Inorganica Chimica Acta, 41 (1980) 253–257
©Elsevier Sequoia S A , Lausanne – Printed in Switzerland

Photostereochemical Cleavage of the Ni–PMe$_3$ bond in Pentacoordinate d^8 Trigonal Bipyramidal Complexes: NiX$_2$(PMe$_3$)$_3$ (X = Br, CN)

MARIE-FRANCE LUDMANN
Laboratoire de Chimie Inorganique Moléculaire et de Catalyse, Université L Pasteur, Strasbourg, France

FRITZ WASGESTIAN
Institut fur Anorganische Chemie, Koln, F R G

MICHÈLE DARTIGUENAVE* and YVES DARTIGUENAVE
Laboratoire de Chimie de Coordination du C N R S , Associe à l'Université P Sabatier, 205 Route de Narbonne, 31030 Toulouse, France

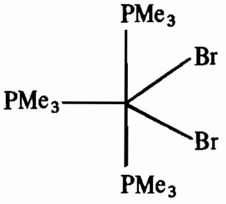
Received January 23, 1980

The photochemical elimination of PMe$_3$ from cis-eq-eq-*NiBr$_2$(PMe$_3$)$_3$ and* trans-*Ni(CN)$_2$(PMe$_3$)$_3$ was studied in chlorobenzene solutions The photochemical quantum yields were found to be wavelength dependent NiBr$_2$(PMe$_3$)$_3$ showed a maximum at 590 nm (position of the second ligand field band $^1A_1 \rightarrow {}^1B_1$) of ϕ = 0 04 The quantum yield of Ni(CN)$_2$(PMe$_3$)$_3$ increased with decreasing wavelength Excitation of the first spin allowed ligand field band did not lead to photoreaction with both compounds The second excited singlet state is supposed to be the photoactive state*

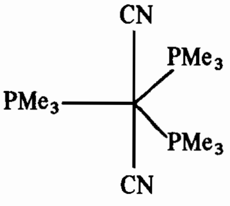
Introduction

Pentacoordinate species have been postulated as intermediates in many thermal [1, 2] and photochemical reactions [3, 4] In order to understand their reactivity, the photochemistry of pentacoordinate nickel(II) complexes has been initiated Up to now, the photochemical properties of Ni(II) d^8 complexes have not been investigated This is easily related to the complicate chemistry of these compounds *i e* their numerous geometries, coordinations, their kinetic labilities and complicate equilibria *etc*, in such a way that their studies have been qualified of "rather unattractive" [3]

In a previous work [5], we have observed that pentacoordinate Ni(II) complexes NiX$_2$(PMe$_3$)$_3$ (X = halide) exhibit a photoactivity upon irradiation and we have tried to use that property on a preparative scale Since no quantitative photochemical studies have been, to our knowledge, made on pentacoordinate d^8 Ni(II) species, it was of interest to develop a more accurate qualitative and quantitative study on these complexes Thus, we report here the results of the photochemical investigation of the two low spin pentacoordinate complexes NiBr$_2$(PMe$_3$)$_3$ and Ni(CN)$_2$(PMe$_3$)$_3$ Both present a trigonal bipyramidal geometry, *TBP*, but their stereochemistries are different isomer (1) (*cis-eq-eq-TBP*) for X = Br and isomer (2) (*trans-TBP*) for X = CN [6]



isomer 1



isomer 2

In this case, we have the opportunity to investigate the photostereochemistry of pentacoordinate d^8 TBP complexes, that is, following Adamson's labilized axis terminology [7], to see if these complexes can be classified as either axially or equatorially labilized

Experimental Section

The nickel complexes NiX$_2$(PMe$_3$)$_3$ (X = Br, I, CN) were prepared as described previously [6] Chlorobenzene was dried and stored on molecular sieves. It was distilled before use

Photochemical conversion was determined from the change in optical density, Electronic spectra were recorded on a Cary 14 spectrophotometer in 1.000

---

*Author to whom correspondence should be addressed

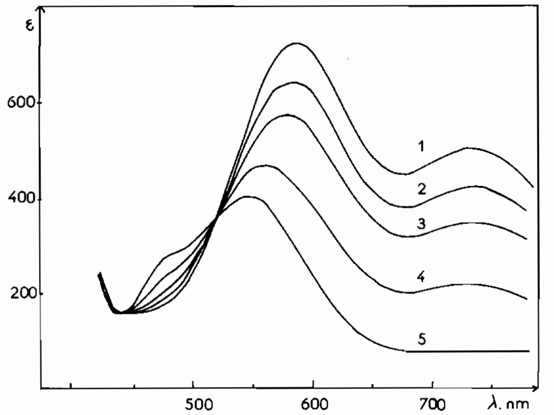


Fig. 1. Irradiation of a 1.2 10^{-3} *M* chlorobenzene solution of $NiBr_2(PMe_3)_3$ (Exposure time: 5 sec).

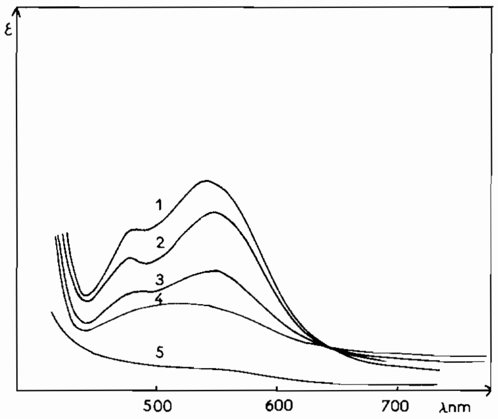


Fig. 2. Irradiation of a 1.2 10^{-3} *M* chlorobenzene solution of $NiBr_2(PMe_3)_2$ (Exposure time: 5 sec).

cm cells. The samples ($c = 10^{-3}$ mole l^{-1}) were irradiated in the cell, which was located on an optical bench. The source of the exciting radiation was a 100 W mercury lamp (OSRAM HBO 100W/2) in combination with SCHOTT interference filters for qualitative work. For quantitative measurement of the quantum yields, a home built actinometer [8] was used.

Results

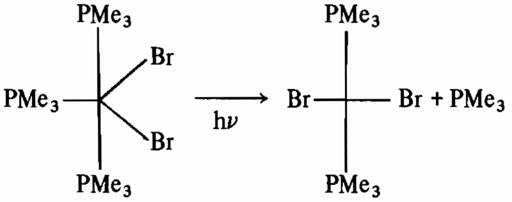
The difficulty of this study was the finding of a convenient solvent *i.e.* *1*) not absorbing energy in the irradiation range (360 to 700 nm) to prevent any secondary reaction which could complicate or hide the studied phenomena *2*) being a good solvent for the Ni(II) complexes in keeping the thermal dissociation reaction slow (Reaction 1)

$$NiX_2(PMe_3)_3 \rightleftharpoons NiX_2(PMe_3)_2 + PMe_3 \qquad (1)$$

This dissociation can be prevented *i.e.* the pentacoordinate species preserved in solution, by adding excess PMe_3, which results in displacing equilibrium (1) toward the left. However this was not possible for the photochemical study because equilibrium (1) is very fast restored so that no photochemical process can be detected on excess PMe_3 (*vide infra*).

After having tried many solvents, the photochemical study was done in chlorobenzene, which was the only solvent where the thermal reaction was negligeable compared to the photochemical one (as, checked by electronic spectroscopy, the electronic spectrum presented no detectable change for one hour and half).

Typical spectrophotometric curves of the photolysis experiment for $NiBr_2(PMe_3)_3$ are shown in Fig. 1. All reactions were done in chlorobenzene solution. After irradiation of the solution ($c = 1.2.10^{-3}$ mole l^{-1}) in the region of the second ligand field transition (580 ± 5 nm) a decrease of the two ligand field bands at 590 and 720 nm ($^1A_1 \rightarrow {}^1A_1$; $^1A_1 \rightarrow {}^1B_2$) allowed in a d^8 TBP complex of C_{2v} symmetry, is observed, consistent with the color of the solution which is modified from royal blue to light pink. The presence of two isobestic points at 522 nm and 440 nm indicates that two species are present in solution. The curve 5 (Fig. 1), characterized by two maxima at 542 nm and 470 nm, is similar to the one obtained when $NiBr_2(PMe_3)_2$ is dissolved in solution ($c = 10^{-3}$ mole l^{-1}). This species has been unambiguously characterized in the solid state as a *trans*-square planar compound, as reported by its X-ray structure [9]. Thus, the photoinduced reaction of $NiBr_2(PMe_3)_3$ can be written as:



(2)

When the photoreaction is going on, the solution becomes colourless (Fig. 2). The ligand field transitions disappear totally, with formation of either a 'three coordinate $NiBr_2L'$' or $NiBr_2$. No solid however, is observed to precipitate ($NiBr_2$ is not soluble in C_6H_5Cl) but due to the low concentration of the solution, this observation is not conclusive. The photolysis of the Ni–Br bond is not observed, in agreement with the molecular nature of the solution as checked by conductivity measurements.

The tetracoordinate species $NiBr_2(PMe_3)_2$, obtained by irradiation remains stable in solution, at room temperature, for several hours (in absence of oxygen).

TABLE I. Quantum Yield Values.

$NiBr_2(PMe_3)_3$	
λ(nm)	ϕ
700	<0.003 (limit of the measurement)
630	0.025 - 0.030
580	0.03 - 0.035
545	0.035 - 0.040
465	0.020
405	0.01
360	0.005
$Ni(CN)_2(PMe_3)_3$	
λ(nm)	ϕ
415	<0.0003
385	0.0007
365	0.00175
355	0.0320
345	0.0060

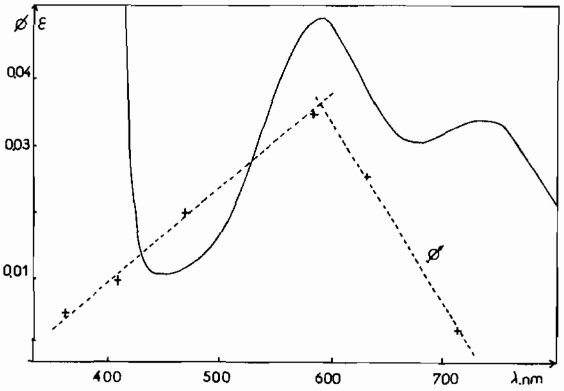


Fig. 3. Wavelength dependence of the quantum yield in photolysis of $NiBr_2(PMe_3)_3$.

However, after one day, the originally light pink solution turns dark-red without any remarkable change in the visible spectrum other than a large increase of the absorption coefficient of the two lower energy bands (from $\epsilon = 400$ to 2000 at 555 nm and from $\epsilon = 300$ to 1100 at 470 nm). No reaction occurs in the dark. The formation of an ionic species is easily ruled out by the conductimetric measurement which shows a nearly zero value of Λ. Attempts to isolate the corresponding species in the solid state have failed until now.

Thus, the photoinduced reaction of $NiBr_2(PMe_3)_3$ seems to be, as a whole, totally analogous to the thermal reaction, which has recently been proven to follow the dissociative reaction path (Reaction 2) [10].

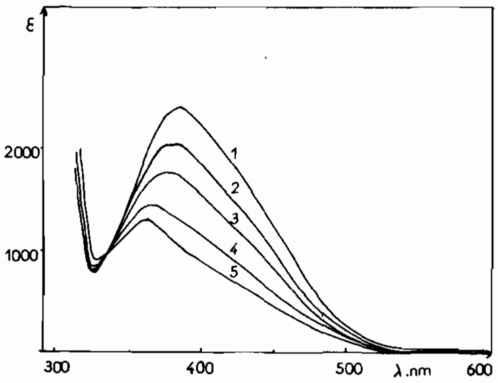


Fig. 4. Irradiation of a 2.35 10^{-4} *M* chlorobenzene solution of $Ni(CN)_2(PMe_3)_3$ (Exposure time: (1–2), (2–3) = 20 min; (3–4) = 40 min; (4–5) = 30 min).

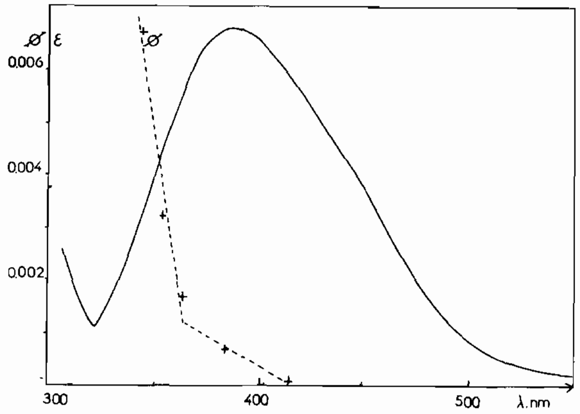


Fig. 5. Wavelength dependence of the quantum yield in photolysis of $Ni(CN)_2(PMe_3)_2$

In order to get some quantitative values of this reaction, the wavelength dependence of the quantum yield has been determined and is reported in Table I. As expected, the quantum yield values are low. They are wavelength dependent, as shown in Fig. 3, which emphasises the comparison between the electronic spectrum and the quantum yield. Interestingly, increase of the quantum yield is observed when the photolysis occurs in the second ligand field transition, while irradiation in the least energetic ligand field band and in the charge transfer range gives no photoreaction. It is the first time, to our knowledge, that the participation of a higher energy excited ligand field state in a Ni–PMe_3 cleavage has been so well established.

Analogous spectral changes have been observed in the photolysis of $NiI_2(PMe_3)_3$ and similar conclusions have been obtained. $NiCl_2(PMe_3)_3$ has not been studied due to the unstability of the complex at room temperature in the solid state and in solution.

Figure 4 shows the absorption spectrum of a chlorobenzene solution of $Ni(CN)_2(PMe_3)_3$. The

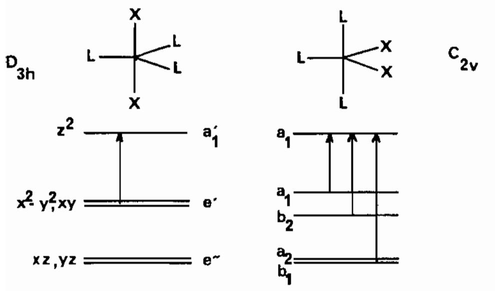
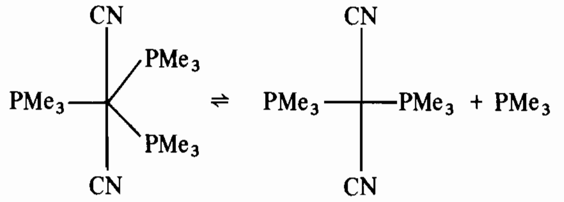


Fig. 6. Ligand field levels of trigonal bipyramidal complexes of D_{3h} and C_{2v} geometries.

390 nm band, broad and assymmetric, has been attributed to the allowed ligand field transition $^1E' \rightarrow {}^1A_1'$ ($d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$) of the *trans-TBP* structure of D_{3h} symmetry. Irradiation of a 2.35 10^{-4} mole l^{-1} solution at room temperature, with a 400 nm light beam (in the maximum of the ligand field band) shows a decrease in the intensity of the band at 390 nm and the appearance of a new transition at 355 nm due to the photochemical dissociation process (Reaction 3)

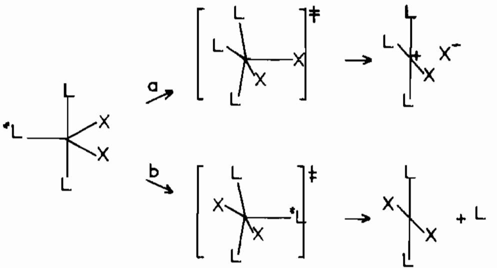
$$Ni(CN)_2(PMe_3)_3 \rightleftharpoons Ni(CN)_2(PMe_3)_2 + PMe_3 \qquad (3)$$



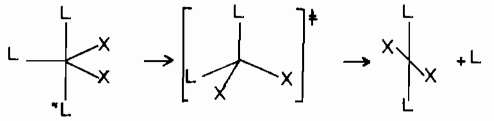
No further photoreaction of the square planar $Ni(CN)_2(PMe_3)_2$ has been observed. The wavelength dependence of the quantum yields is reported in Table I and Fig. 5. Their values are lower than the ones obtained for the bromocomplex. In contrast to $NiBr_2(PMe_3)_3$, the photoreaction is not large when the complex is irradiated in the ligand field band, but increases when exposed to higher energy.

Discussion

The photoreactions observed in this study are simple elimination reactions (breaking of a metal–ligand bond). The final products can be formed in one dissociative step followed by ligand rearrangement. From the maximum in quantum yield, observed at the wavelength of the second ligand field band of $NiBr_2(PMe_3)_3$, we conclude that the photoreactions proceed from the ligand field states.



Scheme 1



Scheme 2

Fig. 7. Equatorial PMe_3 labilization reaction paths (Scheme 1) and axial labilization reaction path (Scheme 2) in the d^8 trigonal bipyramidal low spin Ni(II) complexes.

In a trigonal low-spin d^8 complex, the only empty orbital is the d_{z^2} orbital (Fig. 6). Any ligand field excitation must occupy this orbital and hence should destabilize the axial positions. Predominant axial labilisation explains the phosphine dissociation observed in $NiBr_2(PMe_3)_3$ and the lower quantum yield of $Ni(CN)_2(PMe_3)_3$ where the phosphine ligands are in equatorial positions. Such a mechanism has also been invoked to explain the stereochemical nonrigidity of $NiBr_2(PMe_3)_3$ [10]. However, it is difficult to understand why the first spin allowed ligand field band is not photoactive, since destabilisation by the antibonding d_{z^2} orbital should be equally effective.

If, however, equatorial PMe_3 is labilized, which is the process occurring in the thermal reaction [10], it is associated with a trigonal bipyramidal, square pyramidal, square planar geometric reaction path, which involves in the lower excited state a square pyramidal transitional species (Scheme 1, Fig. 7). Since there are two different ligands in the equatorial plane, it is tempting to speculate on the presence of two different stereoisomers in the excited state: one of lower energy, photoinactive *i.e.* a square pyramidal structure with Br in apical position and one of higher energy, photoactive, *i.e.* a square pyramidal structure with PMe_3 in apical position.

However, in view of the facile geometrical rearrangements effective in Ni^{2+} stereochemistry, any explanation remains very tentative at this time.

The low photochemical quantum yields show that other deactivation processes play a major role. Since below the singulet state, reached by direct excitation, one triplet state, at least, must exist ($^3E'$ in D_{3h} symmetry), intersystem crossing to this state will be an important pathway for deactivation. According to the energy gap law of radiationless transitions [12], intersystem crossing from the higher singulet state will be less effective and therefore less competing with the photoreaction, provided no other triplet states lie in between. The fact, that the maximum quantum yield of the bromocomplex coincides with the absorption maximum indicates that the photoreaction starts from the spectroscopic state and not from a thermally equilibrated one.

Dissociation of a ligand from a *TBP* complex will lead to a distorted tetrahedron or a square planar depending if the ligand leaves from an axial or an equatorial position. In the further relaxation, the phosphine will tend to rearrange giving in both cases a *trans* square planar product, therefore the same geometrical isomer can be expected for the axial and equatorial labilization.

Acknowledgements

We would like to thank Professor H. B. Gray, California Institute of Technology, Pasadena, for simulating discussions. Financial assistance of the Centre National de la Recherche Scientifique and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References;

1 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Second Edition, J. Wiley, N.Y. (1967).

2 C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', W. A. Benjamin, N.Y. (1965).

3 V. Balsani and V. Carassiti, 'Photochemistry of Coordination Compounds', Acad. Press, London (1970).

4 A. W. Adamson and P. D. Fleischauer, Ed., 'Concepts of Inorganic Photochemistry', J. Wiley, N.Y. (1975).

5 A. Merle, M. Dartiguenave and Y. Dartiguenave, *J. Chem. Phys., 10,* 1408 (1971).

6 J. W. Dawson, T. J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H. B. Gray, *J. Am. Chem. Soc., 96,* 4428 (1974).

7 A. W. Adamson, *J. Phys. Chem., 71,* 798 (1967).

8 F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankf.), 51,* 208 (1966).

9 A. Mari, A. Gleizes, M. Dartiguenave and Y. Dartiguenave, to be submitted.

10 P. Meier, A. Merbach, M. Dartiguenave and Y. Dartiguenave, *Inorg. Chem., 18,* 610 (1979).

11 A. Merle, M. Dartiguenave, Y. Dartiguenave, J. W. Dawson and H. B. Gray, *J. Coord. Chem., 3,* 199 (1974).

12 R. Englman and J. Jortner, *Molec. Phys., 18,* 145 (1970).