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Photochemistry of μ-hydrido-tetrakis(tertiary phosphine)-diplatinum complexes

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Abstract

The present work examines the photochemistry of μ-hydrido-tetrakis(ethylphosphine)diplatinum complexes, *trans–trans* monohydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) and *trans–cis* dihydrido-bridged $[(PEt_3)_2HPt(\mu\text{-}H_2)Pt(PEt_3)_2][BPh_4]$ (**2**). The primary photoprocess of these complexes is homolysis of their Pt–Pt bonds. Interesting consequences of Pt–Pt bond dissociation include cleavage of Pt(μ-H)Pt and Pt(μ-H_2)Pt yielding the reactive complexes $[(PEt_3)_2PtH_2]$ (**3**) and $[(PEt_3)_2PtH(S)][BPh_4]$ (**4**) (S: solvent). Depending on experimental conditions, photoproducts **3** and **4** can undergo a multiplicity of reactions. In acetone photoproducts **3** and **4** undergo a thermal coupling reaction forming the *trans–cis* isomer **2**. Selective photolysis of **3** and **4** gives elimination of H_2 and solvent with generation of reactive intermediates $[(PEt_3)_2Pt]$ (**5**) and $[(PEt_3)_2PtH]^+$ (**6**). Photogenerated **5** and **6** fragments react cleanly with CO to form 18 electron compounds $[(PEt_3)_2Pt(CO)_2]$ (**7**) and $[(PEt_3)_2Pt(H)(CO)]^+$ (**8**). In CH_2Cl_2, the photoproducts **5** and **6** could abstract halide from the solvent to form as the only final products $[(PEt_3)_2Pt(Cl)CH_2Cl]$ (**9**) and $[(PEt_3)_2Pt(H)Cl]$ (**10**). The photoreactions are interpreted in terms of excited state decay channels. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photolysis; Hydridodiplatinum complexes; Absorption spectra

1. Introduction

Binuclear complexes containing bridging hydride ligands are common in organometallic chemistry [1]. These hydride complexes are critical to many transition-metal photo-assisted or catalyzed organic transformations [2].

Among the group of compounds containing the M–H–M unit, the following binuclear trihydridodiplatinum complexes are known:

Monohydrido-bridged *trans–trans* complexes (1).
Trans–cis dihydrido-bridged complexes (2).

This paper reports the photochemistry of complexes of **1** and **2** (Scheme 1) demonstrating the potential of photoirradiation as a means of preparing: (i) dihydrido mononuclear platinum(II) intermediate $[(PEt_3)_2PtH_2]$ (**3**) and (ii) Pt(II) monohydrido solvent complexes $[(PEt_3)_2PtH(S)]^+$ (**4**) (S: solvent).

The photoproducts **3** and **4** afford a rich chemistry depending on reactions conditions (λ_{exc}, solvent used, and the presence of donor ligands) and their reactivity constitute a versatile entry point in the organometallic chemistry of the Pt(II) phosphine complexes.

2. Results and discussion

The dinuclear Pt(II) complexes **1** and **2** exhibit absorptions in the UV–Vis region (Table 1) and these can be attributed to transitions between metal–metal bonding and antibonding orbitals. In reality molecular orbital diagrams coupled with an analysis of the bonding and antibonding energies indicate that the LUMO energy level in these complexes has antibonding metal d-orbital characteristics [3–5]. Thus one would expect irradiation using 336 nm light to lead to the HOMO–LUMO transition not only with the cleavage of Pt–Pt bond but also with a significant weakening of the Pt(μ-H)Pt and Pt(μ-H_2)Pt bridges.

Photolysis ($\lambda = 336$ nm) of degassed acetone solution of **1** and **2** induces a gradual disappearance of the absorption at 340 nm due to the starting materials with a concomitant presence of two isosbestic points at 282 and 378 nm. (Fig. 1).

Quantum yields of 0.50 and 0.48 are determined, respectively, for the disappearance of complexes **1** and **2**.

When the irradiated solution is kept in the dark, the original absorption at 340 nm is re-established. Photochemical and thermal reactions can be cycled several times without causing the complexes to decompose.

Irradiation of **1** in NMR tube gives rise to ^{1}H NMR spectra which are much richer in lines than the original system. The relative intensity of the observed peaks strongly depends on

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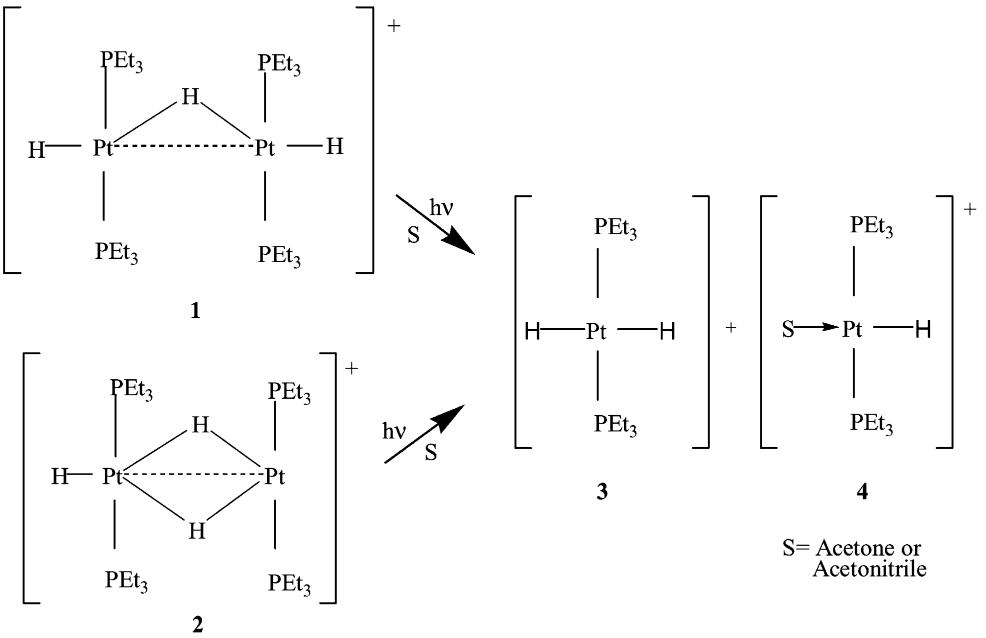


Scheme 1.

the time of observation after irradiation has been stopped and the temperature at which the sample is maintained during NMR observations. Even with the utmost speed, there is always some return to the original **1** species. In order to keep this back reaction under control, the temperature and time for NMR measurements were rigorously controlled. Thus the photolysis of **1** at room temperature, followed by quenching at 195 K and observation of the NMR spectra within 5 min, results in a gradual loss of its characteristic ^{1}H NMR resonance at -8.20 ppm δ_{Ht} and at -6.42 δ_{Hb} and emergence of peaks at -3.00(t) and -14.2(m) ppm assigned to complexes $[(PEt_3)_2PtH_2]$ (**3**) and $[(PEt_3)_2PtH(S)]^+$ (**4**), respectively.

The formation of **3** and **4** as principal products in the photolysis of **1** is confirmed by following additional spectroscopic evidence:

1. The hydride resonance at -3.00 ppm is a 1:2:1 triplet ($^2J_{\mathrm{P-H}} = 20$ Hz) arising from coupling to two P atoms *trans* to a hydride. The $^1J_{\mathrm{Pt-H}}$ is 792 Hz. These

Table 1
Electronic absorption spectral band maxima for trihydridodiplatinumphosphine complexes in acetone at 20°C

Complex	λ_{abs} (nm)[a]	ε (l mol^{-1} cm^{-1})[b]
$[(PEt_3)_2HPt(\mu\text{-}H)PtH(Pet_3)_2]$ $[BPh_4]$ (**1**)	340	4015
	300 (sh)	6100
$[(PEt_3)_2HPt(\mu\text{-}H_2)Pt(PEt_3)_2]$ $[BPh_4]$ (**2**)	341	4310
	300 (sh)	6730

[a] Absorption maximum.
[b] Molar absorption coefficient.

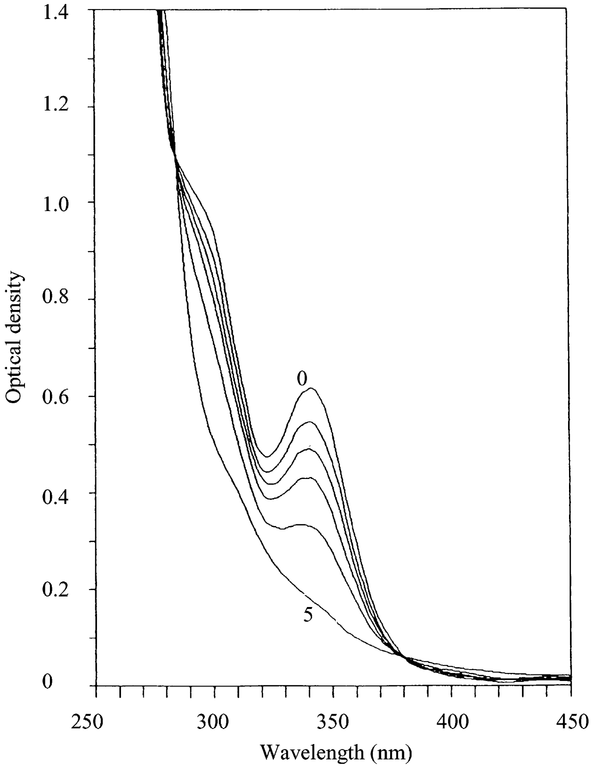


Fig. 1. Electronic spectral changes during λ = 336 nm photolysis of 9×10^{-5} M solution of $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) in acetone. Band maxima and molar absorptivity are given in Table 1. Curves 0–4 correspond to 0, 1, 2, 4, 6 min and curve 5–10 min of irradiation.

parameters resemble very closely to those reported for the *trans* form of **3** [6].

The signal at −14.2 ppm with the usual ^{195}Pt satellites exhibits the following parameter: $^{1}J_{\mathrm{Pt-H}} = 1215$ Hz; $^{2}J_{\mathrm{P-H}\,trans} = 198$ Hz as expected for cationic monohydride Pt(II) complexes [7].

2. Phosphorous ^{31}P{H}NMR spectra, recorded at 223 K, shows:
   - Complete, post-photolysis disappearance of the central multiplet δ_{P} 20.1 ppm of complex **1**.
   - A new signal at 28 ppm (s, $^{1}J_{\mathrm{Pt-P}} = 2758$ Hz) for **3** and at −12.7 ppm (s, $^{1}J_{\mathrm{Pt-P}} = 2545$ Hz) for **4**.

The ratio of **3** and **4** photoproducts monitored by ^{31}P NMR depends on the solvent: in CD_3CN it is 1:1. The photochemistry of complex **2**, under the same conditions described for complex **1**, gave UV–Vis and NMR spectral changes like those described above for complex **1**.

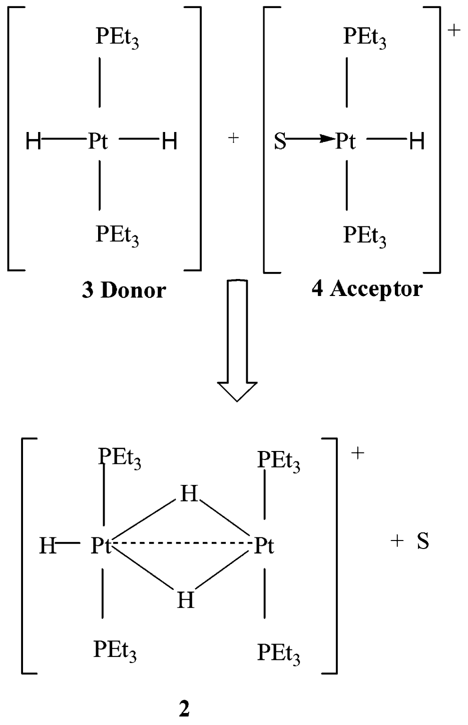
Taken together, the electronic and NMR (^{1}H and ^{31}P) spectral changes, demonstrate that the principal result of the excited state decay is an efficient cleavage of the Pt–Pt bond, implying that rapid rupture of the Pt(μ-H)Pt and Pt(μ-H_2)Pt bridges in the complexes **1** and **2**, respectively, occurs to give the dihydrido complex **3** and the monohydrido solvent complex **4** (Scheme 1).

In the dark or upon irradiation of **1** and **2** for 1 h, the original absorption at 340 nm is re-established, indicating the high reactivity of the products **3** and **4**. Monitoring the photolyzed solution (in NMR tube) by ^{1}H NMR spectroscopy at 298 K, there is clear evidence only of signals of complex **2**. These results indicated that the generated intermediates **3** and **4** recombine thermally according to the donor–acceptor formalism [8] illustrated in Scheme 2. That complex **2** is preferentially formed is consistent with the observed high thermodynamic stability of complexes **2** vs. complex **1** [1].

The results reported above indicate that it would be worth investigating the photoreactivity of such organometallic complexes as **3** and **4** since they are promising candidates for the formation of electron-rich fragments due to their high energy, high intensity electronic charge-transfer excitations associated with high absorption at 300 nm. Indeed promotion of the parent molecules to different regions of the electronically excited manyfold may lead to dissociation channels that result in H_2 evolution from **3** and solvent displacement from **4**. The correlations between the excited states and the observed intermediates were demonstrated by the photoreactions of **1** and **2** at 300 nm in the presence of CO or using CH_2Cl_2 as solvent.

2.1. Photoreaction in acetonitrile under a CO atmosphere

Photolysis (λ = 300 nm) of a degassed acetonitrile solutions of **1** or **2** under a CO atmosphere led to CO uptake and the production of carbonyl complexes $[(PEt_3)_2Pt(CO)_2]$ (**7**) and $[(PEt_3)_2Pt(H)(CO)]^+$ (**8**) in a ratio of 1:1. GC/MS studies of the gas phase of the irradiated solutions showed that 0.4 ± 0.1 mol of H_2 was formed for each mole of **1** or **2** photolyzed. None of these reactions occur thermally and light is essential to induce H_2 and solvent displacement from the parent complexes **3** and **4** formed in the photolysis of complexes **1** or **2**.



Scheme 2.

The following sequence of reactions for the formation of **7** and **8** are proposed:

1. After photoexcitation of **1** or **2** with 300 nm light, species **3** and **4** are formed.
2. Intermediate **3** also has near-UV absorption and irradiation in this region could produce an excited state in which *cis*-$[(PEt_3)_2PtH_2]$ (**3′**) is formed. A secondary photolysis of **3′** could produce the 14e species $[(PEt_3)_2Pt]$ (**5**) and loss of H_2. The NMR spectral data obtained in the first stage of photoreactions indicate that the complex $[(PEt_3)_2PtH_2]$ (**3**), in these experimental conditions, is formed in an equilibrium mixture of *cis* and *trans* isomers. This result show the *trans–cis* isomerization of **3** occurs before reductive elimination of H_2.
3. Efficient interception of the transient 14e species $[(PEt_3)_2Pt]$ (**5**) by CO with formation of the final product **7**.

Several groups have been established precedents for the reactions postulated here showing that H_2 photoevolution in transition metal hydrides occurs from the *cis* form, forming in situ electronically and coordinatively unsaturated species [8,9].

Another type of reaction involves the solvent complex **4** which, in the presence of CO, gives **8**. Most likely, after solvent photodissociation, the coordinatively unsaturated fragment $[(PEt_3)_2Pt(H)]^+$ (**6**) is formed. Lastly, the latter is expected to react with CO forming the final product **8**.

2.2. Photolysis of **1** and **2** in dichloromethane

Markedly different behavior was observed in the prolonged photolysis ($\lambda = 300\,\mathrm{nm}$) of **1** or **2** in CH_2Cl_2. The primary photoevent is always Pt–Pt bond dissociation. This process is followed by the cleavage of Pt–H–Pt bonds with the formation of complexes **3** and **4**.

The ^1H NMR spectral data obtained in the first stage of photoreaction, indicate that the complex $[(PEt_3)_2PtH_2]$ (**3**) in these experimental conditions is formed in an equilibrium mixture of *cis* and *trans* isomers. During this time no appreciable amount of H_2 was generated, indicating that *trans–cis* isomerization occurs before reductive elimination of hydrogen from *cis*-$[(PEt_3)_2PtH_2]$ (**3′**) (Eq. (4)). Gas chromatographic analysis of the gas phase after complete photolysis showed the presence of $0.4 \pm 0.1\,\mathrm{mol}$ of H_2. The expected product of the reductive elimination of H_2 $[(PEt_3)_2Pt]$ (**5**) was not isolated but rather the Pt(II) complexes $[(PEt_3)_2Pt(Cl)CH_2Cl]$ **9** and $[(PEt_3)PtHCl]$ (**10**) were obtained. The complexes **9** and **10** are the products of the oxidative addition of C–Cl bond of the solvent CH_2Cl_2 to the reactive intermediates **5** and **6**, respectively. To assess the mechanism of C–Cl bond activation of CH_2Cl_2 by the platinum fragment $[(PEt_3)_2Pt]$, an ESR spin-trapping study was performed. Thus, photolysis of **1** or **2** in CH_2Cl_2 containing the radical scavenger $PhCH(NO)CMe_3$ (PBN) yielded ESR signals ($a_N = 15.46\,\mathrm{G}$, $a_H = 1.6\,\mathrm{G}$) that can be attributed to the $PBN{\cdot}CH_2Cl$ spin adduct [10]. This points to the formation of $^{\bullet}CH_2Cl$ radicals in the overall process. No evidence for thermal Cl-atom abstraction can be observed when solutions identical to those used in the photochemical studies are refluxed for 2 h in the dark. A possible sequence of reactions of the intermediates produced in the photolysis of **3** in CH_2Cl_2 with respect to the platinum products is given in Eqs. (1)–(3):

$$\underset{\mathbf{3}}{trans\text{-}[(PEt_3)_2PtH_2]} \xrightarrow{h\nu} \underset{\mathbf{3'}}{cis\text{-}[(PEt_3)_2PtH_2]} \xrightarrow{h\nu} \underset{\mathbf{5}}{[(PEt_3)_2Pt]} + H_2 \qquad (1)$$

$$\underset{\mathbf{5}}{[(PEt_3)_2Pt]} + CH_2Cl_2 \rightarrow [(PEt_3)_2PtCl^{+\bullet}\text{–}CH_2Cl^{-\bullet}] \qquad (2)$$

$$[(PEt_3)_2PtCl^{+\bullet}\text{–}CH_2Cl^{-\bullet}] \rightarrow \underset{\mathbf{9}}{[(PEt_3)_2Pt(Cl)CH_2Cl]} \qquad (3)$$

The C–Cl bond activation could take place through an electron-transfer process (Eq. (2)) similar to the one proposed for alkyl halide addition to Ir(I) and Pt(0) complexes [11]. The hydrido intermediate $[(PEt_3)_2PtH]^+$ (**6**) which results from the primary solvent displacement from complex **4** can also be viewed as a reactive species whose reaction with CH_2Cl_2 is expected to give $[(PEt_3)_2PtHCl]$ (**10**) upon continuous photolysis, according to Eqs. (4) and (5).

$$\underset{\mathbf{4}}{[(PEt_3)_2PtH(S)][BPh_4]} \xrightarrow[-S]{h\nu} \underset{\mathbf{6}}{[(PEt_3)_2PtH][BPh_4]} \qquad (4)$$

$$\underset{\mathbf{6}}{[(PEt_3)_2PtH][BPh_4]} \xrightarrow{CH_2Cl_2} \underset{\mathbf{10}}{[(PEt_3)_2PtHCl]} + HBPh_4 + \text{radical-derived products} \qquad (5)$$

The acid $HBPh_4$ could not be detected directly, presumably because it is very unstable and rapidly decomposes into benzene and BPh_3 [8].

The results presented demonstrate that the type of solvent used or the presence of CO exerts great control over the binuclear forming reactions illustrated in Scheme 2. The CO atmosphere as well as the use of CH_2Cl_2 as solvent thus suppress the recombination between the photoproducts $[(PEt_3)_2PtH_2]$ and *trans*-$[(PEt_3)_2PtH(S)]$ and enables observation of the reactions presented in Sections 2.1 and 2.2.

The informations obtained in this study will prove helpful in construction of reaction coordinates for complex platinum hydrides reactions, providing a basis for understanding the primary photochemical reactions and the chemistry of the resulting reactive intermediates which are of great importance in catalytic systems.

3. Experimental details

3.1. General procedure

All operations were performed under nitrogen using conventional Schlenk-line techniques. All solvents were freshly distilled from standard drying agents and degassed by three freeze–thaw cycles before use. All NMR solvents were dried and distilled before use. Sample preparation was carried out under dry oxygen-free nitrogen using standard inert atmosphere techniques. Both $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) and $[(PEt_3)_2HPt(\mu\text{-}H_2)Pt(PEt_3)_2][BPh_4]$ (**2**) were prepared according to the procedure in literature [1].

3.2. Photochemical reactions

The photochemical reactions were performed with the output of a 500 W ORIEL Hg lamp fitted with an IR blocking filter and a water filter to remove excess heat. An applied photophysics f3/4 monochromator was used to obtain the irradiation wavelength. The progress of the photoreactions was monitored by UV–Vis spectral measurements. For the quantum-yield determination, the conversions to products were kept below 10%, and over this period, plots of conversions vs. time were linear. Potassium ferrioxalate actinometry was used to determine the radiation intensity at the wavelength of irradiation.

3.3. Instrumentation

UV–Vis spectra were recorded on a JASCO Uvidec-650 spectrophotometer. ^{1}H and ^{31}P NMR were recorded on a BRUKER AC 200 spectrometer operating at 200.13 MHz for ^{1}H and at 81.0 MHz for ^{31}P. The chemical shift scales are relative to internal TMS for ^{1}H and the external H_3PO_4 for ^{31}P NMR. FT-IR spectra were recorded with a Bruker IFS 88 spectrophotometer.

*3.4. Photolysis of the complex $[(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2][BPh_4]$ (**1**) in acetone*

A solution of complex **1** (0.15 mmol) in acetone was irradiated with $\lambda = 336$ nm. After 1 h of irradiation a yellow precipitate was formed. The precipitate was collected and identified by its ^{1}H and ^{31}P NMR spectra as *trans–cis* $[(PEt_3)_2HPt(\mu\text{-}H_2)Pt(PEt_3)_2][BPh_4]$ (**2**).

^{1}H NMR: bridging hydride, δ_{Hb}, ppm: $-3.55(^{1}J_{Pt\text{–}H} = 361, 592$ Hz; $^{2}J_{P\text{–}H\,trans} = 106$ Hz); terminal hydride, δ_{Ht}, ppm: -4.92 ($^{1}J_{Pt\text{–}H} = 1316$ Hz; $^{2}J_{P\text{–}H} = 13.31$ Hz; $^{2}J_{Pt\text{–}H} = 192$ Hz).

^{31}P NMR (in acetone-d_6): central multiplet, δ_P, ppm: $20.1(^{1}J_{Pt\text{–}P} = 2580$ Hz; $^{3}J_{Pt\text{–}P} = 18$ Hz).

3.5. Photochemical experiments in the NMR tube

A typical analytical photolysis was carried out as follows: an NMR tube with a vacuum line adapter was charged with the complex **1** in acetone-d_6. After capping, the tube was placed in a water-cooled quartz cuvette set before the focused photolysis beam. The reactions were monitored periodically by examining the recognizable groups of the signals in the NMR spectrum of complex **1** at 193 K.

Upon photoexcitation at $\lambda = 336$ nm (3 min) there is, at first, a depletion of the parent adsorptions in the ^{1}H and ^{31}P NMR spectra and a new series of peaks at -3.00 ppm (t, $^{1}J_{Pt\text{–}H} = 792$ Hz; $^{2}J_{P\text{–}H} = 20$ Hz) and at -14.2 ppm (m, $^{1}J_{Pt\text{–}H} = 1215$ Hz; $^{2}J_{P\text{–}H\,trans} = 198$ Hz) are observed. The signals at -3.00 and -14.2 ppm were assigned to the photoproducts *trans*-$[(PEt_3)_2PtH_2]$ (**3**) and $[(PEt_3)_2PtH(S)]^+$ (**4**), respectively. The relative abundance of **3** and **4**, derived from ^{31}P NMR spectra, is found to be a ratio of 1:1. After 30 min of irradiation at 336 nm, the ^{1}H and ^{31}P NMR spectra showed the resonances of **3** and **4** as major products (>95%). In other cases, the NMR analysis was performed 2 h after the end of photolysis. Only the *trans*-isomer **2** was detected.

Photochemical experiments with 300 nm light were monitored by ^{1}H NMR using 0.1 M CD_3CN (or CD_2Cl_2) solutions of **1**. Samples were photolyzed for 15 min. Spectra were recorded at 3 min intervals. During this time, the ^{1}H NMR spectrum of the irradiated solution of **1** shows: (1) the triplet pattern expected for the *trans*-isomer **3**, with ^{195}Pt satellite ($J_{Pt\text{–}H} = 792$ Hz centered at -3.00 ppm); (2) a complex resonance for the *cis*-isomer **3′** upfield centered at -3.8 ppm about a ^{195}Pt satellite of the *trans* isomer; (3) a signal at -14.2 ppm (s, $^{1}J_{Pt\text{–}H} = 1215$ Hz, $^{2}J_{P\text{–}H} = 198$ Hz) assigned to the complex $[(PEt_3)_2PtH]^+$ **4**. Analogous results were obtained when complex **2** was photolyzed in the same experimental conditions. The ^{1}H NMR results of the bulk photolysis are reported in Sections 3.6 and 3.8.

*3.6. Photochemical preparation of $[(PEt_3)_2Pt(CO)_2]$ (**7**) and $[(PEt_3)_2Pt(H)(CO)][BPh_4]$ (**8**)*

A solution of complex **1** (0.1 M) in acetonitrile was prepared in a quartz cuvette where photochemical reaction was to be carried out. The cuvette was sealed with a septum equipped with a suitable vent-hole. A slow stream of CO was bubbled through the solution during irradiation at 300 nm (1 h, 20°C). Removal of the solvent under vacuum at room temperature gave a residue identified as a mixture of $[(PEt_3)_2Pt(CO)_2]$ (**7**) (FT-IR: ν(CO) 1945, 1990 cm^{-1} in THF), and $[(PEt_3)_2Pt(H)(CO)][BPh_4]$ (**8**) (FT-IR: ν(CO) 1915 cm^{-1} in THF; ν(Pt–H) 2210 cm^{-1}) [12,13]. The same products **7** and **8** were obtained using complex **2**.

The photoreactions of **1** or **2** in the presence of CO were complete within 1 h. Gas chromatographic analysis of the gas phase (after a preliminary calibration) showed that the total H_2 evolved was $0.4 \pm 0.1 \times 10^{-1}$ mol.

3.7. ESR radical trapping experiments

Solutions of **1** or **2** (10^{-3} M) in carefully purified CH_2Cl_2 were introduced into a 4 mm cylindrical ESR tube containing the spin trap phenyl-*tert* butylnitrone (PBN) at concentration of 2×10^{-3} M. The degassed solutions prepared in the dark did not show any ESR signals. Upon direct irradiation ($\lambda = 300$ nm) in the ESR cavity, the signals of $[PBN{\cdot}CH_2Cl]$ spin adduct was observed ($g = 2.0060$, $a_N = 15.4$ G, $a_H = 15.4$ G) [11].

3.8. Photoreactions in dichloromethane

Photolysis ($\lambda = 336$ nm) of thoroughly degassed CH_2Cl_2 solution of complex **1** gave the UV–Vis spectral changes shown in Fig. 1. The extent of the reaction was determined by monitoring the decrease in optical density at 340 nm and, after correcting for the inner filter effects, a plot of the degree of conversion vs. irradiation time proved linear. The key result in these experiments was the changes in ^{1}H NMR spectra in CD_2Cl_2 accompanying photolysis of **1** in the NMR tube. After 15 min of photolysis, it is clear that the complexes **3** and **4** were formed. Prolonged photolysis of **1** led to further changes in the ^{1}H NMR spectra, indicating that the complexes **3** and **4** react undergo secondary photolysis forming the complexes $[(PEt_3)_2Pt(Cl)CD_2Cl]$ (**9′**) and $[(PEt_3)_2Pt(D)(Cl)]$ (**10′**). Completely analogous results are obtained when complex **2** was photolyzed in CD_2Cl_2 at 300 nm.

3.9. Bulk photolysis

Solutions 0.1 M of **1** or **2** in CH_2Cl_2 were photolyzed to completion as monitored by ^1H NMR. The solvent was removed in vacuo and the white residue identified as a mixture of $[(PEt_3)_2Pt(Cl)CH_2Cl]$ (**9**) (^1H NMR in CD_2Cl_2: $\delta(CH_2)$, 3.46 ppm; dd, $^2J_{Pt\text{–}H} = 45$ Hz; $^3J_{P\text{–}Pt\text{–}H} = 2$ Hz) and $[(PEt_3)_2Pt(H)(Cl)]$ (**10**) (^1H NMR in CD_2Cl_2, δ(Pt–H), -17.0 ppm; $^1J_{Pt\text{–}H} = 1230$ Hz; $^2J_{P\text{–}H} = 14$ Hz).

Acknowledgements

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