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OXIDATIVE ADDITION – REDUCTIVE ELIMINATION SEQUENCES IN THE PHOTOCHEMISTRY OF SOME BIS(PHOSPHINE)PLATINUM COMPLEXES

CARLO BARTOCCI, ANDREA MALDOTTI, SILVANA SOSTERO and ORAZIO TRAVERSO*

Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del C.N.R., Istituto Chimico, Università di Ferrara, Ferrara (Italy)

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Summary

The photolysis of [$L_2Pt(C_2H_4)$] ($L = PPh_3$, $P(p\text{-}C_6H_4CH_3)_3$ complexes in halocarbon solvents (CH_2Cl_2, CH_2Br_2) gives C_2H_4 and the coordinatively unsaturated species [L_2Pt]. Photolysis of platinum metallacycles [$L_2Pt(CH_2)_4$] ($L = PPh_3$, P(n-Bu)$_3$) generates alkanes, alkenes and [L_2Pt]. The [L_2Pt] centers are very reactive, and under prolonged photolysis undergo oxidative addition of CH_2Cl_2 forming the *trans*-[$L_2Pt(CH_2Cl)Cl$] complexes. Under appropriately controlled conditions the *trans* complexes isomerize to *cis* species before bimolecular C_2H_4 elimination occurs and [L_2PtCl_2] is formed as the final product. The oxidative addition–reductive elimination mechanism is discussed on the basis of spin-trapping experiments, quantum yield values, and the sensitivity to radical inhibitors and to solvents.

Introduction

The chemical reactivity of olefin complexes of platinum(0) and platinum metallacycles has been the subject of extensive studies [1,2]. In many of these studies the formation of [L_2Pt] (L = tertiary phosphines) centers was induced in situ by photochemical or thermal means and their presence revealed by kinetic and spectroscopic measurements. The 14-valence electron [L_2Pt] intermediates are quite reactive. Depending on the conditions used (excitation wavelength, solvent, etc.), [L_2Pt] intermediates undergo a broad spectrum of reactions. Examples include insertion, metallation, dimer formation, and oxidative addition [3–6].

The oxidative addition of an organic substrate to zerovalent platinum complexes has often been postulated in homogeneous catalytic cycles. Mechanistic and theoretical aspects of oxidative addition have continued to be the subject of many studies [7–10]. Widely different mechanisms have been proposed for the oxidative addition of organic substrate to d^{10} metal complexes including nucleophilic, free radical, and electron transfer pathways. The last is especially interesting since the electron

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transfer process might be photochemically accelerated.

While such a mechanism assumes paramagnetic transition-metal intermediates, such species have not as yet been observed in photoinduced oxidative-addition processes. We now report that the spin-trapping method, coupled with ESR spectroscopy, has been used to detect platinum(I) intermediates formed in the photoinduced halocarbon solvent addition to phosphine-platinum(0) complexes. Kinetic and spectroscopic results are also described which provide evidence for the operation of oxidative addition–reductive elimination sequences in platinum metallacycle photochemistry.

Experimental

Materials. The starting materials $[L_2Pt(C_2H_4)]$ (I, L = PPh_3; II, L = $P(p\text{-}C_6H_4CH_3)_3$). $[L_2Pt(CH_2)_4]$ (III, L = PPh_3; IV, L = $P(n\text{-}Bu)_3$) were prepared by established procedures [2,3,11]. Merck spectroquality solvents were dried before use by distillation from phosphorus pentoxide under nitrogen. The *N*-t-butyl-α-phenylnitrone and galvinoxyl were commercial samples used as received. Manipulations were conducted under vacuum or under purified nitrogen or argon.

General irradiation procedures. Irradiations were conducted using an Applied Photophysics Reactor equipped with the appropriate lamps and/or a Hanau Q 400 Mercury source. The complex to be studied was placed in an evacuable quartz UV cell, and after degasing on a vacuum line the appropriate solvent was distilled on to the sample. Solutions for NMR studies were transferred inside an inert atmosphere glove box into the NMR tubes. NMR spectra were periodically recorded with a Bruker WH 90 spectrometer. Samples for ESR experiments were similarly prepared. The ESR experiments were carried out with a Bruker ER 200 D spectrometer. Mass spectra were obtained with an AEI MS 902 mass spectrometer. GLC analyses were carried out with a Perkin–Elmer 990 chromatograph. All kinetic runs were carried out by monitoring the photoreactions by ^{31}P NMR spectroscopy. The quantum yield calculation was based on two actinometric measurements, performed in the reaction cell before and after each photochemical run.

Photolysis of $[(PPh_3)_2Pt(C_2H_4)]$ (I). Irradiation of I in halocarbon solvents RX (RX = CH_2Cl_2, CH_2Br_2, CD_2Cl_2) with λ 334 nm induced a color change from yellow to cream. Mass spectral analysis of the gases above the irradiated solutions showed the presence of C_2H_4 [3]. The ^1H and ^{31}P NMR spectra of the irradiated solutions showed only the presence of resonances typical of $[(PPh_3)_2Pt]$. Similar behavior was observed for complex II.

Prolonged photolysis (3 h) of solutions of I led to bleaching of the initial cream color. The solution was in each case concentrated by solvent evaporation in a stream of N_2 and *cis*-$[(PPh_3)_2Pt(CH_2Cl)Cl]$ (Va) was crystallized by gradual addition of benzene. After removal of the *cis*-isomer by filtration the solvent was evaporated from the solution to yield *trans*-$[(PPh_3)_2Pt(CH_2Cl)Cl]$ (Vb). Identification [4] of the *trans*- and *cis*-isomers was principally by ^1H and ^{31}P NMR spectroscopy (Table 1).

Photolysis of trans-$[(PPh_3)_2Pt(CH_2Cl)Cl]$ (Vb). No thermal isomerization of Vb to the *cis* form occurred during several days at 20°C. A 1 h irradiation (λ 280 nm) of Vb (5×10^{-2} mol dm^{-3} in CD_2Cl_2 gave the following ^{31}P NMR changes: original solution, −27.25 ppm (relative to H_3PO_4); irradiated solution, reduced intensity at −27.25 ppm, new peak at −19.00 ppm. The observed shift of the ^{31}P resonance is

TABLE 1

NMR PARAMETERS FOR $[(PPh_3)_2Pt(CH_2Cl)Cl]$

Parameter	Va	Vb
$\delta(CH_2)$[a], ppm	3.48 (dd)	2.95
J(Pt-H)[a], Hz	50	54
J(P-H)[a], Hz	2.5	8.5
P-shift[b], ppm	19.0 (d)	27.2 (s)
J(Pt-P)[b], Hz	4460	3140

[a] ^1H NMR spectrum in CH_2Cl_2, 20°C, TMS int. [b] ^{31}P NMR spectrum in CD_2Cl_2, 20°C, shift relative to external H_3PO_4.

the same as that found for the *trans–cis*-isomerization of similar complexes [11,12]. A ^{31}P NMR profile of the photoreaction indicated the absence of the free-ligand ^{31}P resonance at 33 ppm. These results indicate that the only photochemical process occuring is that shown in eq. 1.

$$\underset{\text{(Vb)}}{trans\text{-}\left[(PPh_3)_2Pt(CH_2Cl)Cl\right]} \xrightarrow{h\nu} \underset{\text{(Va)}}{cis\text{-}\left[(PPh_3)_2Pt(CH_2Cl)Cl\right]} \tag{1}$$

Photolysis of cis-[(PPh₃)₂Pt(CH₂Cl)Cl] (Va). Irradiation (254 nm) of Va in CD_2Cl_2 caused no photochemical isomerization. The only product isolated was $[(PPh_3)_2PtCl_2]$ (VI), which was formulated as the *cis* complex on the basis of spectroscopic properties [11]. Analysis of the ^1H NMR of the irradiated Va solution showed the presence of free C_2H_4, indicating bimolecular ethylene elimination (eq. 2).

$$2cis\text{-}\left[(PPh_3)_2Pt(CH_2Cl)Cl\right] \xrightarrow{h\nu} 2cis\text{-}\left[(PPh_3)_2Cl_2\right] + C_2H_4 \tag{2}$$

Photolysis of [(PPh₃)₂Pt(C₂H₄)] (I) in CH₂Br₂. A solution of I (0.15 mol dm^{-3}) in CH_2Br_2 was photolyzed at 365 nm for 4 h. C_2H_4 production was observed by mass spectroscopy. The solvent was then quickly removed and replaced by CD_2Cl_2 and the ^{31}P NMR spectrum was recorded. Two platinum containing species were identified, $[(PPh_3)_2Pt(CH_2Br)Br]$ (18.4 ppm, J(Pt–P) 4350 Hz) and $[(PPh_3)_2PtBr_2]$. The presence of $[(PPh_3)_2Pt(CH_2Br)Br]$ was confirmed by the appearance of a set of signals in the ^1H NMR spectra centered at δ 3.45 (J(Pt–H) 44.5 Hz, J(P–H) 6.8 Hz).

Photolysis of 1,4-tetramethyleneplatinum(II) derivatives [L₂Pt(CH₂)₄] (III, L = PPh₃; IV, L = P(n-Bu)₃). Photolysis of degassed CH_2Cl_2 solutions of III and IV with 313-nm light caused a rapid color change from white to pale yellow. GLC of the irradiated solutions showed the presence of substantial amounts of cyclobutane and 1- and 2-butene; relative yields (%) were: III: cyclobutane 7, 1-butene 80, 2-butene 13; IV: cyclobutane 48, 1-butene 50, 2-butene 2.

^{31}P NMR analysis of the irradiated (1 h) CH_2Cl_2 solutions indicated the presence of the *trans*-species $[L_2Pt(CH_2Cl)Cl]$ (Vb, L = PPh_3; IX, L = $P(n\text{-}Bu)_3$: ^{31}P NMR, δ 14.5 ppm, J(Pt–P) 2710 Hz). ^{31}P NMR spectroscopic examination of solutions obtained after prolonged (3 h) photolysis of III and IV in CH_2Cl_2 indicated the presence of three platinum-containing species: *trans*-$[L_2Pt(CH_2Cl)Cl]$, *cis*-

$[L_2Pt(CH_2Cl)Cl]$ and $[L_2PtCl_2]$. Concentration and cooling of the CH_2Cl_2 solution obtained by irradiation (6 h) gave a solid which was identified as *cis*-$[L_2PtCl_2]$. Mass spectral analysis of the gases above the irradiated solutions showed substantial amounts of C_2H_4.

Mechanistic studies

(i) ESR experiments. Attempts were made to assess the role of radical pathways in the photochemically induced oxidative-addition of CH_2Cl_2 to $[L_2Pt]$ ($L = PPh_3$, $P(p\text{-}C_6H_4CH_3)_3$, $n\text{-}Bu_3P$) intermediates as follows. Irradiation (λ 313 nm) of an ESR cavity containing degassed solution (2×10^{-2} *M*) of the compound (I, II, III, IV) and N-t-butyl-α-phenylnitrone (10^{-3} *M*, at which concentration light absorption by the spin-trap is negligible) led, after an induction period which corresponded to the photoproduction of $[L_2Pt]$ intermediates, to an 12-line spectrum. This is attributed to the spin-trapped platinum(I) complex, $L_2Pt(CHPhN(O)Bu^t)Cl$ [13]. The hyperfine coupling constants (to ^1H, ^{14}N and ^{195}Pt) are reported in Table 2.

(ii) Experiments with galvinoxyl, a free radical inhibitor. Galvinoxyl ($GO^\cdot$) has been found to inhibit the addition of certain alkyl halides to some Rh^I, Pd^0 and Pt^0 complexes, this being evidence for a radical mechanism [7,10]. In this work, $[L_2Pt(C_2H_4)]$ and $[L_2Pt(CH_2)_4]$ photoreactions in the presence or absence of $GO^\cdot$ were monitored by ^{31}P NMR using ^{31}P resonances characteristic of the original complex and its products. It was found that photoproduction of platinum(II) complexes $[L_2Pt(CH_2Cl)Cl]$ was inhibited by ca. 1% of $GO^\cdot$ in CH_2Cl_2. This is not due to reaction or complexation of the platinum compounds with the inhibitor since the intense galvinoxyl absorption at 425 nm is unchanged. The observation of inhibition is evidence for a radical reaction pathway for photoinduced oxidative addition of CH_2Cl_2 to platinum(0) species.

(iii) Quantum yields. Measurement of the apparent quantum yield for $[(PPh_3)_2Pt(CH_2Cl)Cl]$ formation at 334 nm using I in CH_2Cl_2 gave a value of 0.45 ± 0.02 which is very low compared with those observed in radical chain mechanisms ($\phi > 1$) [14]. This points to the existence of a radical non-chain mechanism.

Quantitative measurements were also carried out in 10, 15, and 25% CH_2Cl_2/THF solvent mixtures and showed that the apparent quantum yield for $[(PPh_3)_2Pt(CH_2Cl)Cl]$ formation generally decreases with increasing THF concentration. Rough estimation of product ratios, by ^{31}P NMR spectroscopy based on the average of 4 experiments, using I in a CH_2Cl_2/THF binary mixture, gave:

TABLE 2

ESR PARAMETERS FOR THE SPIN ADDUCT $L_2Pt(CHPhN(O)Bu^t)Cl$ [a,b]

L	$a(^1H)$ (mT)	$a(^{14}N)$ (mT)	$a(^{195}Pt)$ (mT)
PPh_3	0.40	1.48	0.35
$P(p\text{-}C_6H_4CH_3)$	0.40	1.48	0.41
$n\text{-}Bu_3P$	0.38	1.42	0.55

[a] Spectra recorded in CH_2Cl_2 at 18°C. [b] A photodecomposition of the spin adduct was observed when non-monochromatic light was used.

$[(PPh_3)_2Pt(CH_2Cl)Cl]$ as sole product in CH_2Cl_2; $[(PPh_3)_2PtCl_2]/[(PPh_3)_2Pt(CH_2Cl)Cl] = 2.6$ in 8/2 CH_2Cl/THF. The platinum(II) complex product ratio seems very sensitive to the presence of THF. This partitioning is probably affected by several factors, especially solvent participation in the photoinduced oxidative addition reaction and the fate of the solvent-derived radical $^{\bullet}CH_2Cl$.

Discussion

The new results reported pertain mainly to the mechanism of photochemistry of I, II, III and IV complexes. Previous photochemical studies showed that I undergoes quantum efficient ethylene dissociation upon photolysis leading to the 14-valence electron $[(PPh_3)_2Pt]$ intermediate [3,4]. Depending on the conditions used (solvent, wavelength of irradiation) the intermediate can undergo an oxidative addition and form an alkylplatinum(II) complex by an insertion. Equations 3-9 represent the experimental observations and current speculations about the course of the photochemical reactions of phosphineplatinum(0) (I, II) and platinum(II) (III, IV) complexes.

$$[L_2Pt(C_2H_4)] \xrightarrow{h\nu} [L_2Pt] + C_2H_4 \tag{3}$$

$$[L_2Pt(CH_2)_4] \xrightarrow{h\nu} [L_2Pt] + \text{alkanes} + \text{alkenes} \tag{4}$$

$$[L_2Pt] + CH_2Cl_2 \xrightarrow{h\nu} [L_2Pt^I]^{\bullet +}[CH_2Cl_2]^{\bullet -} \tag{5}$$

$$[L_2Pt^I]^{\bullet +}[CH_2Cl_2]^{\bullet -} \xrightarrow{h\nu} [L_2Pt^ICl] + {}^{\bullet}CH_2Cl \tag{6}$$

$$[L_2Pt^ICl] + {}^{\bullet}CH_2Cl \rightarrow \textit{trans-}[L_2Pt(CH_2Cl)Cl] \tag{7}$$

$$[L_2Pt(CH_2Cl)Cl] \xrightarrow{h\nu} \textit{cis-}[L_2Pt(CH_2Cl)Cl] \tag{8}$$

$$2[L_2Pt(CH_2Cl)Cl] \xrightarrow{h\nu} 2[L_2PtCl_2] + C_2H_4 \tag{9}$$

The major pathway from $[L_2Pt(C_2H_4)]$ and $[L_2Pt(CH_2)_4]$ to $[L_2Pt]$ intermediates, involving formation of $[L_2Pt(CH_2Cl)Cl]$ by oxidative addition of CH_2Cl_2 to $[L_2Pt]$ and decomposition of the *cis*-isomers $[L_2Pt(CH_2Cl)Cl]$ by elimination of C_2H_4 is supported by five experimental observations. First, irradiation of I and II leads to loss of C_2H_4, while III and IV undergo photoinduced elimination of alkanes and alkenes. The ^1H and ^{31}P NMR spectra show that the primary photoproduct of reaction 3 and 4 is the 14-electron-valence species $[L_2Pt]$. Second, oxidative addition compounds $[L_2Pt(CH_2Cl)Cl]$ derived from CH_2Cl_2 and $[L_2Pt]$ intermediates can be isolated (for $L = PPh_3$) or detected as intermediates ($L = P(n\text{-}Bu)_3$) in the prolonged photolysis of III and IV. Third, radical trapping experiments, the effect of a radical inhibitor, and quantum yields measurements are in agreement with expectations for a radical pathway involving initial electron transfer (eq. 5) for the photoinduced oxidative addition of CH_2Cl_2 to $[L_2Pt]$ (eq. 7). Fourth, irradiation of $[L_2Pt(CH_2Cl)Cl]$ at 254 nm causes conversion into a *cis*-isomer (eq. 8). In some cases the expected *cis*-isomer is observed only in mixtures with the *trans* form and $[L_2PtCl_2]$, possibly because the sequential photochemical processes are too rapid.

Fifth, the *cis*-isomer $[L_2Pt(CH_2Cl)Cl]$ undergoes photoinduced reductive elimination of C_2H_4 to form the final product $[L_2PtCl_2]$ upon photolysis at 254 nm. Monitoring of the ^1H and ^{31}P NMR spectra during the photoreactions indicates that photoisomerization (eq. 8) occurs prior to the bimolecular reductive elimination of C_2H_4 (eq. 9). For $[L_2Pt]$ intermediates in CH_2Cl_2 all the evidence presented in this and in previous papers [3,4] involving use of a radical inhibitor, trapping of $[L_2Pt^ICl]$ species by PBN, and determination of the quantum yields of the photoinduced addition reactions supports the occurrence of a radical non-chain pathway.

From the results it seems that halogen abstraction to generate a halogen platinum(I) intermediate and the $^{\cdot}CH_2Cl$ radical (eq. 6) is the key reaction. Such an abstraction of halide from RX takes place by means of an electron-transfer step (eq. 5) similar to that proposed for alkyl halide addition to iridium(I) [10] and platinum(0).

The reaction of eq. 6 is assumed to be rate determining, since the rate has been found to depend on the halogen (much greater for CH_2Br_2 than CH_2Cl_2). This is reasonable, because capture of the $^{\cdot}CH_2Cl$ radical by unsaturated metal centers (eq. 7) is much more quicker than halide abstraction by $[L_2Pt]$ species.

The observation that the use of a CH_2Cl_2/THF mixture as solvent promotes the formation of L_2PtCl_2 at the expense of $[L_2Pt(CH_2Cl)Cl]$ is consistent with the proposed mechanism. The radical $^{\cdot}CH_2Cl$ rapidly abstracts a hydrogen atom from THF to generate a bulky radical [7]; this attacks the $[(PPh_3)Pt^ICl]$ less effectively, and hence dihalide formation is increasingly favoured over the formation of $[(PPh_3)_2Pt(CH_2Cl)Cl]$ observed in pure CH_2Cl_2.

The reactions postulated in equations 3–9 suggest two conclusions. First, it appears that reductive elimination–oxidative addition sequences are important photoreactions in platinum(0) and platinum(II) organometallic chemistry. Second, since other processes (isomerization, orthometallation, insertion reactions) are also photochemically accelerated [3,5], care must be taken in the choice of solvent and the use of the irradiation wavelength.

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