Journal of Organometallic Chemistry, 241 (1983) 119–130
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOCHEMISTRY OF SOME ALKOXYCARBONYLPLATINUM(II) COMPLEXES

CONRAD F. SHIBA * and WALTER H. WADDELL

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213 (U.S.A.)

(Received March 29th, 1982)

Summary

Alkoxycarbonylplatinum(II) complexes *trans*-$Pt(CO_2CH_2R)Cl(PPh_3)_2$, where R = H, Me and Ph, were synthesized in two steps and were characterized by infrared and ultraviolet absorption, proton and phosphorus-31 nuclear magnetic resonance, and mass spectral techniques, and by elemental analysis. Irradiation of the complexes in the solid state or in fluid solution with 254 nm light causes a steady decrease in the intensities of the infrared absorptions in the 1650 and 1070 cm^{-1} regions, which is interpreted as signifying labilization of the alkoxycarbonyl ligand. In dichloromethane solution, irradiation causes dissociation of the alkoxycarbonyl ligand, which then decomposes into carbon monoxide and an alkoxide ion. The carbon monoxide is thought to re-coordinate to afford the stable product *trans*-$PtCl(CO)(PPh_3)_2^+$. In the presence of oxygen, triphenylphosphine which dissociates from the metal, is photooxidized to form triphenylphosphine oxide in a parallel photoreaction. Disappearance quantum yields for the alkoxycarbonyl complexes are quite small, $\Phi \sim 10^{-4}$–10^{-3} mol/einstein, and follow the trend H > Me > Ph.

Introduction

Although thermal substitution reactions of square-planar complexes of platinum(II) have been extensively studied and systematized [1–3], corresponding photochemical reactions have been examined for only a limited number of systems. Yet, a variety of interesting photochemical reactions have been reported [4–6] including aquation [7–10], dimerization [11–13], oxidation-reduction [14–16], *ortho*-metalation [17], photosubstitution [13, 18–20], and *cis-trans* isomerization [7, 8, 13, 21–28] reactions. Many of these reactions proceed via the formation of highly reactive, coordinatively unsaturated transients. Since intermediates of this nature are postulated to participate in many homogeneous catalysis schemes, it is of interest to

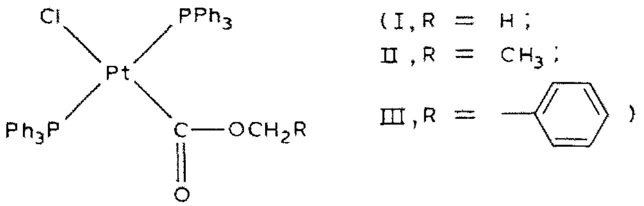
---

* Address correspondence to this author at the Department of Chemistry, Centre College, Danville, Kentucky 40422.

0022-328X/83/0000–0000/$03.00

investigate the photochemistry of square-planar d^8 complexes of platinum(II), particularly those containing organic ligands.

Since alkoxycarbonyl complexes have been postulated as intermediates in oxo-type catalytic reactions [29–31], the investigation of their chemical and physical properties has been of interest [32]. A number of alkoxycarbonyl complexes of platinum(II) have been prepared [33–41] and their thermal chemistry examined; however, the photochemical properties of these compounds have not been investigated. Hence, we have examined the spectroscopic and photochemical properties of alkoxycarbonyl complexes of platinum(II), which represent stable derivatives of metalated formic acid. In particular, we have prepared and characterized the *trans* isomers of chloro(alkoxycarbonyl)bis(triphenylphosphine)platinum(II), where the alkyl group is methyl (structure I), ethyl (II) and benzyl (III) and have studied their solution photochemistry. Ultraviolet absorption spectroscopy and difference infrared spectroscopy were employed to identify the reaction products and gain insight into their mechanism of formation.



Results

Preparation and characterization

trans-Chloro(methoxycarbonyl)bis(triphenylphosphine)platinum(II) (I), *trans*-chloro(ethoxycarbonyl)bis(triphenylphosphine)platinum(II) (II), and *trans*-(benzoxycarbonyl)chlorobis(triphenylphosphine)platinum(II) (III) were prepared in two steps using a modification of the procedure of Clark and coworkers [33, 34]. The desired intermediate carbonyl complex *trans*-$[\mathrm{PtCl(CO)(PPh_3)_2}]\mathrm{PF_6}$ (IV) was synthesized directly from *cis*-dichlorobis(triphenylphosphine)platinum(II) in nearly quantitative yield following the procedure of Church and Mays [42], eq. 1.

$$\mathrm{PtCl_2(PPh_3)_2} + \mathrm{NH_4PF_6} \xrightarrow[\text{1 atm}]{\mathrm{CO}} trans\text{-}\underset{\text{(IV)}}{[\mathrm{PtCl(CO)(PPh_3)_2}]\mathrm{PF_6}} + \mathrm{NH_4Cl} \qquad (1)$$

IV reacts with alcohols to form the corresponding alkoxycarbonyl complexes (eq. 2).

$$[\mathrm{PtCl(CO)(PPh_3)_2}]\mathrm{PF_6} + \mathrm{ROH} \rightleftarrows trans\text{-}\mathrm{Pt(CO_2R)Cl(PPh_3)_2} + \mathrm{HPF_6} \qquad (2)$$

The room temperature ultraviolet absorption spectrum of IV in dichloromethane exhibits an absorption maximum at 285 nm ($\epsilon = 2.17 \times 10^4$ M^{-1} cm^{-1}) and a shoulder at 309 nm ($\epsilon = 1.44 \times 10^4$ M^{-1} cm^{-1}) [37]. The UV spectra of I–III are similar, Table 1. The UV spectrum of I in aerated dichloromethane solution is illustrated as Fig. 1, which shows a series of three shoulders in the region 255–275 nm with extinction coefficients of the order of 10^4 M^{-1} cm^{-1} superimposed upon the tail of a very intense absorption at shorter wavelengths. There are no assignable

TABLE I

ULTRAVIOLET SPECTRAL DATA [a]

Complex	λ_{max} (nm)	$\epsilon \times 10^{-4}$ M^{-1}cm^{-1}
I, $Pt(CO_2CH_3)Cl(PPh_3)_2$	257	2.3
	268	1.6
	275	1.1
II, $Pt(CO_2C_2H_5)Cl(PPh_3)_2$	255	2.3
	267	1.6
	275	1.1
III, $Pt(CO_2CH_2C_6H_5)Cl(PPh_3)_2$	257	2.3
	268	1.7
	275	1.2
IV, $[PtCl(CO)(PPh_3)_2]PF_6$	285	2.2
	309	1.4

[a] Approximately 10^{-4} M solutions in CH_2Cl_2, room temperature.

features at wavelengths longer than 300 nm.

The IR spectra of I–III exhibit bands arising from vibrations of the coordinated triphenylphosphine ligands [43]. The IR spectrum of IV exhibits an intense band at

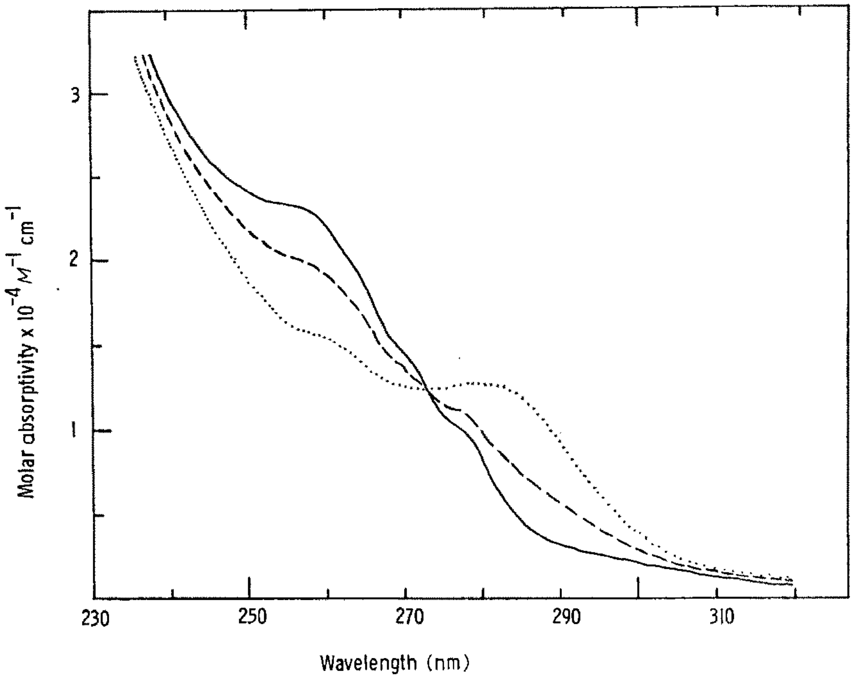


Fig. 1. Room temperature ultraviolet absorption spectra of *trans*-chloro(methoxycarbonyl)bis(triphenylphosphine)platinum(II) (I) in aerated dichloromethane solution were recorded as a function of irradiation time using 60–120 seconds excitation intervals for up to one hour. Representative spectra are displayed: (————)nonirradiated; (- - - - - -) after 280 seconds of 254 nm irradiation; (· · · · · ·) after 760 seconds of 254 nm irradiation.

2100 cm^{-1}, characteristic of a terminal carbonyl ligand in a cationic complex, and a very strong, broad band centered at 835 cm^{-1}, which is attributed to the PF$_6^-$ anion [44] (literature value of 2120 cm^{-1} [34]). The IR spectra of I (Fig. 2A), II, and III are similar, exhibiting characteristic absorptions in the 1630–1660 cm^{-1} region and the 1060–1075 cm^{-1} region, assigned to the C=O and C–O vibrations, respectively, of a coordinated alkoxycarbonyl ligand. Compounds I–III are assigned *trans* stereochemistry based upon the lack of a strong infrared absorption in the 550 cm^{-1} region [45].

The proton NMR spectrum of I is consistent with that reported by Clark et al. [34], although coupling of the methoxy protons to ^{195}Pt ($I = 1/2$, 33.8% abundance) was not clearly observed. The phosphorus-31 NMR spectrum consists of an approximately 1/4/1 triplet centered at 19.08 ppm (with respect to external H_3PO_4), ^1J(Pt-P) 3061 Hz. The splitting pattern of the resonance signal and the coupling constant are consistent with *trans* geometry for the complex [46]. NMR spectral data are presented in Table 2.

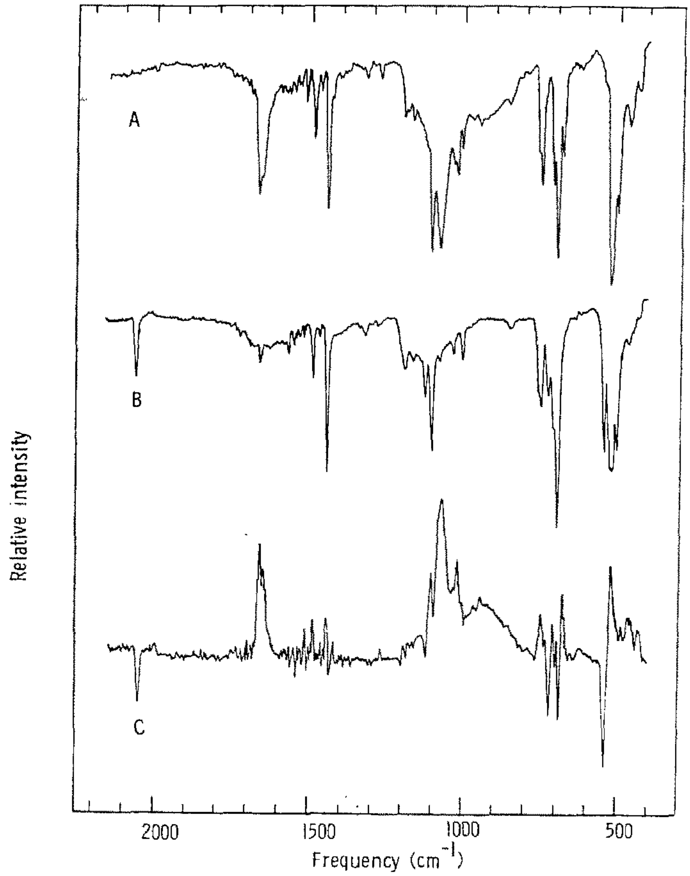


Fig. 2. Infrared spectra of *trans*-chloro(methoxycarbonyl)bis(triphenylphosphine)platinum(II) (I) were recorded as a function of irradiation time using 120–900 sec excitation periods for up to 3 h: (A) nonirradiated; (B) after 900 sec of 254 nm irradiation of a deaerated dichloromethane solution; (C) difference spectrum of A minus B.

TABLE 2

NMR SPECTRAL DATA [a]

Complex	Proton			Phosphorus-31	
	$\tau(CH_3)$	$\tau(CH_2)$	$\tau(C_6H_5)$	δ	^1J(Pt-P) (Hz)
I, $Pt(CO_2CH_3)Cl(PPh_3)_2$	7.66(s)	–	2.22, 2.62(m)	19.08	3061
II, $Pt(CO_2C_2H_5)Cl(PPh_3)_2$	9.56	7.29	2.20, 2.53(m)	–	–
III, $Pt(CO_2CH_2C_6H_5)Cl(PPh_3)_2$	–	6.34(s)	2.24, 2.66(m)	18.74	3061
IV, $[PtCl(CO)(PPh_3)_2]PF_6$	–	–	2.12, 2.32(m)	20.40	2035

[a] $CDCl_3$ + 1% TMS solutions.

Mass spectral data of I (solid samples, direct inlet probe), exhibited only a very weak molecular ion peak ($m/e = 813$) under the conditions employed. Fragments containing platinum and chlorine gave rise to clusters of peaks owing to isotope effects. Peaks corresponding to primary fragmentation products were observed at m/e values of 785, 782, and 754. The most significant primary fragmentation process appears to be the loss of the methoxycarbonyl ligand, with loss of the methoxide group or carbon monoxide apparently also observed (15/8/4 ratio). Primary fragmentation patterns involving the presumed loss of chloride ion, or molecular benzene or carbon dioxide are not observed. As in the case of the methoxycarbonyl complex, loss of the ethoxycarbonyl ligand is the most important primary fragmentation process of II. III reveals a loss of a fragment with molecular weight corresponding to that of the alkoxycarbonyl ligand as the predominant initial process, Table 3. The mass spectra of complexes I–III are dominated by fragments of lower mass number ($m/e < 400$) with a base peak at $m/e = 262$, probably corresponding to the triphenylphosphine ion.

Photochemistry

In an initial investigation, room temperature photochemical studies of I were made in dichloromethane and tetrahydrofuran solutions and in the solid state. Pressed KBr wafers of I were irradiated with unfiltered light from a medium

TABLE 3

MASS SPECTRAL DATA

Assignment	I		II		III	
	m/e	relative intensity	m/e	relative intensity	m/e	relative intensity
M^+	813	1	827	2	889	< 1
$M-CO$	785	4	799	1	861	< 1
$M-Cl$	778	< 1	792	5	854	6.5
$M-CO_2$	769	< 1	783	11	845	< 1
$M-OCH_2R$	782	8	782	10	782	< 1
$M-CO_2CH_2R$	754	15	754	22	754	98
$M-PPh_3$	551	1	565	2	627	1

pressure mercury arc. IR spectra were recorded prior to and at intervals between irradiations. The only notable spectral changes were the steady decrease in intensity of the 1665 and 1075 cm^{-1} bands with increasing irradiation time.

The photochemistry of I in tetrahydrofuran solutions was examined upon excitation with 254 nm light. However, in both aerated or deaerated solution it was not possible to deduce structural information based upon the observed spectral changes, which were difficult to reproduce.

Aliquots of a 10^{-4} *M* aerated solution of I in dichloromethane were irradiated with 254 nm light and UV spectra recorded. After 60 sec of irradiation, the absorption intensity of the 257 nm band maximum decreased while the absorption in the 280–290 nm region increased (Fig. 1). Irradiation for up to 760 sec reveals the presence of an isosbestic point (273 nm) as a new species with an absorption maximum at 283 nm is formed. Upon prolonged irradiation, the intensity of the 283 nm band steadily decreases and the isosbestic point is no longer maintained. The quantum efficiency of disappearance of I is 0.002 ± 0.0006, determined within an irradiation time span in which the isosbestic point was maintained.

Upon irradiation of aerated dichloromethane solutions of I with 254 nm light, changes are observed in its IR spectrum. After 100 sec of irradiation, a decrease in the intensities of the alkoxycarbonyl vibrational bands at 1665 and 1075 cm^{-1} is observed, and a weak band has appeared at 2100 cm^{-1}. After irradiating for a total of 760 sec the bands at 1665 and 1075 cm^{-1} have totally disappeared, and the band at 2100 cm^{-1} attains its maximum intensity, then decreases with further irradiation. Upon irradiation, additional infrared absorptions appear at 1185, 1120, 724, and 543 cm^{-1}. These bands have been presented as evidence of the formation of triphenylphosphine oxide [47].

Difference infrared spectroscopy was used in order to more clearly ascertain the changes occurring in the IR spectrum of I upon irradiation of deaerated dichloromethane solutions, Fig. 2. It can be clearly seen that the bands at 1665, 1075, and 520 cm^{-1} in the spectrum of the nonirradiated complex decreased in intensity upon irradiation, while new bands at 2100 and 543 cm^{-1} appeared upon irradiation, Fig. 2C. The band at 2100 cm^{-1} displays interesting behavior in that it appears within 300 sec and steadily increases in intensity with irradiation times of up to 1200 sec, then decreases in intensity, disappearing after 2400 sec of irradiation.

To verify that the observed behavior of I is in fact due to a photochemical rather than a thermal reaction, a dichloromethane solution of the complex was saturated with carbon monoxide gas at ambient pressure and maintained at room temperature for 1 h. After evaporation of the solvent, the infrared spectrum was found to be unchanged from that of the starting material. Hence, thermal substitution of carbon monoxide for the methoxycarbonyl ligand does not readily occur at room temperature. When a carbon monoxide-saturated solution of the complex was irradiated with 254 nm light for 1800 sec the infrared spectral changes observed were similar to those observed for deaerated solutions, but the 2100 cm^{-1} band was more intense in the case of the CO-saturated solution. The 2100 cm^{-1} band is not observed upon irradiation in the solid state (KBr pellet).

That this photochemical behavior is general is illustrated by irradiation of II and III. Upon irradiation of aerated 10^{-4} *M* dichloromethane solutions of II and/or III, their UV spectra exhibit decreases in absorption intensity in the 250–260 nm region and increases in absorption intensity in the 280–290 nm region. Isosbestic points of

272 and 275 nm are maintained at irradiation times of up to 720 sec for II and up to 1720 sec for III. At longer irradiation times, the absorption intensity in the 280–290 nm region steadily decreases. The quantum yields for disappearance of II and III in aerated dichloromethane solutions upon 254 nm irradiation are 0.001 ± 0.0003 and 0.0004 ± 0.0002, respectively.

When deaerated solutions of II or III are irradiated with 254 nm light, the IR spectra exhibit changes similar to those observed for I. The alkoxycarbonyl bands steadily decrease in intensity upon irradiation and disappear after ca. 1000 sec of irradiation. A new absorption at 2100 cm^{-1} appears within ca. 300 sec, attains maximum intensity after ca. 1000 sec, and decreases in intensity with longer irradiation times. At long irradiation times, the IR spectra of all three alkoxycarbonyl complexes showed evidence of triphenylphosphine oxide formation (bands at 1185, 1120, 724 and 543 cm^{-1}). These bands are even obtained in deaerated solutions, but to a lesser extent. Oxide formation is thought to result from incomplete removal of oxygen upon argon bubbling since photooxidation of free triphenylphosphine in solution is reported to be extremely facile [47].

Discussion

The isosbestic point in the electronic absorption spectra (Fig. 1) indicates that a two-component system is initially formed upon irradiation of I. The simultaneous growth of the band at 2100 cm^{-1} and decrease in the bands at 1665 and 1075 cm^{-1} provide IR spectral evidence that a carbonyl complex is probably formed at the same time that the methoxycarbonyl ligand disappears. The carbonyl complex is postulated to be the cationic carbonyl complex $PtCl(CO)(PPh_3)_2^+$, essentially the synthetic precursor, IV. The IR spectrum of *trans*-$[PtCl(CO)(PPh_3)_2]PF_6$ (IV), exhibits a carbonyl absorption at 2100 cm^{-1}. The bathochromic shift in the ultraviolet spectrum of $Pt(CO_2CH_3)Cl(PPh_3)_2$ upon irradiation is also consistent with the formation of a cationic complex, since the electronic absorption spectrum of IV exhibits an absorption maximum at 285 nm, Table 1.

It should be noted that it is not possible to make a direct time correlation of the electronic and infrared absorption spectral changes since the volumes and cell path lengths for the irradiated samples differed. However, parallel photochemical behavior is observed in that new bands are formed which increase in intensity with increasing irradiation time but later decrease with continued irradiation. These general results occur for aerated and deaerated solutions.

The photochemical behavior of II and III in dichloromethane solution parallels that of $Pt(CO_2CH_3)Cl(PPh_3)_2$ (I), in every respect except the rate of reaction. The parallel decrease and increase in intensities of new absorptions in both the electronic and infrared absorption spectra with increasing irradiation time is similar to the observed behavior of the methoxycarbonyl derivative. The new bands at 2100 cm^{-1} in the IR spectra and in the 280 nm region of the electronic absorption spectra of both II and III upon irradiation are both consistent with the formation of a carbonyl complex, postulated to be *trans*-$PtCl(CO)(PPh_3)_2^+$ (IV) as the initial photoproduct.

It is possible that the proposed photochemical intermediate IV may be formed by direct photodissociation of a methoxide anion from I. This reaction would then be similar to the thermal reaction of I with strong acids for which Byrd and Halpern

[37] report that IV is obtained, eq. 3.

$$Pt(CO_2CH_3)Cl(PPh_3)_2 + H^+ \rightarrow PtCl(CO)(PPh_3)_2^+ + CH_3OH \quad (3)$$

An alternative pathway can be suggested, namely photodissociation to a methoxycarbonyl anion and the coordinatively unsaturated species $PtCl(PPh_3)_2^+$ (V), followed by rapid thermal dissociation of the anion into carbon monoxide and methoxide ion and subsequent coordination of carbon monoxide. Some support for this mechanism may be derived from the observations that the infrared absorptions of the methoxycarbonyl ligand of I disappear after ca. 900 sec of irradiation, whereas the infrared band of the carbonyl ligand continues to increase in intensity with up to ca. 1200 sec of irradiation. In addition, mass spectral studies of I indicate that loss of a component with a *m/e* ratio of 59 is a major primary fragmentation process. No loss of a component with *m/e* ratio of 31 is observed. Hence, under the high energy conditions of the mass spectral experiments, the entire methoxycarbonyl ligand is labile. That the latter photodissociation may be important is supported by the photochemical behavior of II and III, which apparently undergo very similar photochemical behavior to I. Mass spectral experiments on II and III show the presence of peaks that may correspond to the loss of $CO_2C_2H_5$ and $CO_2CH_2C_6H_5$ as major reaction pathways.

Yet a third mechanism can be considered, namely initial dissociation of triphenylphosphine and rearrangement of the alkoxycarbonyl ligand to form $PtCl(OCH_3)(CO)(PPh_3)$ (VI); subsequent substitution of triphenylphosphine for methoxide would then afford IV. Triphenylphosphine oxide formation may support this mechanism; however, the isosbestic point in the UV spectra indicates that upon irradiation of I a two-species equilibrium is initially established and the UV and IR spectral properties of the primary photochemical product are essentially those of IV.

Alternatively, analysis of the IR spectral data of irradiated samples of I may provide some evidence of another photochemical reaction. A band at 543 cm^{-1} steadily increased in intensity with increasing irradiation time and, while the origin of this band is unclear, it gains intensity out of proportion to the other triphenylphosphine oxide bands in the present case. Since it has been postulated that a strong absorption at 550 ± 5 cm^{-1} denotes *cis* stereochemistry in bis(triphenylphosphine)platinum(II) complexes [45], this band may be evidence for *trans–cis* isomerization of the complex upon irradiation. However, the electronic absorption spectral changes observed upon irradiation are not readily explained if isomerization is the major photochemical reaction. The isosbestic point suggests the probable presence of only two absorbing species, one of which is evidently the carbonyl complex $PtCl(CO)(PPh_3)_2^+$. The infrared absorption at 2100 cm^{-1} is consistent with *trans* stereochemistry for this complex. In addition, while it is known that upon irradiation of *trans*-chlorophenylbis(triethylphosphine)platinum(II) a *trans–cis* photoisomerization occurs, the electronic absorption spectrum of the *cis* isomer has a lower ϵ_{280} than that of the trans isomer [48], behavior opposite to that observed upon irradiation of I–III.

It is noteworthy that the major reaction observed upon irradiation of alkoxycarbonylplatinum(II) complexes appears to be labilization of the alkoxycarbonyl ligand. Infrared spectral data for acylmetal complexes of Group VIII elements have been interpreted as an indication that acyl ligands exert a large *trans*-bond weakening effect in these complexes [49]. A similar effect might be expected for alkoxycarbonyl ligands, since they are structurally similar. While the Pt–Cl stretching band has not been assigned, the IR spectrum of I displays weak bands at 280, 252 and 227 cm^{-1}. Bands in this region are indicative of a strong *trans*-influence by the ligand *trans* to chloride [50]. The labilization of the alkoxycarbonyl ligand in preference to the chloride ligand is accordingly unusual. Similar unexpected photochemical behavior was observed in the case of $PtCl_3(C_2H_4)^-$, in which photoaquation of the ethylene ligand was observed [10]. It must be concluded that the thermal and photochemical behavior of these complexes are fundamentally different.

Experimental

Materials

Dichlorobis(triphenylphosphine)platinum(II) ($PtCl_2(PPh_3)_2$, Strem), ammonium hexafluorophosphate (NH_4PF_6, 96%, Alfa Ventron), ethanol (Rossville Gold Shield, IMC), and benzyl alcohol (99%, Aldrich), were all used as received. Absolute methanol (Baker) was dried over 3A molecular sieves. Dichloromethane (Baker) was dried over 4A molecular sieves for use in syntheses and was refluxed over phosphorus pentoxide and distilled through a 61-cm-long Pyrex column packed with glass helices for spectroscopic and photochemical use. Carbon monoxide (C. P., Matheson), and argon and oxygen (West Penn Laco) were used without further purification. Prepurified nitrogen gas (West Penn Laco) was dried by passage through a column containing anhydrous calcium sulfate (Drierite),

Instrumentation

Ultraviolet-visible absorption spectra were recorded on a Perkin–Elmer Model 575 spectrophotometer, correcting for solvent absorption and cell mismatch effects.

Infrared spectra were recorded on a Perkin–Elmer Model 580 spectrophotometer controlled by an Interdata Model 6/16 computer, using the Perkin–Elmer CDS-2 software. Samples were mounted as pressed potassium bromide or cesium iodide pellets, or evaporated films on a KRS-5 (TlBr-TlI) multiple internal reflection crystal (45° incidence angle, 25 reflections). Spectra were calibrated relative to bands of a polystyrene film and were recorded with a precision of ± 2 cm^{-1}. Flattening, smoothing, expansion, accumulated scans, and difference spectra were performed using the CDS-2 computer system. Difference spectra were normalized on the 1440 cm^{-1} band and presented in absorbance. Infrared spectra of irradiated solutions (typically 1.5–2 ml of 1×10^{-4} solution) were recorded after concentrating to a few drops. The solution was applied to a KRS-5 MIR crystal (52 × 20 × 2 mm), allowed to evaporate to dryness, placed in an evacuated dessicator for ten minutes, then removed and mounted in the spectrophotometer. The instrument was purged with dry air or nitrogen gas for fifteen minutes and the spectrum recorded.

Proton magnetic resonance spectra were recorded at 250 MHz in the correlation mode using tetramethylsilane as internal reference and lock signal. Phosphorus-31 NMR spectra were observed at 101.2 MHz with chemical shifts relative to external aqueous phosphoric acid. (Positive δ values are downfield from H_3PO_4). All NMR spectra were recorded at room temperature.

Mass spectral data were obtained at 70 eV and 50°C on a Varian MAT 112 mass spectrometer. The instrument was calibrated with perfluorokerosene.

Syntheses

trans-Chlorocarbonylbis(triphenylphosphine)platinum(II) hexafluorophosphate, trans-$[PtCl(CO)(PPh_3)_2]PF_6$. 2.069 g (2.62 mmol) of $PtCl_2(PPh_3)_2$ and 0.44 g (2.68 mmol) of ammonium hexafluorophosphate was added to 150 ml of dichloromethane/acetone (2/1, v/v), purged with carbon monoxide and stirred at room temperature under a flow of carbon monoxide for 18 h. The precipitated ammonium chloride was removed by filtration and the volume of the filtrate reduced to about 25 ml. Upon cooling the filtrate in a freezer, the product formed as white crystals, which were collected on a fritted glass filter, washed with diethyl ether, and dried overnight in vacuo. Yield: 2.314 g, 95.3%. IR spectrum (KBr pellet): ν(C=O) 2100 s and ν(P–F of PF_6^-) 840 s,br cm^{-1} (Lit. [34] ν(C=O) 2120 cm^{-1}). Analysis (Galbraith Labs). Found: C, 46.95; H, 3.19; P, 9.93. $C_{37}H_{30}ClF_6OP_3Pt$ calcd.: C, 47.88; H, 3.26; P, 10.01%.

trans-Chloro(methoxycarbonyl)bis(triphenylphosphine)platinum(II), trans-$Pt(CO_2CH_3)Cl(PPh_3)_2$. 0.485 g (0.522 mmol) of $[PtCl(CO)(PPh_3)_2]PF_6$ was added to 50 ml of absolute methanol, stoppered, and stirred at room temperature for 4 h. The product was collected on a fritted filter, washed successively with 5 ml each of water, methanol, and diethyl ether, and dried overnight in vacuo. The crude product was recrystallized from a dichloromethane/hexane mixture, washed with diethyl ether, and dried in vacuo. Yield: 0.328 g, 77%. IR spectrum (KBr pellet): ν(C=O) 1665 s, ν(C–O) 1075 cm^{-1} vs (Lit. [34] 1664, 1060 cm^{-1}). Analysis. Found: C, 54.76; H, 4.12; Cl, 4.50; P, 7.66. $C_{38}H_{33}ClO_2P_2Pt$ calcd.: C, 56.06; H, 4.09; Cl, 4.35; P, 7.61%.

trans-Chloro(ethoxycarbonyl)bis(triphenylphosphine)platinum(II), trans-$Pt(CO_2C_2H_5)$-$Cl(PPh_3)_2$. 0.592 g (0.638 mmol) of $[PtCl(CO)(PPh_3)_2]PF_6$ and 50 ml of absolute ethanol was stirred at room temperature for 23 h. The precipitate was collected on a fritted filter, washed with 5 ml each of water, ethanol, and diethyl ether, and dried. The crude product was recrystallized from a dichloromethane/hexane mixture, washed with diethyl ether, and dried in vacuo. Yield of the white, crystalline product was 0.456 g, 86.3%. IR spectrum (KBr pellet): ν(C=O) 1630 s, ν(C–O) 1075 s, br cm^{-1} (Lit. [34] 1638, 1080 cm^{-1}). Analysis. Found: C, 56.30; H, 4.14. $C_{39}H_{35}ClO_2P_2Pt$ calcd.: C, 56.56; H, 4.26%.

trans-(Benzoxycarbonyl)chlorobis(triphenylphosphine)platinum(II), trans-$Pt(CO_2CH_2C_6H_5)Cl(PPh_3)_2$. 0.485 g (0.523 mmol) of $[PtCl(CO)(PPh_3)_2]PF_6$ and 0.058 g of sodium carbonate was diluted with 30 ml of dichloromethane and 20 ml of benzyl alcohol and stirred for 24 h. The reaction solution was concentrated, treated with diethyl ether and petroleum ether, and cooled in a freezer. The crystallized product was collected on a filter, washed with water, benzyl alcohol, and diethyl ether, and dried. Yield: 0.275 g, 59%. IR spectrum (KBr pellet): 1646 and 1061 cm^{-1}, bands attributed to the benzoxycarbonyl ligand (Lit. [37] 1642 cm^{-1}). Analysis. Found: C, 59.20; H, 4.24. $C_{44}H_{37}ClO_2P_2Pt$ calcd.: C, 59.36; H, 4.19%.

Photochemical procedures

The irradiation source used was a Hanovia 450-watt medium-pressure mercury-vapor immersion lamp (Ace Glass). Degassed fluid solutions were contained in long-stemmed quartz cells of 10-mm path length equipped with Teflon stopcocks. Solutions were deaerated by passing a fine stream of argon gas bubbles through the samples for 10 minutes with cooling to prevent excessive solvent loss. Oxygenated solutions were similarly prepared. Samples were also degassed using a vacuum line by freeze-pump-thaw cycles (– 196°C, four cycles each). Solid samples were mounted as pressed potassium bromide pellets. 254 nm radiation was isolated using combinations of chemical filters contained in cylindrical quartz cells of 10- and 20-mm path length. Samples were mounted directly behind the filters. Ferrioxalate actinometry was used to measure the lamp intensity for the purpose of determining quantum yields. Stock solutions of all platinum complexes studied were stored in a freezer and prepared and handled only under red illumination.

Acknowledgements

We wish to thank Mr. Andrew W. Steele for technical assistance and Professor Charles H. Van Dyke for helpful discussions on this work, and the Carnegie-Mellon University NMR Facility for Biomedical Studies (NIH RR 00292) for use of the 250 MHz NMR Spectrometer.

References

1 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd Ed., J. Wiley, New York, 1967, p. 351–453.
2 C.H. Langford and H.B. Gray, Ligand Substitution Processes, W.A. Benjamin, New York, 1966, p. 18–54.
3 G.K. Anderson and R.C. Cross, Chem. Soc. Rev., 9 (1980) 185.
4 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic, New York, 1970, p. 245–256; and ref. cited therein.
5 P.D. Fleischauer, A.W. Adamson and G. Sartori, Prog. Inorg. Chem., 17 (1972) 1; and ref. cited therein.
6 A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley-Interscience, New York, 1975; p. 237–247; and ref. cited therein.
7 V. Balzani and V. Carassiti, J. Phys. Chem., 72 (1968) 383.
8 J.R. Perumareddi and A.W. Adamson, J. Phys. Chem., 72 (1968) 414.
9 F. Scandola, O. Traverso, and V. Carassiti, Mol. Photochem., 1 (1969) 11.
10 P. Natarajan and A.W. Adamson, J. Am. Chem. Soc., 93 (1971) 5599.
11 F. Pesa and M. Orchin, Inorg. Chem., 14 (1975) 994.
12 P. Courtot, R. Rumin, and A. Peron, J. Organometal. Chem., 144 (1978) 357.
13 R. Rumin and P. Courtot, J. Organometal. Chem., 193 (1980) 407.
14 D.M. Blake and C.J. Nyman, Chem. Commun., (1969) 483.
15 D.M. Blake and C.J. Nyman, J. Am. Chem. Soc., 92 (1970) 5359.
16 C. Bartocci and F. Scandola, Chem. Commun., (1970) 531.
17 S. Sostero, O. Traverso, M. Lenarda and M. Graziani, J. Organometal. Chem., 134 (1977) 259.
18 C. Bartocci, F. Scandola, and V. Balzani, J. Am. Chem. Soc., 91 (1969) 6948.
19 C. Bartocci, F. Scandola, and V. Carassiti, J. Phys. Chem., 78 (1974) 2349.
20 C. Bartocci, A. Ferri, V. Carassiti, and F. Scandola, Inorg. Chim. Acta, 24 (1977) 251.
21 P. Haake and T.A. Hylton, J. Am. Chem. Soc., 84 (1962) 3774.
22 V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, Inorg. Chem., 4 (1965) 1243.
23 F. Scandola, O. Traverso, V. Balzani, G.L. Zucchini, and V. Carassiti, Inorg. Chim. Acta, 1 (1967) 76.
24 L. Moggi, G. Varani, N. Sabbatini, and V. Balzani, Mol. Photochem., 3 (1971) 141.
25 S.H. Goh and C.Y. Mok, J. Inorg. Nucl. Chem., 39 (1977) 531.
26 J.H. Price, J.P. Birk, and B.B. Wayland, Inorg. Chem., 17 (1978) 2245.
27 P. Courtot, R. Rumin, A. Peron and J.P. Girault, J. Organometal. Chem., 145 (1978) 343.
28 R. Rumin and P. Courtot, J. Organometal. Chem., 169 (1979) 225.
29 H.W. Sternberg and I. Wender, Chem. Soc. Spec. Publ. No. 13, 1959, p. 35.
30 L. Marko, Chem. Ind. (London), (1962) 260.
31 L. Marko, Proc. Chem. Soc., (1962) 67.
32 R.J. Angelici, Accounts Chem. Res., 5 (1972) 335.

33 H.C. Clark, K.R. Dixon and W.J. Jacobs, Chem. Commun., (1968) 93.
34 H.C. Clark, K.R. Dixon and W.J. Jacobs, J. Am. Chem. Soc., 91 (1969) 1346.
35 D.M. Barlex, R.D.W. Kemmitt, and G.W. Littlecott, Chem. Commun., (1969) 613.
36 W.J. Cherwinski and H.C. Clark, Inorg. Chem., 10 (1971) 2263.
37 J.E. Byrd and J. Halpern, J. Am. Chem. Soc., 93 (1971) 1634.
38 D.M. Barlex and R.D.W. Kemmitt, J. Chem. Soc., Dalton Trans., (1972) 1436.
39 H. Kurosawa and R. Okawara, J. Organometal. Chem., 71 (1974) C35.
40 E.D. Dobrzynski and R.J. Angelici, Inorg. Chem., 14 (1975) 59.
41 H. Kurosawa, Inorg. Chem., 14 (1975) 2148.
42 M.J. Church and M.J. Mays, Chem. Commun., (1968) 435.
43 Infrared bands are observed at 3050w, 1485w, 1440s, 1310w, 1190w, 1160w, 1100s, 1000w, 750s, 695vs, 525vs, 500s and 430w cm^{-1} ($\pm$10 cm^{-1}).
44 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Wiley-Interscience, New York, 1978, p. 154.
45 S.H. Mastin, Inorg. Chem., 13 (1974) 1003.
46 A. Pidcock, R.E. Richards, and L.M. Venanzi, Proc. Chem. Soc., (1962) 184.
47 G.L. Geoffroy, D.A. Denton, and C.W. Eigenbrot, Inorg. Chem., 15 (1976) 2310.
48 L.L. Costanzo and S. Giuffrida, Inorg. Chim. Acta, 38 (1980) 31.
49 B.L. Shaw and N.I. Tucker, Organo-Transition Metal Compounds and Related Aspects of Homogeneous Catalysis, Pergamon, Oxford, 1973, p. 812.
50 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Wiley-Interscience, New York, 1978, p. 319.