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PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION METAL COMPLEXES

IV *. THERMAL AND PHOTOCHEMICAL REACTIONS OF $PtCl_6^{2-}$ AND $PtCl_4^{2-}$ WITH OLEFINS AND ALCOHOLS: CONVENIENT SYNTHESIS OF π-OLEFIN COMPLEXES OF PLATINUM(II)

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Summary

Olefinplatinum(II) π-complexes can be synthesized by the following methods: (i) heating a solution of an olefin, alcohol or alkyl acetate and $PtCl_6^{2-}$ in acetic acid; (ii) light irradiation of a solution of $PtCl_6^{2-}$ and an olefin in acetone; and (iii) light irradiation of a solution of $PtCl_4^{2-}$ and an olefin in aqueous acetone. The possible mechanisms of the thermal and photoinduced reactions are discussed.

Introduction

π-Olefin complexes of platinum(II) were the first organometallic compounds known since 1830 and much work has been devoted to these substances [1–3]. Despite this, there are no convenient methods for preparing π-olefin complexes of platinum(II). Historically, the first method was to reflux a solution of platinum(IV) chloride in alcohol [4]. More recently, Hartley described a synthesis in which the normal alcohols containing two, three or four carbon atoms are treated with sodium tetrachloroplatinate(II) at room temperature [5]. The branched alcohols do not form olefin complexes by this method. Finally, olefinplatinum(II) complexes can be prepared by the reaction of olefins with $PtCl_4$ or $PtCl_4^{2-}$ [1–3]. It is interesting that the platinum complexes PtX_6^{2-} and PtX_4^{2-} (X = Cl, Br, I) catalyse the oxidation of

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* For part III see ref. 18.

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alcohols, $C_nH_{2n+1}OH$ ($n = 2$–6), to esters, $C_nH_{2n+1}OCOC_{n-1}H_{2n-1}$, with I_2 in aqueous solution [6].

We wish to report here a novel convenient synthesis of π-olefin complexes of platinum(II) in which a solution of the $PtCl_6^{2-}$ ion and an olefin in acetone or acetic acid is heated or irradiated with light. The thermal reaction of $PtCl_6^{2-}$ with alcohols or alkyl acetates in acetic acid can also be used for the synthesis of olefinplatinum(II) complexes. Some parts of this work have been published as preliminary communications [7–9].

Results

Two different methods were used to prepare π-olefin complexes of platinum(II). These were heating a solution of platinum(IV) chloride complex with an olefin (eq. 1) or alcohol or alkyl acetate (eq. 2) (method A), and light irradiation of a solution of $PtCl_6^{2-}$ with an olefin (eq. 1) (method B). Acetone (denoted here as a) or acetic acid (denoted as b) was used as the solvent. In all cases, the π-olefin complexes were isolated in the dimer form, $[(\text{olefin})PtCl_2]_2$, or as the pyridine adduct, $(\text{olefin})PtCl_2py$

TABLE 1

SYNTHESES OF π-OLEFIN COMPLEXES OF PLATINUM(II)

Starting complex of platinum [a]	Organic substrate	Method [b]	Temperature (°C)	Time (min)	Product, complex of platinum(II)	Yield (%)
I	$PhCH{=}CH_2$	Aa	62	600	$[(PhCH{=}CH_2)PtCl_2]_2$	35
II	$PhCH{=}CHPh$	Aa	62	660	$[(PhCH{=}CHPh)PtCl_2]_2$	70
I	$PhCH{=}CH_2$	Ab(py)	120	10	$(PhCH{=}CH_2)PtCl_2py$	18
I	$PhCH{=}CH_2$	Ab	71	180	$[(PhCH{=}CH_2)PtCl_2]_2$	71
I	$PhCH{=}CHPh$	Ab(py)	120	5	$(PhCH{=}CHPh)PtCl_2py$	47
I	$CH_3(CH_2)_3CH{=}CH_2$	Ab(py)	120	30	$(\text{Hex-1-ene})PtCl_2py$	6
I	$Ph_2C{=}CH_2$	Ab(py)	50	5	$(Ph_2C{=}CH_2)PtCl_2py$	18
I	$CH_3CH(OH)CH_3$	Ab(py)	120	120	$(CH_3CH{=}CH_2)PtCl_2py$	34
I	$CH_3CH_2CH_2CH_2OH$	Ab(py)	120	120	$(C_2H_5CH{=}CH_2)PtCl_2py$	21
I	$PhCH(OH)CH_3$	Ab	71	240	$[(PhCH{=}CH_2)PtCl_2]_2$	38
I	$C_2H_5OCOCH_3$	Ab(py)	120	150	$(CH_2{=}CH_2)PtCl_2py$	42
I	$(CH_3)_2CHCH_2OCOCH_3$	Ab	120	120	$[(CH_2{=}C(CH_3)_2)PtCl_2]_2$	27
I	$PhCH(OCOCH_3)CH_3$	Ab	71	240	$[(PhCH{=}CH_2)PtCl_2]_2$	17
II	$PhCH{=}CH_2$	Ba	10	50	$[(PhCH{=}CH_2)PtCl_2]_2$	98
II	$PhCH{=}CH_2$	Ba(py)	10	50	$(PhCH{=}CH_2)PtCl_2py$	50
II	$CH_2{=}CH_2$	Ba(py)	15	15	$(CH_2{=}CH_2)PtCl_2py$	32
I	$CH_2{=}CH_2$	Bb(py)	15	45	$(CH_2{=}CH_2)PtCl_2py$	13
I	$CH_3(CH_2)_3CH{=}CH_2$	Bb(py)	8	150	$(\text{Hex-1-ene})PtCl_2py$	70
I	$PhCH{=}CH_2$	Bb	15	20	$[(PhCH{=}CH_2)PtCl_2]_2$	19
I	$Ph_2C{=}CH_2$	Bb(py)	15	35	$(Ph_2C{=}CH_2)PtCl_2py$	13
III	$PhCH{=}CH_2$	Ba	15	60	$[(PhCH{=}CH_2)PtCl_2]_2$	91
III	$FcCH{=}CH_2$ [c]	Ba	15	60	$[(FcCH{=}CH_2)PtCl_2]_2$	77
III	$CH_3(CH_2)_3CH{=}CH_2$	Ba(py)	15	60	$(\text{Hex-1-ene})PtCl_2py$	39

[a] $H_2PtCl_6 \cdot 6H_2O$ (I), $Na_2PtCl_6 \cdot 6H_2O$ (II) or $Na_2PtCl_4 \cdot 4H_2O$ (III). [b] Thermal (A) or photoinduced (B) reaction. Solvent: acetone (a) or acetic acid (b). [c] Fc: ferrocenyl, $C_5H_5FeC_5H_4$.

(the latter is denoted as py).

$$\mathrm{PtCl_6{}^{2-} + RCH{=}CHR^1 \xrightarrow[\text{or } h\nu]{\Delta} [(RCH{=}CHR^1)PtCl_2]_2 \xrightarrow{py} (RCH{=}CHR^1)PtCl_2py} \quad (1)$$

$$\mathrm{PtCl_6{}^{2-} + RCH_2CHR^1OX \xrightarrow{\Delta} [(RCH{=}CHR^1)PtCl_2]_2 \rightarrow (RCH{=}CHR^1)PtCl_2py} \quad (2)$$

$(X = H \text{ or } COCH_3)$

Examples of the syntheses are summarized in Table 1.

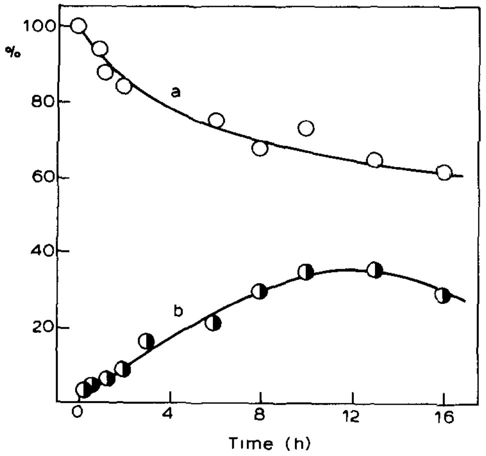

Fig. 1. Thermal reaction of H_2PtCl_6 (0.035 *M*) with styrene (0.62 *M*) at 62 °C in CH_3COCH_3/H_2O (2.2/1, v/v). Consumption of $PtCl_6{}^{2-}$ (a) and the yield of $[(PhCH{=}CH_2)PtCl_2]_2$ (b) versus time.

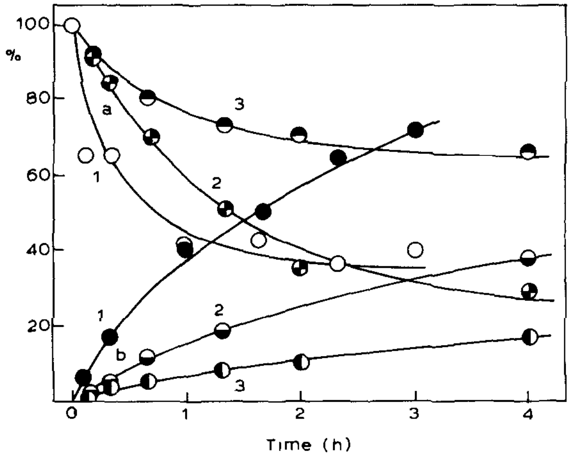

Fig. 2. Consumption of H_2PtCl_6 (initial concentration $[PtCl_6{}^{2-}]_0$ 0.1 *M*) (a) and the yield of complex $[(PhCH{=}CH_2)PtCl_2]_2$ (b) versus time in the thermal reaction of $H_2PtCl_6 \cdot 6H_2O$ with styrene (initial concentration 1.75 *M*) (1), $PhCH(OH)CH_3$ (1.5 *M*) (2) or $PhCH(OCOCH_3)CH_3$ (1.1 *M*) (3) in CH_3COOH at 70.5 °C.

Thermal reaction (method A)

The thermal reaction can be carried out using $H_2PtCl_6 \cdot 6H_2O$ or $Na_2PtCl_6 \cdot 6H_2O$ as the starting complex of platinum(IV) and acetone or acetic acid as the solvent. Olefins, alcohols and alkyl acetates have been used as organic substrates. The best results are obtained if the reaction is carried out in CH_3COOH and if $H_2PtCl_6 \cdot 6H_2O$ and an olefin are used as starting compounds. Unfortunately, the salt $Na_2PtCl_6 \cdot 6H_2O$ is only sparingly soluble in acetic acid. The thermal reaction of H_2PtCl_6 with styrene in aqueous acetone is rather slow (Fig. 1). The rate of the reaction in CH_3COOH, in the case of styrene, is higher than that for the reaction with the alcohol $PhCH(OH)CH_3$ or the acetate $PhCH(OCOCH_3)CH_3$ (Fig. 2). The plot of the styreneplatinum(II) π-complex concentration versus the initial concentration of H_2PtCl_6 is shown in Fig. 3. It can be concluded that the reaction is first order in the platinum(IV) complex. The dependence of the initial rate of the reaction on $[styrene]_0$ in the range 0–0.8 *M* is close to linear, but at large concentrations of styrene the rate does not depend on this concentration (Fig. 4). It should be noted that styrene reacts readily with acetic acid in the presence of H_2PtCl_6 to afford the acetate and the rate of reaction with $PtCl_6^{2-}$ decreases in the course of the reaction.

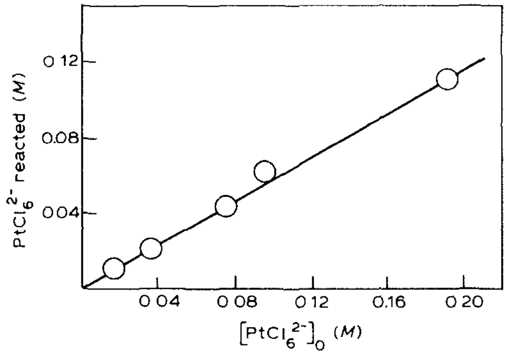

Fig. 3. Plot of the consumption of $PtCl_6^{2-}$ in the thermal reaction with styrene (1.75 *M*) in CH_3COOH at 70.5 °C for 20 min versus $[PtCl_6^{2-}]_0$.

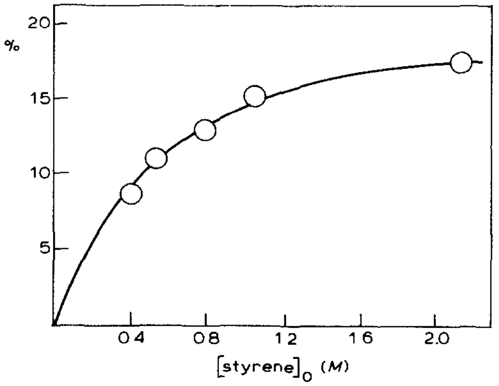

Fig. 4. Plot of the yield (based on Pt) of complex $[(PhCH{=}CH_2)PtCl_2]_2$ in the thermal reaction of H_2PtCl_6 (0.1 *M*) with styrene in CH_3COOH at 70.5 °C for 20 min versus $[styrene]_0$.

Photoinduced reaction (method B)

The photoinduced reaction of $Na_2PtCl_6 \cdot 6H_2O$ with olefins in acetone is a very convenient synthetic method for preparing olefinplatinum(II) π-complexes because the rate of the reaction is high and excellent yields of the complexes can be obtained. We used a halogen tungsten lamp for these syntheses but a high-pressure mercury lamp or sunlight is also effective. A white precipitate of NaCl salt is deposited during irradiation with light. The rate of the reaction does not depend on temperature, within experimental error. The kinetics of the reaction are shown in Fig. 5. The photoinduced reaction is first order in $PtCl_6^{2-}$ (Fig. 6) and zero order in styrene (Fig. 7). It should be noted that the $PtCl_6^{2-}$ ion reacts under light irradiation with acetone [8,10], but the rate of the reaction with an olefin is much higher.

The reaction using acetic acid as the solvent (irradiation of a high-pressure mercury lamp was used) is similar to that in acetone (Figs. 8 and 9). The rate of the reaction depends on light intensity (Fig. 10) and decreases with increasing concentration of LiCl added (Fig. 11). The synthetic importance of the reaction in acetic

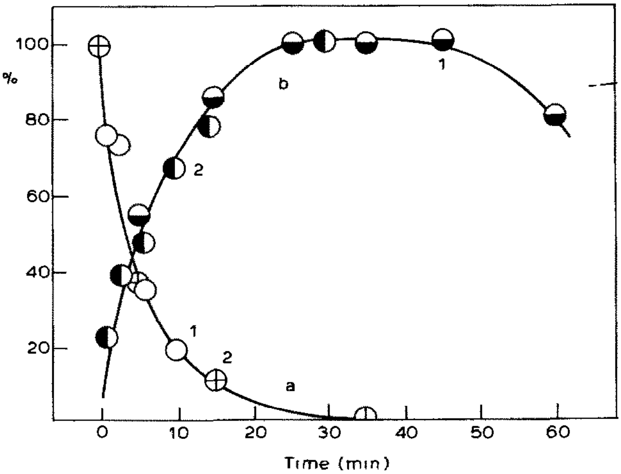

Fig. 5. Plot of the consumption of $PtCl_6^{2-}$ (a) and the yield of complex $[(PhCH{=}CH_2)_2PtCl_2]_2$ (b) in the reaction of $Na_2PtCl_6 \cdot 6H_2O$ (0.035 *M*) with styrene (0.865 *M*) in acetone under irradiation of a halogen tungsten lamp at 9 °C (1) and 25 °C (2) versus irradiation time.

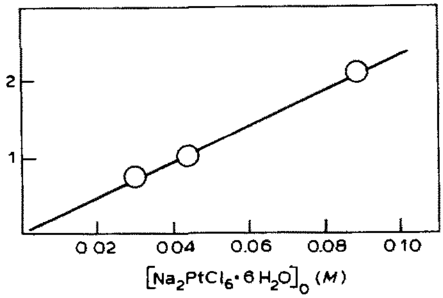

Fig. 6. Plot of the initial relative rate of consumption of $PtCl_6^{2-}$ of the photoinduced reaction of $Na_2PtCl_6 \cdot 6H_2O$ with styrene (0.865 *M*) in acetone versus $[PtCl_6^{2-}]_0$ (a halogen tungsten lamp was used).

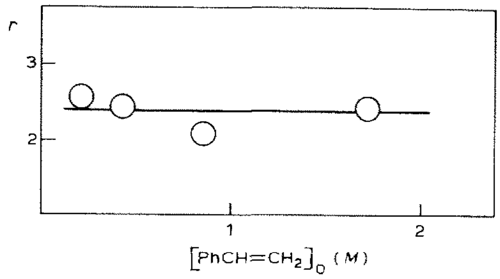

Fig. 7. Plot of the initial relative rate of the photoinduced reaction of $Na_2PtCl_6 \cdot 6H_2O$ (0.089 *M*) with styrene in acetone versus [styrene]$_0$ (a halogen tungsten lamp was used).

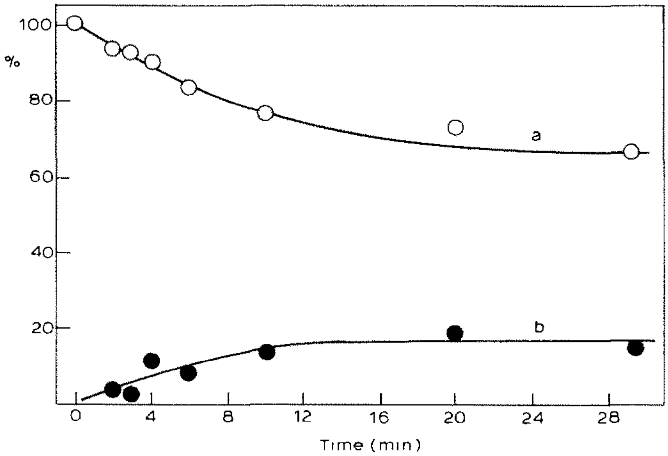

Fig. 8. Plot of the consumption of $PtCl_6^{2-}$ (a) and the yield of complex $[(PhCH{=}CH_2)PtCl_2]_2$ (b) in the photoinduced reaction of $H_2PtCl_6 \cdot 6H_2O$ (0.039 *M*) with styrene (0.35 *M*) in CH_3COOH at 18 °C versus time of irradiation with light of a high-pressure mercury lamp.

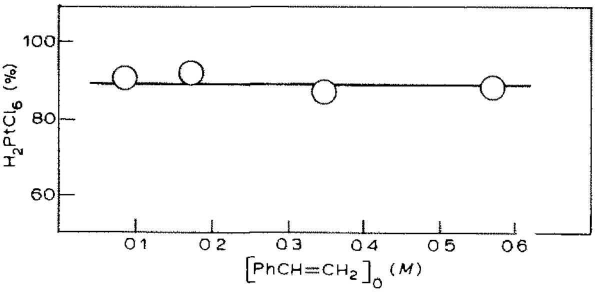

Fig. 9. Plot of the consumption of $PtCl_6^{2-}$ in the photoinduced reaction of $H_2PtCl_6 \cdot 6H_2O$ (0.02 *M*) with styrene in CH_3COOH for 3 min versus [styrene]$_0$ (a high-pressure mercury lamp was used).

acid is less than that of the reaction in acetone because of the difficulty in isolating the complex.

It is interesting to note that the photoinduced reaction of $PtCl_6^{2-}$ with *trans*-stilbene does not produce the π-olefin complex of platinum(II) either in acetone or in acetic acid. However, the thermal reaction of $PtCl_6^{2-}$ with *trans*-stilbene gives the olefinplatinum(II) complex in a good yield (see Table 1). The photoinduced reaction of $PtCl_6^{2-}$ with alcohols or alkyl acetates does not afford π-olefin complexes. No photoinduced reaction of $PtCl_6^{2-}$ with ethylenes bearing electron-withdrawing substituents (methyl methacrylate, methacrylic and acrylic acids) occurs.

The photochemical (as well as thermal) reaction of $PtCl_6^{2-}$ with olefins gives rise to complex mixtures of organic products of the olefin oxidation (more than seven compounds according to thin-layer chromatography). The structures of these organic products were not established.

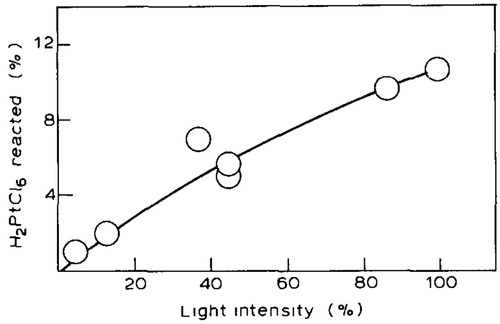

Fig. 10. Plot of the conversion of $PtCl_6^{2-}$ in the photoinduced reaction of H_2PtCl_6 (0.02 M) with styrene (0.17 M) in CH_3COOH for 6 min versus light intensity (full light of a high-pressure mercury lamp was 100%).

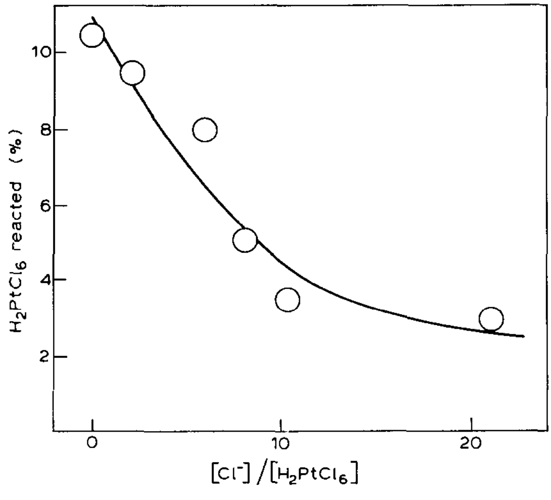

Fig. 11. Plot of the conversion of $PtCl_6^{2-}$ in the photoinduced reaction of H_2PtCl_6 (0.02 M) with styrene (0.17 M) in CH_3COOH for 6 min versus concentration of LiCl added (relative to [$PtCl_6^{2-}$]).

Upon light irradiation of a frozen solution of styrene and $PtCl_6{}^{2-}$ in acetone or acetic acid at 77 K, the ESR spectrum can be observed. The spectrum exhibits signals due to platinum(III) complexes (see, for example, Fig. 2 in ref. 10) and organic radicals.

Finally, we have found that light irradiation of a solution of $PtCl_4{}^{2-}$ ion and an olefin in aqueous acetone affords the π-olefin complex of platinum(II) in a good yield (up to 90%). This reaction is also a convenient synthetic method for preparing olefinplatinum(II) π-complexes. This method is denoted as Ba in Table 1 and can be used when the olefin is very expensive.

Discussion

The mechanisms of the reactions of $PtCl_6{}^{2-}$ with olefins appear to be similar to those of the reactions of $PtCl_6{}^{2-}$ with arenes [8,11,12]. On the other hand, the reactions of $PtCl_6{}^{2-}$ with arenes and olefins resemble the corresponding reactions of mercury(II), thallium(III) and lead(IV) compounds. The oxidation reactions of olefins by the latter compounds are known to involve σ-organyl intermediates formed by the electrophilic addition of mercury(II), thallium(III) or lead(IV) to the double bond [13]. Analogously, it may be assumed that the thermal reaction of $PtCl_6{}^{2-}$ with an olefin starts from the electrophilic addition of the coordinatively unsaturated species $PtCl_5{}^-$ to the double bond:

$$PtCl_5{}^- + RCH{=}CHR^1 \rightarrow R^1H\overset{+}{C}{-}C(HR){-}PtCl_5{}^{2-} \quad (3)$$

The zwitterionic species thus formed may be stabilized by the addition of a nucleophile, X^- (e.g. Cl^-, CH_3COO^-, H_2O):

$$R^1H\overset{+}{C}{-}C(HR){-}PtCl_5{}^{2-} + X^- \rightarrow R^1HCX{-}C(HR){-}PtCl_5{}^{2-} \quad (4)$$

It should be noted that analogous σ-alkyl complexes of platinum(IV) have been prepared by the addition of Cl_2 to the complex $(CH_2{=}CH_2)PtCl_3{}^-$ [14]. The complex formed in eq. 4 can be converted into a platinum(II) compound by the following routes [14–16]:

$$R^1HCX{-}C(HR){-}PtCl_5{}^{2-} \rightarrow R^1HCX{-}C(HR)Cl + PtCl_4{}^{2-} \quad (5)$$

$$R^1HCX{-}C(HR){-}PtCl_5{}^{2-} \rightarrow R^1XC{=}CHR + PtCl_4{}^{2-} + H^+ + Cl^- \quad (6)$$

Both these reactions can be accelerated by heating or light irradiation. The platinum(II) chloride complex then reacts with the olefin to give the olefinplatinum(II) complex.

As for the photoinduced reaction, one may propose that the first stage is excitation of the complex $PtCl_6{}^{2-}$ followed by electron transfer from the olefin to the platinum(IV) complex and formation of a cation-radical and the platinum(III) complex:

$$PtCl_6{}^{2-} \rightarrow [PtCl_6{}^{2-}]^\star \quad (7)$$

$$RHC{=}CHR^1 + [Pt^{IV}Cl_6{}^{2-}]^\star \rightarrow [RHC{=}CHR^1]^{+\cdot} + Pt^{III}Cl_5{}^{2-} + Cl^- \quad (8)$$

Such a mechanism is in accordance with those of the photoinduced reactions of $PtCl_6{}^{2-}$ [17] with arenes [11,12], acetone [10], and Alk_4M (M = Sn, Ge) [18]. Both the radicals derived from the olefin and the platinum(III) complex can be observed in the ESR spectra. The formation of the analogous cation-radicals was detected in the ESR spectra for the reaction of $Co(OCOCF_3)_3$ with several olefins in CF_3COOH solutions [19,20].

The cation-radicals can add nucleophiles, X^- (Cl^-, CH_3COO^- etc.):

$$R\dot{C}H{-}\overset{+}{C}HR^1 \leftrightarrow R\overset{+}{C}H{-}\dot{C}HR^1 \xrightarrow{X^-} R\dot{C}H{-}CHXR^1 + RCHX{-}\dot{C}HR^1 \qquad (9)$$

The radicals formed in reaction 9 can dimerize, e.g.:

$$2R\dot{C}H{-}CHXR^1 \rightarrow R^1XHCHCHRCHRCHXR^1, \qquad (10)$$

or, after oxidation by platinum(III) or platinum(IV),:

$$R\dot{C}H{-}CHXR^1 + Pt^{III} \rightarrow R\overset{+}{C}H{-}CHXR^1 + Pt^{II} \qquad (11)$$

$$R\dot{C}H{-}CHXR^1 + Pt^{IV} \rightarrow R\overset{+}{C}H{-}CHXR^1 + Pt^{III} \qquad (12)$$

they can react with a second nucleophilic species:

$$R\overset{+}{C}H{-}CHXR^1 + X^- \rightarrow RCHX{-}CHXR^1 \qquad (13)$$

Complexes of platinum(III) are capable of disproportionating:

$$2Pt^{III}Cl_5{}^{2-} \rightarrow Pt^{II}Cl_4{}^{2-} + Pt^{IV}Cl_6{}^{2-} \qquad (14)$$

and the platinum(II) compounds thus formed react with the olefin to afford the π-olefin complex of platinum(II):

$$PtCl_4{}^{2-} + RCH{=}CHR^1 \xrightarrow{(h\nu)} (RCH{=}CHR^1)PtCl_3{}^- + Cl^- \qquad (15)$$

The radical formed in reaction 9 and the platinum(III) complex can recombine in the solvent cage to afford a σ-alkyl complex of platinum(IV):

$$R\dot{C}H{-}CHXR^1 + Pt^{III}Cl_5{}^{2-} \rightarrow (R^1HX)C(HR)CPt^{IV}Cl_5{}^{2-} \qquad (16)$$

This complex then gives the π-olefin complex of platinum(II) (eq. 5 and 6).

The fact that the first stages of both the thermal and photoinduced reactions are common, i.e. electron transfer from the olefin to platinum(IV) occurs to afford the cation-radical and a platinum(III) complex, should not be excluded. Recombination of these species as shown in eq. 16 gives the σ-alkyl complex of platinum(IV) in both cases. Such a mechanism may be denoted as $Ad_{E}e.t.$ (electrophilic addition involving an electron transfer step). The complex nature of the mixture of olefin oxidation products indicates that a few routes lead to the olefin π-complex formation.

Alternatively, one may assume that the excited species formed in eq. 7 dissociates to produce $Pt^{III}Cl_5{}^{2-}$ and $Cl^{\bullet}$. The latter reacts with the olefin, and the former disproportionates (eq. 14). The platinum(II) complex thus formed coordinates to the olefin. However, this route seems to be less probable because in this case the reaction of $Cl^{\bullet}$ with acetone enol [10] should lead to the formation of chloroacetone simultaneously with the formation of a σ-acetonyl complex. Moreover, methyl acrylate is a good acceptor of $Cl^{\bullet}$, but we have not detected the formation of either the π-olefin complex of methyl acrylate with platinum(II), or the $PtCl_4{}^{2-}$ ion. The photoinduced reaction of $PtCl_6{}^{2-}$ with olefins resembles, in this respect, the reaction with arenes induced by irradiation [11,12]. Indeed, neither reaction occurs with organic π-substrates (arenes or olefins) bearing electron-withdrawing substituents. This fact is in good agreement with the proposed electron transfer from the π-substrate to the platinum(IV) complex.

Experimental

All procedures were carried out in air. Photochemical reactions were carried out in a quartz cylindrical vessel irradiated with full light of a high-pressure mercury lamp (1000 W) or in a Pyrex vessel irradiated with full light of a halogen tungsten lamp under vigorous stirring. The concentrations of the complexes in kinetic experiments were measured spectrophotometrically using absorption in the visible region (Specord UV-VIS). The ^{1}H NMR spectra were recorded on a Bruker SXP-4-100 spectrometer.

Examples of the syntheses of olefinplatinum(II) π-complexes by different methods are described below. All other complexes were prepared analogously and the data are summarized in Table 1.

Thermal reaction of Na_2PtCl_6 with trans-stilbene in acetone (method Aa)

A solution of 0.3 g of $Na_2PtCl_6 \cdot 6H_2O$ and 0.5 g of PhCH=CHPh in 10 ml of acetone and 2 ml of H_2O was refluxed for 11 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (eluent: acetone/hexane, 3/5). The yield of complex $[(PhCH{=}CHPh)PtCl_2]_2$ was 0.085 g (70% based on Pt).

Thermal reaction of H_2PtCl_6 with styrene in acetic acid (method Ab)

A solution of 0.5 g of $H_2PtCl_6 \cdot 6H_2O$, 2 ml of $PhCH{=}CH_2$ and 0.2 ml of H_2O in 7.5 ml of acetic acid was heated at 71°C for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (eluent: acetone/hexane, 3/5). The yield of complex $[(PhCH{=}CH_2)PtCl_2]_2$ was 71%.

Thermal reaction of H_2PtCl_6 with propan-2-ol in acetic acid [method Ab(py)]

A solution of 0.5 g of $H_2PtCl_6 \cdot 6H_2O$ and 3 ml of $CH_3CH(OH)CH_3$ in 5 ml of acetic acid was heated at 120°C for 2 h. The solvent was removed under reduced pressure and the residue was extracted with chloroform. The solution was shaken with aqueous pyridine (0.03 ml of pyridine per 10 ml of water), washed with water, and dried over Na_2SO_4. Chloroform was removed under reduced pressure and the residue was chromatographed on silica gel (eluent: chloroform). The yield of complex $(CH_2{=}CHCH_3)PtCl_2py$ was 0.13 g (34%).

Photoinduced reaction of Na_2PtCl_6 with styrene in acetone (method Ba)

A solution of 0.2 g of $Na_2PtCl_6 \cdot 6H_2O$ and 1 ml of $PhCH{=}CH_2$ in 20 ml of acetone was irradiated with full light of a halogen tungsten lamp at 10°C for 50 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (eluent: acetone/hexane, 1/1). The yield of complex $[(PhCH{=}CH_2)PtCl_2]_2$ was 0.13 g (98%).

Photoinduced reaction of Na_2PtCl_6 with ethylene in acetone [method Ba(py)]

Ethylene was bubbled through a solution of 0.1 g of $Na_2PtCl_6 \cdot 6H_2O$ in 5 ml of acetone during light irradiation of a high-pressure mercury lamp for 15 min. Acetone was removed under reduced pressure, the residue was extracted with chloroform, and the solution was treated with aqueous pyridine (0.03 ml of pyridine per 10 ml of water) and dried over Na_2SO_4. Chloroform was removed under reduced pressure and the residue was chromatographed on silica gel (eluent: chloroform). The yield of complex $(CH_2{=}CH_2)PtCl_2py$ was 0.023 g (32%).

Photoinduced reaction of H_2PtCl_6 with hex-1-ene in acetic acid [method Bb(py)]

A solution of 0.2 g of $H_2PtCl_6 \cdot 6H_2O$, 0.5 ml of hex-1-ene and 0.1 ml of H_2O in 4.3 ml of acetic acid was irradiated with full light of a high-pressure mercury lamp at 8 °C for 2.5 h. The solvent was removed under reduced pressure and the residue was extracted with chloroform. The solution was shaken with aqueous pyridine, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (eluent: chloroform). The yield of complex $[CH_3(CH_2)_3CH{=}CH_2]PtCl_2py$ was 70%.

Photoinduced reaction of Na_2PtCl_4 with styrene in aqueous acetone (method Ba)

A solution of 0.2 g of $Na_2PtCl_4 \cdot 4H_2O$, 0.4 ml of H_2O and 1 ml of $PhCH{=}CH_2$ in 18 ml of acetone was irradiated with full light of a halogen tungsten lamp at 15 °C for 1 h. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. The yield of complex $[(PhCH{=}CH_2)PtCl_2]_2$ was 0.12 g (91%).

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References

1 M.I. Rybinskaya, in Metody Elementoorganicheskoi Khimii, π-Kompleksy Monoolefinov, Nauka, Moskva, 1975.

2 M. Herberhold, Metal π-Complexes, Elsevier, Amsterdam, 1972.

3 A.Z. Rubezhov, in Metody Elementoorganicheskoi Khimii, Platina, Nauka, Moskva, 1978.

4 W.C. Zeise, Mag. Pharmakol., 35 (1830) 105.

5 F.R. Hartley, Inorg. Chim. Acta, 5 (1971) 197.

6 Yu.N. Kukushkin, V.N. Demidov and N.P. Fedyapin, Zh. Obshch. Khim., 53 (1983) 2393.

7 G.B. Shul'pin and G.V. Nizova, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 669.

8 G.B. Shul'pin, G.V. Nizova and A.E. Shilov, J. Chem. Soc., Chem. Commun., (1983) 671.

9 G.V. Nizova, J.V.Z. Krevor, A.N. Kitaigorodskii and G.B. Shul'pin, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2805.

10 G.V. Nizova, M.V. Serdobov, A.T. Nikitaev and G.B. Shul'pin, J. Organomet. Chem., 275 (1984) 139.

11 G.B. Shul'pin, G.V. Nizova, A.E. Shilov, A.T. Nikitaev and M.V. Serdobov, Izv. Akad. Nauk SSSR, Ser. Khim., in press.

12 G.B. Shul'pin, G.V. Nizova and A.T. Nikitaev, J. Organomet. Chem., 276 (1984) 115.

13 R.A. Sheldon and J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981, p. 135.

14 J. Halpern and R.A. Jewsbury, J. Organomet. Chem., 181 (1979) 223.

15 V.V. Zamashchikov, E.S. Rudakov, S.A. Mitchenko and S.L. Litvinenko, Teor. Eksp. Khim., 18 (1982) 510.

16 V.V. Zamashchikov, E.S. Rudakov, S.A. Mitchenko, A.N. Kitaigorodskii and G.B. Shul'pin, Dokl. Akad. Nauk Ukr. SSR, Ser. B, No. 6 (1983) 33.

17 G.B. Shul'pin, G.V. Nizova, A.E. Shilov, A.T. Nikitaev, M.V. Serdobov and A.N. Kitaigorodskii, Proceedings of 4-th Int. Symp. on Homogen. Catal., Leningrad, 1984.

18 G.B. Shul'pin, G.V. Nizova, A.N. Kitaigorodskii and M.V. Serdobov, J. Organomet. Chem., 275 (1984) 273.

19 R.M. Dessau, J. Am. Chem. Soc., 92 (1970) 6356.

20 R. Tang and J.K. Kochi, J. Inorg. Nucl. Chem., 35 (1973) 3845.