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# Novel ketene formation by reactions of acid chlorides with low-valent platinum complexes

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## Abstract

$Pt(CO)_n(PPh_3)_{4-n}$ ($n = 0$–$2$) reacts with $Ph_2CHCOCl$ under CO to afford diphenylketene and *trans*-$PtHCl(PPh_3)_2$. For this reaction, the rate law is zero order in the platinum complex, first order in $Ph_2CHCOCl$, and first order in free $PPh_3$. A primary isotope effect ($k_H/k_D = 4.5$) was observed in the reaction of $Ph_2CDCOCl$. A mechanism is proposed which involves the rate-determining enolization of $Ph_2CHCOCl$ by $PPh_3$ followed by fast abstraction of HCl by a platinum(0) complex.

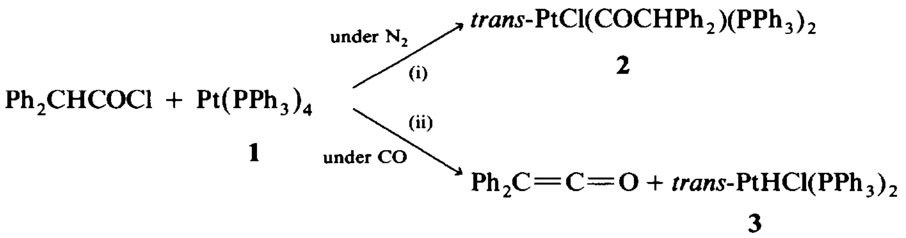
## Introduction

Ketenes and ketene complexes have received increasingly more attention as important intermediates in transition metal-promoted reactions such as CO hydrogenation [1] and carbonylation of organic or organometallic compounds [2]. A variety of transition metal-ketene complexes have been reported [3]. Although it is well-known that ketenes can be prepared by treatment of acid halides with bases such as tertiary amines [4], reactions of low-valent metal complexes with acid halides usually result in the formation of metal acyl complexes instead of ketenes in spite of their basic character. Only a few ruthenium complexes have been reported to give ketenes when treated with acid chlorides [5,6]. However, the reaction mechanism of this dehydrohalogenation has been ambiguous, although a cationic acylruthenium complex has been proposed as an intermediate.

We recently developed a novel palladium- or platinum-catalyzed cyclocarbonylation of cinnamyl compounds which yields fused aromatic compounds [7,8]. A possible mechanism of this reaction involves a vinyl ketene intermediate [8]. We have therefore embarked on an investigation of ketene formation in the presence of palladium and platinum complexes. Here we describe the novel formation of diphenylketene by reaction of platinum(0) complexes with diphenylacetyl chloride.

## Results and discussion

When an excess amount of $Ph_2CHCOCl$ was allowed to react with $Pt(PPh_3)_4$ (**1**), under $N_2$ in benzene or toluene at r.t., the usual oxidative addition occurred to give



Scheme 1

a colorless acyl complex *trans*-PtCl(COCHPh$_2$)(PPh$_3$)$_2$ (**2**) [9]. In contrast, when a similar reaction was conducted under CO, the color of the solution gradually turned the characteristic yellow of diphenylketene. Formation of diphenylketene was confirmed from the strong absorption at 2100 cm$^{-1}$ [4] in the IR spectrum of the solution. However, no absorption due to **2** was observed. The yield of diphenylketene determined by the absorbance at 2100 cm$^{-1}$ reached 88% based on **1**, although it could not be isolated because of its instability. Addition of hexane to the reaction mixture afforded *trans*-PtHCl(PPh$_3$)$_2$ (**3**) in 89%. This result indicates that only under CO the reaction path ii proceeds and the usual oxidative addition path i is completely suppressed (Scheme 1).

This type of ketene formation was found to depend largely on the acid chloride used. Phenylacetyl chloride was also found to react with **1** under CO at r.t. to give **3** (68%) and the IR spectrum of the reaction mixture exhibited absorptions at 1905, 1878, and 1710 cm$^{-1}$ indicating the formation of phenylketene dimer [10]. Other acid chlorides such as acetyl chloride, isobutyryl chloride, 2-phenylpropionyl chloride did not react with **1** under CO at r.t., although these chlorides gave the corresponding acyl complexes under N$_2$. A similar reaction of Ph$_2$CHCOCl with Pt[P(OPh)$_3$]$_4$ also produced diphenylketene, but the reaction was very sluggish and therefore not investigated in detail. It should be mentioned that the ketene formation does not proceed with palladium complexes. Thus, the reactions of Ph$_2$CHCOCl under CO with Pd(PPh$_3$)$_4$ or Pd(CO)(PPh$_3$)$_3$ gave only *trans*-PdCl(COCHPh$_2$)(PPh$_3$)$_2$, and no diphenylketene was detected by IR.

Since **1** is known to establish an equilibrium with Pt(CO)(PPh$_3$)$_3$ (**4**) and Pt(CO)$_2$(PPh$_3$)$_2$ (**5**) under CO (Scheme 2) [11], reactions of excess Ph$_2$CHCOCl with **1**, **4**, and **5** were monitored by measuring the IR absorption at 2100 cm$^{-1}$ at different times. As can be seen from Fig. 1, the amount of diphenylketene increased linearly with the reaction time, which suggests that the reaction rate is zero order with respect to the platinum complex concentration. The reaction rates were found to fall in the order **1** > **4** > **5**. In view of this fact, PPh$_3$, dissociated from the platinum complexes, seems to accelerate the reaction, although no reaction was observed by either $^1$H NMR or IR when Ph$_2$CHCOCl was allowed to stand in contact with PPh$_3$ in benzene under CO.

In order to elucidate the mechanism of this ketene formation, the kinetics of the reaction were studied at 29 °C in benzene. When the initial concentration of **1** was fixed, the initial rate was proportional to the initial concentration of Ph$_2$CHCOCl (Fig. 2). On the other hand, when the initial concentration of Ph$_2$CHCOCl was

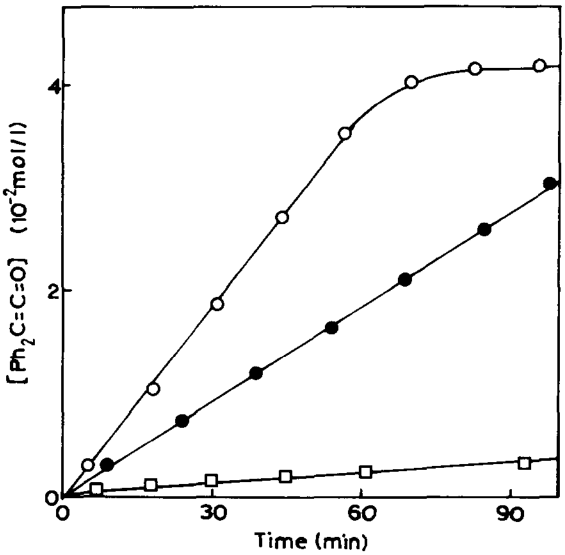
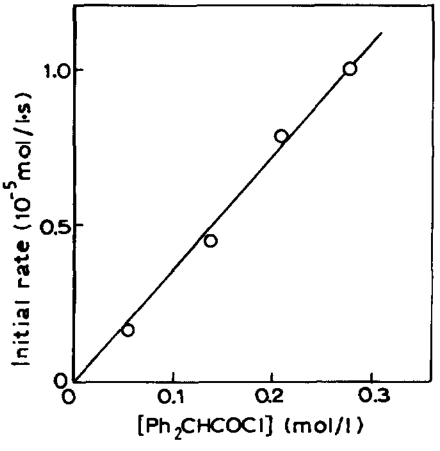


Fig. 1. Relation between reaction time and diphenylketene concentration. Reaction conditions; $Ph_2CHCOCl$ 0.28 mol/l, platinum complexes 0.055 mol/l, in benzene 5 ml, 29 °C, CO 1 atm. ○, **1**; ●, **4**; □, **5**.

fixed in the presence of a large excess of $PPh_3$, the initial rate was found to be almost independent of the initial platinum complex concentration (Fig. 3). In addition when the concentrations of $Ph_2CHCOCl$ and platinum complex are constant, addition of $PPh_3$ to the reaction system clearly increased the rate (Fig. 4).



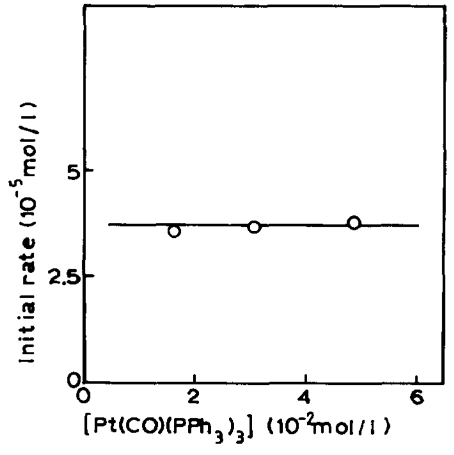


Fig. 2. Effect of concentration of $Ph_2CHCOCl$ on the reaction. Reaction conditions; $Pt(PPh_3)_4$ 0.055 mol/l, in benzene 5 ml, 29 °C, CO 1 atm.

Fig. 3. Effect of concentration of platinum complex on the reaction. Reaction conditions; $Ph_2CHCOCl$ 0.24 mol/l, $PPh_3$ 0.19 mol/l, in benzene 5 ml, 29 °C, CO 1 atm. Because **4** is the major platinum species in a solution containing excess $PPh_3$ under CO [11], **4** was used as the platinum species charged, instead of **1**, in order to minimize the change of $PPh_3$ concentration by $PPh_3$ dissociation.

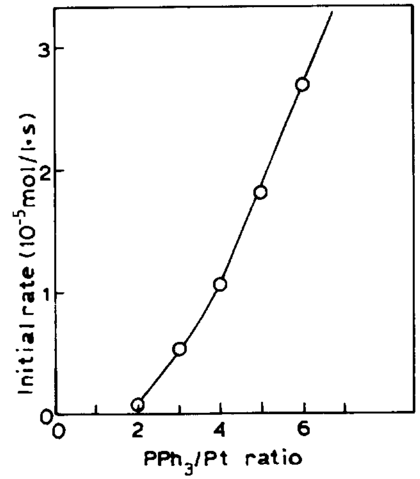


Fig. 4. Effect of $PPh_3$/Pt ratio on the reaction. Reaction conditions; $Ph_2CHCOCl$ 0.28 mol/l, platinum complexes 0.055 mol/l, in benzene 5 ml, 29° C, CO 1 atm. **5**, **4**, and **1** were used as the platinum species charged where $PPh_3$/Pt were 2, 3, $\geq 4$, respectively.

Unfortunately, the precise concentration of free $PPh_3$ could not be determined by $^{31}P$ NMR because **1** showed only a broad signal under $N_2$, or under CO, at r.t. owing to fast phosphine exchange. However, according to the equilibrium shown in Scheme 2, it may be assumed that **4** which contains 3 molecules of $PPh_3$ is the major platinum species at high $PPh_3$/Pt ratios under CO [11]. The initial rate is almost proportional to the value $(PPh_3/Pt) - 3$ at high $PPh_3$/Pt ratio. This indicates that the initial rate is first order in the free $PPh_3$ concentration $[PPh_3]$. The deviation from linearity at low $PPh_3$/Pt ratio is probably due to $PPh_3$ dissociation from **4** to form **5**. The rate expression was estimated from the kinetic data to be:

$$\text{rate}_{\text{obsd}}(\mathrm{d}[Ph_2C{=}C{=}O]/\mathrm{d}t) = k[Ph_2CHCOCl][PPh_3] \qquad (1)$$

$$k = (7.1 \pm 1.2) \times 10^{-4}\ \mathrm{l/mol \cdot s}\ (\text{at } 29\,^{\circ}\mathrm{C})$$

Furthermore, a primary kinetic isotope effect ($k_H/k_D = 4.5$) was observed in the reaction of 2-deuteriodiphenylacetyl chloride at 29° C, which suggests that the rate-determining step is the $\alpha$-C–H bond cleavage in $Ph_2CHCOCl$.

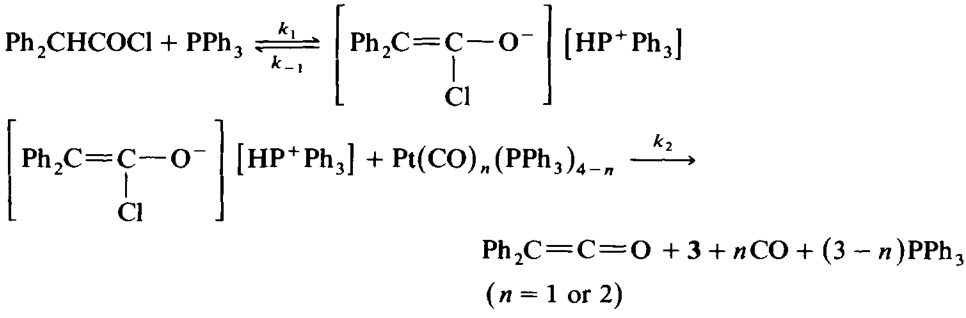
$$\underset{\mathbf{1}}{Pt(PPh_3)_4} \rightleftharpoons Pt(PPh_3)_3 + PPh_3$$

$$Pt(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_2 + PPh_3$$

$$Pt(PPh_3)_3 + CO \rightleftharpoons \underset{\mathbf{4}}{Pt(CO)(PPh_3)_3}$$

$$Pt(PPh_3)_2 + 2CO \rightleftharpoons \underset{\mathbf{5}}{Pt(CO)_2(PPh_3)_2}$$

Scheme 2



Scheme 3

A possible mechanism which is consistent with the kinetic data is depicted in Scheme 3. The first step is the rate-determining enolization of $Ph_2CHCOCl$ by $PPh_3$. Participation of an enol phosphonium salt has been assumed in the diphenylketene formation from $\alpha$-bromodiphenylacetyl bromide and $PPh_3$ [12]. Since the reaction of $Ph_2CHCOCl$ with $PPh_3$ produced no changes in the IR and $^1H$ NMR spectra as mentioned above, $k_1$ must be far smaller than $k_{-1}$. The second step is the fast formation of diphenylketene and **3** by the reaction of a platinum carbonyl complex $Pt(CO)_n(PPh_3)_{4-n}$ ($n = 1$ or 2) with the enolized $Ph_2CHCOCl$. Carbonyl ligands diminish the nucleophilicity of the platinum and prevent the oxidative addition of $Ph_2CHCOCl$ to give **2**. However, the platinum complex is basic enough to abstract the proton from $HP^+Ph_3$. Subsequent $Cl^-$ abstraction from the $Ph_2CHCOCl$ enolate anion results in the formation of **3** and diphenylketene.

The rate equation obtained by applying the steady-state treatment with respect to the enolized $Ph_2CHCOCl$ in Scheme 3 is described as follows:

$$\text{rate}_{\text{calcd}} = \frac{k_1 k_2 [Ph_2CHCOCl][PPh_3][Pt(CO)_n(PPh_3)_{4-n}]}{k_1[Ph_2CHCOCl] + k_{-1} + k_2[Pt(CO)_n(PPh_3)_{4-n}]} \qquad (2)$$

Assuming that $k_2[Pt(CO)_n(PPh_3)_{4-n}] \gg k_1[Ph_2CHCOCl]$, $k_{-1}$, eq. 2 can be approximated as follows:

$$\text{rate}_{\text{calcd}} = k_1[Ph_2CHCOCl][PPh_3] \qquad (3)$$

This is in agreement with the observed rate expression eq. 1.

Interestingly, a cationic ruthenium acyl complex was previously considered to be an intermediate in the ketene formation by the reactions of acid chlorides and a ruthenium carbonyl complex [5]. Mechanisms including $\beta$-hydrogen elimination of the acyl ligand or proton dissociation from the acyl complex have been proposed. However, in the case of platinum, mechanisms involving platinum acyl complexes are unambiguously excluded because the reaction rate is independent of the platinum complex concentration. The fact that **2** did not liberate diphenylketene under CO in benzene also supports the argument above.

Finally, the Arrhenius plot of $k_1$ is shown in Fig. 5, for which the equilibrium of Scheme 2 was assumed to be unchanged over the temperature range of 10–50 °C. The overall activation energy was determined to be 11.9 ± 1.4 kcal/mol.

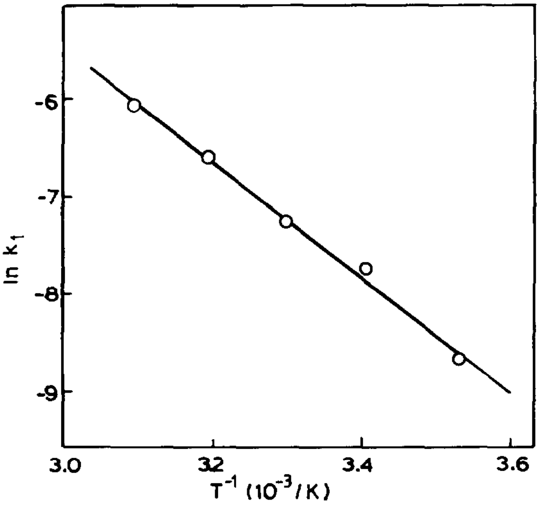


Fig. 5. Arrhenius plot of $k_1$. Reaction conditions; $Ph_2CHCOCl$ 0.28 mol/l, $Pt(PPh_3)_4$ 0.055 mol/l, in benzene 5 ml, CO 1 atm.

The results described here reveal the novel reactivity of low-valent platinum complexes and provide important information on the mechanism for ketene formation from acid chlorides and platinum complexes. Participation of the ketene formation in catalytic reactions such as the cyclocarbonylation [7,8] is now under investigation.

## Experimental

The $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL GX-400 spectrometer at 400 MHz and 161.8 MHz, respectively. Chemical shifts are relative to internal TMS and external $H_3PO_4$, respectively. Infrared spectra were taken on a JASCO IR-810 spectrophotometer.

The reactions were performed under $N_2$ or CO by Schlenk tube techniques. $Pt(PPh_3)_4$ [13], $Pt(CO)(PPh_3)_3$ [11], $Pt(CO)_2(PPh_3)_2$ [11], $Pt[P(OPh)_3]_4$ [14], $Pd(PPh_3)_4$ [15], and $Pd(CO)(PPh_3)_3$ [16] were prepared by published methods. Diphenylacetyl chloride, 2-deuterodiphenylacetyl chloride, and 2-phenylpropionyl chloride were prepared by the reaction of diphenylacetic acid, 2-deuteriodiphenylacetic acid [17], and 2-phenylpropionyl chloride, respectively, with $SOCl_2$ [18]. All solvents used were purified by standard methods and stored under $N_2$ or CO.

### *Reaction of acid chlorides and platinum or palladium complexes*

The following procedure for the reaction of $Ph_2CHCOCl$ with **1** under CO is representative. In a measuring flask was placed a benzene solution (5 ml) of $Ph_2CHCOCl$ (240 mg, 1.04 mmol) and **1** (343 mg, 0.276 mmol), and the flask was set in a round bottom flask settled in a thermostated oil bath under CO. A small portion of the solution was withdrawn with a syringe every 10–15 min, and diphenylketene in the solution was determined by measuring IR the absorption at

2100 cm$^{-1}$. The initial reaction rate was determined from the linear part of the time–diphenylketene concentration curve.

In a separate reaction of $Ph_2CHCOCl$ (347 mg, 1.5 mmol) with **1** (623 mg, 0.50 mmol) in toluene (10 ml) under CO during 4 h at r.t., *trans*-$PtHCl(PPh_3)_2$ (**3**) [19] (336 mg, 89%) was obtained by adding hexane to the reaction mixture: $^1H$ NMR ($CD_2Cl_2$) $\delta$ −16.19 (t, 1 H, Pt–*H*, $^2J$(P–H) = 13.75 Hz, $^1J$(Pt–H) = 1195 Hz), 7.4–7.7 (m, 30H, Ph); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 28.3 (s, $^1J$(Pt–P) = 3012 Hz); IR (KBr) 2220 cm$^{-1}$ ($\nu$(Pt–H)).

A reaction of $Ph_2CHCOCl$ (0.70 g, 3.0 mmol) and **1** (1.2 g, 1.0 mmol) in toluene (40 ml) under $N_2$ gave the white precipitate of *trans*-$PtCl(COCHPh_2)(PPh_3)_2$ (**2**) and the solution showed no IR absorption due to diphenylketene. After removal of the solvent, recrystallization of the residual solid from $CH_2Cl_2$–hexane gave *trans*-$PtCl(COCHPh_2)(PPh_3)_2 \cdot \frac{1}{2}(CH_2Cl_2)$ (0.65 g, 65%) as white crystals; $^1H$ NMR ($CD_2Cl_2$) $\delta$ 3.15 (s, 1 H, C*H*$Ph_2$), 6.49–7.74 (m, 40 H, Ph); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 19.0 (s, $^1J$(Pt–P) = 3538 Hz); IR (KBr) 1651 cm$^{-1}$ ($\nu$(C=O)). Anal. Found: C, 60.88; H, 4.45. $C_{101}H_{84}Cl_4O_2P_4Pt_2$ calcd.: C, 61.09; H, 4.26%.

Similarly, reaction of $Ph_2CHCOCl$ (0.90 g, 3.9 mmol) with $Pd(PPh_3)_4$ (1.5 g, 1.3 mmol) in benzene (40 ml) afforded *trans*-$PdCl(COCHPh_2)(PPh_3)_2$ (0.92 g, 82%) as yellow crystals: $^1H$ NMR ($CD_2Cl_2$) $\delta$ 3.75 (s, 1 H, C*H*$Ph_2$), 6.62–7.73 (m, 40 H, Ph); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 18.6 (s); IR (KBr) 1670 cm$^{-1}$ ($\nu$(C=O)).

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