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# Substituted ketene elimination from acid chlorides induced by ruthenium(0) compounds

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## Abstract

The compound $Ru(CO)_2$(triphos) (triphos = $MeC(CH_2PPh_2)_3$) reacts with a number of acid chlorides RR'CHCOCl to form $[RuH(CO)_2(triphos)]Cl$ and the corresponding substituted ketenes RR'CCO. A quantitative study of the reaction of $Ph_2CHCOCl$ shows that $Ph_2CCO$ is formed in a 1 : 1 stoichiometry. The compound $Ru(CO)_3(PPh_3)_2$ also reacts with $Ph_2CHCOCl$, forming $Ph_2CCO$ and the unstable hydride $[RuH(CO)_3(PPh_3)_2]Cl$, the chemistry of which is also reported.

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We have previously reported that acetyl chloride reacts with the ruthenium(0) compound $Ru(CO)_2$(triphos) (I) (triphos = $MeC(CH_2PPh_2)_2)_3$) to form ketene and the ruthenium(II) hydride $[RuH(CO)_2(triphos)]Cl$ (II) [1].

$$I + MeCOCl \rightarrow II + CH_2CCO \qquad (1)$$

Because of problems in handling the gaseous, very reactive ketene, however, the yield of the organic product could not be ascertained. In addition, no attempt was made to determine the possible generality of the reaction. In view of the novelty of this mode of ketene formation, we have therefore investigated the system further, and we describe in this paper experiments involving reactions of a variety of acid halides with both I and with a second ruthenium(0) compound, $Ru(CO)_3(PPh_3)_2$ (III). We also determine the stoichiometry of the reaction of I with an acid halide, $Ph_2CHCOCl$, which forms a stable ketene, $Ph_2CCO$.

## Experimental

All experiments were carried out under an atmosphere of purified nitrogen in dried, deaerated solvents, using glassware which had been flame dried under vacuum. IR spectra were run on a Bruker IFS 85 FTIR spectrometer, $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra on a Bruker AM 400 FTNMR spectrometer.

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Compounds I [1], II [1] and III [2] were prepared as described in the literature. The reagents n-butyryl chloride, isobutyryl chloride, trimethylacetyl chloride, hydrocinnamoyl chloride, phenylacetyl chloride and 1,8-bis(dimethylamino)naphthalene (Proton Sponge) were purchased from Aldrich, diphenylacetyl chloride from Lancaster Syntheses, and trifluoroacetylchloride from Fairfield Chemicals. With the exception of the gaseous trifluoroacetyl chloride, the acid halides were generally purified by distillation from *N,N*-diethylaniline or isoquinoline prior to use.

Diphenyl ketene was prepared and purified by distillation at 140–142 °C/9 mmHg [3], and was characterized by its IR ($\nu$(CCO) 2100 $cm^{-1}$ [4]) and $^{13}C\{^1H\}$ NMR ($\delta$ 47.2, $Ph_2\mathit{C}OO$, $\delta$ 201.6, $Ph_2\mathit{C}CO$) [5] spectra. Although the compound was normally stored under nitrogen at −40 °C, monitoring of the IR absorbance at 2100 $cm^{-1}$ of a 4 m*M* methylene chloride solution showed only a 2% decrease in intensity over two days at room temperature.

*Reaction of I with $Ph_2CHCOCl$*

$Ph_2CHCOCl$ (0.24 g, 1.05 mmol) was added to a solution of I (0.82 g, 1.05 mmol) in 50 ml methylene chloride. The mixture was refluxed for 12 h, during which time monitoring by IR spectroscopy demonstrated the smooth disappearance of the $\nu$(CO) of I (1941, 1858 $cm^{-1}$) and the appearance of the $\nu$(CO) of II (2057, 2010 $cm^{-1}$) and $Ph_2CCO$ (2100 $cm^{-1}$). The solution was then concentrated and heptane was added to precipitate pure II in ≈ 85% yield. Solvent was removed from the filtrate at reduced pressure, and the resulting yellow-brown residue was found to exhibit the IR absorption and $^{13}C$ resonances characteristic of $Ph_2CCO$ (see above). The reaction was much faster in refluxing toluene, being completed within a few minutes.

The stoichiometry of the reaction of II with $Ph_2CHCOCl$ was ascertained via two different experiments. In the first, a known amount of I was refluxed in methylene chloride for 12 h with a deficiency of the acid halide (1/0.9). The solvent was then removed under reduced pressure, and the residue was redissolved in $CD_2Cl_2$ containing a slight excess of methanol. Separate experiments had shown that $Ph_2CCO$ and methanol react rapidly and quantitatively to form the corresponding ester, $Ph_2CHCO_2Me$, and $^1H$ NMR spectroscopy was thus utilized to estimate the relative amounts of ester and hydride from the reaction of I with $Ph_2CHCOCl$. Careful integration of the spectrum showed that, within experimental error, the ratio was 1/1.

The stoichiometry was also determined directly through absorbance measurements utilizing a Beer's law plot of the intense $\nu$(CCO) of $Ph_2CCO$ at 2100 $cm^{-1}$. Equimolar amounts of I and $Ph_2CHCOCl$ were reacted and the solution was made up to a known volume. Measurement of the intensity of the 2100 $cm^{-1}$ band confirmed that the concentration of the $Ph_2CCO$ corresponded to the amount of I that had reacted.

*Reactions of I with other acid chlorides*

In a series of reactions, 0.20–0.78 g (0.26–1.0 mmol) of I and slight excesses of $PhCH_2COCl$, $PhCH_2CH_2COCl$, $MeCH_2CH_2COCl$ or $Me_2CHCOCl$ were refluxed in methylene chloride until all the I had disappeared. The times required were 1–1.5 h for the first two, 2–3 days for the others; in contrast, no reaction had occurred with $Me_3CCOCl$ after 4 days. In all cases where reaction occurred, IR spectroscopy showed that II was the major product, generally formed in > 85% yields. Furthermore, in the reactions of $PhCH_2COCl$ and $PhCH_2CH_2COCl$, transient ketenic peaks at 2115 and 2118 $cm^{-1}$, respectively, were also observed, while with $MeCH_2CH_2COCl$, weak absorptions at 1754 and 1819 $cm^{-1}$ were observed in the final spectrum.

In contrast, reaction of I with PhCHClCOCl resulted in an instantaneous change in colour of the solution from orange to yellow. The IR spectrum of the reaction mixture showed that no II had formed, there being evident only two rather intense absorptions at 2086 and 2043 $cm^{-1}$, attributed to $[RuCl(CO)_2(triphos)]Cl)$ [1], and a relatively weak band at 2023 $cm^{-1}$, attributed to $RuCl_2(CO)(triphos)$ [1]. On standing or on work-up, the former complex converted to the latter [1].

Treatment of I with $CF_3COCl$ in methylene chloride was carried out under a variety of conditions, but was found to yield a variety of products (by $^1H$, $^{31}P\{^1H\}$ and $^{19}F$ NMR spectroscopy), none of which could be unambiguously identified as the expected $[Ru(CF_3CO)(CO)_2(triphos)]Cl$. A major product in general was the hydride, II, which was formed even in the presence of an equimolar amount of recrystallized Proton Sponge.

### *Reaction of III with $Ph_2CHCOCl$*

A solution of 0.40 g III (0.57 mmol) and 0.13 g $Ph_2CHCOCl$ (0.57 mmol) in 20 ml methylene chloride was refluxed while being monitored periodically by IR spectroscopy. A weak band at 2052 $cm^{-1}$ appeared within a few minutes but, within a few hours, the only new bands apparent were at 2100, 2059 and 1995 $cm^{-1}$. The first of these is to be attributed to $Ph_2CCO$, an assignment confirmed by the $^{13}C\{^1H\}$ NMR spectrum ($CD_2Cl_2$) which exhibited the expected resonances of $Ph_2CCO$ at $\delta$ 47.2 and $\delta$ 201.6. The other two $\nu(CO)$ may be assigned to $RuCl_2(CO)_2(PPh_3)_2$ (see below). About 50% of the III was still present (IR) after 5 days, although reaction of III with $Ph_2CHCOCl$ in refluxing toluene was complete within 12 h, the same products being obtained.

### *Reactions of III with anhydrous HCl and $CF_3CO_2H$*

Treatment of a solution of III in methylene chloride with an excess of trifluoroacetic acid yielded a solution which exhibited $\nu(CO)$ at 2122w, 2072m and 2050s $cm^{-1}$. Removal of the solvent and dissolution of the residue in $CD_2Cl_2$ resulted in a solution exhibiting a $^1H$ resonance at $\delta$ $-6.14$ (t, $J$(P–H) 13 Hz) and a $^{31}P$ resonance at $\delta$ 34.5(s).

Anhydrous HCl was bubbled through a suspension of 0.54 g III in 25 ml methylene chloride at room temperature for 2 min. At this point, the suspension of III had dissolved and the $\nu(CO)$ (1898 $cm^{-1}$) had disappeared, to be replaced by bands at 2122w, 2072s, 2050vs and 1996w $cm^{-1}$. The solvent was then removed under reduced pressure to give a yellow powder which was redissolved in $CD_2Cl_2$. A $^1H$ NMR spectrum ($CD_2Cl_2$) of the solute exhibited a hydride resonance at $\delta$ $-6.21$ (t, $J$(P–H) 13 Hz), while a $^{31}P\{^1H\}$ NMR spectrum exhibited singlets at $\delta$ 17.7, $\delta$ 34.5 (major product) and $\delta$ 40.0. On further treatment of the solution with HCl, only bands at 2059s and 1996s $cm^{-1}$ remained in the carbonyl region of the IR spectrum. The hydride resonance had disappeared from the $^1H$ NMR spectrum, while the $^{31}P\{^1H\}$ spectrum exhibited only the single resonance at $\delta$ 17.7.

Assignments for all of these spectroscopic data will be made below.

## Results and discussion

Our previous work involved the conversion of acetyl chloride to the very volatile, thermally labile $CH_2CCO$, and accurate estimates of the stoichiometry of the reaction were not obtained. The present investigation therefore began with a study of the reaction of I with $Ph_2CHCOCl$, which was expected to give a substituted ketene ($Ph_2CCO$) which would be sufficiently non-volatile and stable that its formation could be monitored conveniently and accurately. As hoped, I does react with $Ph_2CHCOCl$ to yield $Ph_2CCO$, identified by comparison of its IR, $^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra with those of an authentic sample and with data from the literature [4,5]. In addition, the IR spectra of the solutions indicated the presence of the hydride II as the major ruthenium-containing product. Quantitative estimates of the amounts of $Ph_2CCO$ formed also demonstrated that the stoichiometry of the reaction was

$$\mathrm{I} + Ph_2CHCOCl \rightarrow \mathrm{II} + Ph_2CCO \qquad (2)$$

thus confirming our previous hypothesis [1]. A weak $\nu(CO)$, to be attributed to $RuCl_2(CO)(triphos)$, was also apparent at the end of the reaction, possibly indicating an alternate, radical reaction pathway for I and $Ph_2CHCOCl$ (see discussion below concerning the similar reaction of I with $PhCHClCOCl$). However, separate experiments have shown that I also reacts very slowly with methylene chloride, forming the same chlororuthenium(II) compound.

Reactions of I with other acid halides were also investigated, although not in detail as the anticipated ketene products were expected to be relatively thermally labile. In general, the significant formation of II was taken as evidence that a reaction as in (1) or (2) had occurred. Reactions of I with $PhCH_2COCl$ and $PhCH_2CH_2COCl$ proceeded to completion within 1–2 h in refluxing methylene chloride, yielding in both cases II and, apparently, $PhCHCO$ or $PhCH_2CHCO$. In contrast, the reactions of I with $MeCH_2CH_2COCl$ and $Me_2CHCOCl$ took 2–3 days to go to completion. The ketene products are expected to be unstable under these conditions [6], and indeed no bands at about 2100 $cm^{-1}$ were noted. Ultimately, there were observed weak absorptions at 1754 and 1819 $cm^{-1}$ in the IR spectrum of the $MeCH_2CH_2COCl$ reaction mixture, presumably to be assigned to the products of thermal decomposition of the ketene [7].

In contrast to the above-mentioned reactions, treatment of I with $PhCHClCOCl$ resulted in the immediate formation of $[RuCl(CO)_2(triphos)]Cl$, no hydride or ketene absorptions being apparent in the IR spectrum. Chlorination of I may indicate a radical process [1], but the reaction was not investigated further. No reaction between I and $Me_3CCOCl$ had occurred after 4 days of refluxing, quite likely because of the effects of steric hindrance although, of course, a ketene product could not form in this case. This system was also not investigated further. In an attempt to isolate the type of acyl intermediate postulated previously for the dehydrohalogenation of acetyl chloride by I [1], the latter was treated with trifluoroacetyl chloride. Unfortunately, the attempt was inconclusive, as an apparently acidic impurity in the acid halide preferentially protonated the ruthenium(0) compound. Attempts to deactivate the impurity failed.

In an effort to ascertain the possible generality of reactions such as (1) and (2), we have also found that reaction of $Ru(CO)_3(PPh_3)_2$ (III) with $Ph_2CHCOCl$ does indeed produce the corresponding ketene (identified by IR and $^{13}C\{^1H\}$ NMR spectroscopy), although the expected ruthenium hydride, $[RuH(CO)_3(PPh_3)_2]Cl$ (see below for IR evidence), is apparently formed only as a transient species. This cationic hydride, as the hexafluorophosphate salt, has been reported to exhibit $\nu(CO)$ (Nujol mull) at 2126m, 2076vs, 2056vs and 2024m $cm^{-1}$, and a hydride NMR resonance (liquid $SO_2$) at $\delta$ −6.2 (t, $J$(P–H) 15.5 Hz) [7].

For purposes of comparison, the cationic hydride complex was synthesized by treating III with trifluoroacetic acid in methylene chloride, a reaction which gave solutions exhibiting $\nu(CO)$ at 2122w, 2072m and 2050s $cm^{-1}$ ($CH_2Cl_2$), and a hydride resonance at $\delta$ −6.14 (t, $J$(P–H) 13 Hz). The $^{31}P\{^1H\}$ spectrum exhibited a resonance at $\delta$ 34.5(s) ($CD_2Cl_2$). The IR and $^1H$ NMR data are almost identical to the data reported in the literature for the $[RuH(CO)_3(PPh_3)_2]^+$ cation, and thus this species is clearly formed in the reaction of III with trifluoroacetic acid. The $^{31}P$ chemical shift of this complex is $\delta$ 34.5.

On this basis, a weak IR absorption at 2052 $cm^{-1}$, observed in the early stages of the reaction of III with $Ph_2CHCOCl$, may well correspond to the anticipated cationic hydride complex. It would appear that while the reaction of III with $Ph_2CHCOCl$ initially gives $[RuH(CO)_3(PPh_3)_2]Cl$, the latter is unstable under the reaction conditions and is converted to a complex exhibiting $\nu(CO)$ at 2059s and 1995s $cm^{-1}$, to be identified as $RuCl_2(CO)_2(PPh_3)_2$ (lit. 2059s, 1996s $cm^{-1}$ in $CH_2Cl_2$ [8]). This type of degradation has precedent, as II has been found to react slowly with acetyl chloride to form $[RuCl(CO)_2(triphos)]Cl$ and $RuCl_2(CO)(triphos)$ [9].

In a complementary study of the properties of the hydride, a reaction of III with anhydrous HCl was found to yield solutions exhibiting a weak $\nu(CO)$ at 1996 $cm^{-1}$ (in addition to the above-mentioned $\nu(CO)$ at 2122, 2072 and 2050 $cm^{-1}$), a hydride resonance at $\delta$ −6.21 (t, $J$(P–H) 13 Hz) and $^{31}P$ resonances at $\delta$ 34.5 (major product), $\delta$ 17.7 and $\delta$ 40.0. The first-mentioned $^{31}P$ resonance is clearly to be attributed to $[RuH(CO)_3(PPh_3)_2]Cl$, and thus this compound would appear to be the initial product of HCl addition. On further treatment with HCl, however, all the ruthenium was converted to $RuCl_2(CO)_2(PPh_3)_2$, as evidenced by the appearance of only two $\nu(CO)$ (at 2059 and 1996 $cm^{-1}$ [8]) in the final IR spectrum, and of a single resonance at $\delta$ 17.7 (lit. $\delta$ 17.4 [10]) in the $^{31}P\{^1H\}$ NMR spectrum. Comparison with the spectroscopic data from the initial reaction of III with HCl suggests that this compound was one of the minor products. The other, exhibiting the $^{31}P$ resonance at $\delta$ 40.0, may have been $RuHCl(CO)_2(PPh_3)_2$ (lit. $\delta$ 39.9 in $C_6D_6$) [10]). It is instructive to contrast the results of our protonation studies with those of Collman and Roper, who have found that III reacts with HCl and trifluoroacetic acid to form, presumably under more forcing conditions, only the species $RuX_2(CO)_2(PPh_3)_2$ ($X = Cl, CF_3CO_2$) [11].

In conclusion, we have shown that the previously reported [1] dehydrohalogenation of acetyl chloride by I is not unique, but occurs with other acid chlorides and with at least one other ruthenium(0) compound. We have also determined the stoichiometry for the reaction of I with $Ph_2CHCOCl$, showing that this reaction proceeds as in eq. 2.

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