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# The Oxidative Addition of Methyl Iodide to Acetylacetonatocarbonyltriphenylphosphiterhodium(I) Complex

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Oxidative addition reactions of the alkyl and acyl halogenides are quite typical for the Rh(I) phosphine complexes. $RhCl(PPh_3)_3$ reacts with $CH_3J$ to form the alkyl $[Rh(CH_3)ClJ(PPh_3)_2{\cdot}CH_3J]$ complex [1–3]. Alkyl rhodium(III) compounds ($RhX_2R(CO)L_2$) were obtained by reactions of $RhX(CO)L_2$ with the methyl, acyl, allyl and sulphonyl halogenides [4, 5]. Oxidative addition reactions of the RX and RCOX halogenides to rhodium(I) cyclopentadienyl complexes $C_5H_5Rh(CO)L$ have been studied [6, 7]. Examination of $CH_3J$ addition to metal complexes revealed that the alkyl complex has not always been the only reaction product. If the product of oxidative addition contained the CO group, isomerisation of the compound leading to the acyl complex, e.g., $Rh(COCH_3)XJL_2$, was usually observed [8, 9]. The reverse reaction, *i.e.*, the rearrangement of the pentacoordinated acyl complex $RhCl_2(COR)(PPh_3)_2$ to the hexacoordinated alkyl complex $RhRCl_2(CO)(PPh_3)_2$, was also reported [10].

The subject of this paper is the reaction of the oxidative addition of $CH_3J$ to the Rh(acac)(CO)[$P(OPh)_3$] complex. In the literature only two such reactions with Rh(acac)($PPh_3$)$_2$ [11] and Rh(acac)(CO)($PPh_3$) have been reported [12].

The reaction of Rh(acac)(CO)P ($P = P(OPh)_3$) with $CH_3J$ was investigated by IR and $^1H$ NMR spectroscopy at 20 °C. After addition of $CH_3J$ to Rh(acac)(CO)P solution in $CHCl_3$, the IR spectrum in the 1800–2200 $cm^{-1}$ region shows the new $\nu(CO)$ band at 2080 $cm^{-1}$, as well as the band deriving from the initial compound ($\nu(CO) = 2005$ $cm^{-1}$). During the first hour, the intensity of both bands keeps changing systematically – the intensity of the former declines and that of the latter increases. Simultaneously, a broad band appears at 1720 $cm^{-1}$; its intensity slowly increases. After 4 h the intensity of the bands stabilizes. The literature data [4–10] allowed the assignment of the $\nu(CO)$ band at 2080 $cm^{-1}$ to the alkyl Rh(acac)(CO)($CH_3$)(J)P complex, and the band at 1720 $cm^{-1}$ to the acyl Rh(acac)($COCH_3$)(J)P complex. The oxidative addition reaction of $CH_3J$ to Rh(acac)(CO)P is not too fast, and the complete conversion of the initial complex was observed after 1 h.

For comparison, we have repeated the recently reported reaction of $CH_3J$ addition to Rh(acac)(CO)($PPh_3$) [12]. In this case the $\nu(CO)$ band at 1980 $cm^{-1}$, derived from the initial phosphine complex, disappeared immediately after the addition of $CH_3J$; this indicates that the reaction was much faster. This could be indicative of the influence of the electron density of the metal ion on the rate of the oxidative addition reaction of $CH_3J$ to the Rh(I) complex.

Substitution of the $PPh_3$ ligand by the stronger $\pi$-acceptor $P(OPh)_3$ diminished the electron density and the oxidative addition reaction rate. This explains why there are no products of the reaction between the Rh(acac)$(CO)_2$ complex and $CH_3J$ even after 24 h.

Examination of the reaction between Rh(acac)(CO)P and $CH_3J$ at different concentrations of the reagents revealed that the reaction rate was practically independent of the amount of $CH_3J$ ($[CH_3J]:[Rh] = 1/10$), but the composition of the reaction products changed with variations in $CH_3J$ concentration. At lower $CH_3J$ concentrations, the alkyl and acyl complexes were formed in approximately equal amounts, while at considerable $CH_3J$ excess a larger amount of the alkyl complex formed.

The $^1H$ NMR spectrum of the Rh(acac)(CO)P complex exhibits two signals from the methyl protons of the acetylacetonate ligand (1.65 and 1.99 ppm) and a signal from the –CH– proton at 5.31 ppm. Addition of $CH_3J$ to the solution results in the appearance of new lines at 1.75, 2.06 and 1.45 ppm, and at 5.21, 5.41 and 5.47 ppm, in addition to the line deriving from $CH_3J$ (2.13 ppm). The reaction is accompanied by the stepwise lowering of the lines deriving from Rh(acac)(CO)P and by the intensity increase of the other lines. After ~1.5 h (when the initial complex practically did not exist in the solution), additional signals of lower intensity were observed at 1.85, 2.0 and 2.22 ppm.

The product of the oxidative addition of $CH_3J$ to Rh(acac)(CO)P (or, more precisely, the mixture of products) was isolated in solid form. The IR and $^1H$ NMR spectra of the isolated solid substance are identical to those described above for the solution. The IR spectrum exhibits the $\nu(CO)$ band at 2080 $cm^{-1}$ and one broad band at ~1720 $cm^{-1}$; the $^1H$ NMR spectrum presents all the signals that were previously discussed (Fig. 1a).

Seven $^1H$ NMR lines are observed in the $CH_3$ range of the spectrum. Some of them are broadened; therefore assignment to $CH_3$(acac) and $CH_3(CH_3J)$ protons seems to be quite difficult. It should be also noted that in solution at least three different species, containing acetylacetone ligand showing CH proton signals at 5.21, 5.41 and 5.47 ppm, are present.

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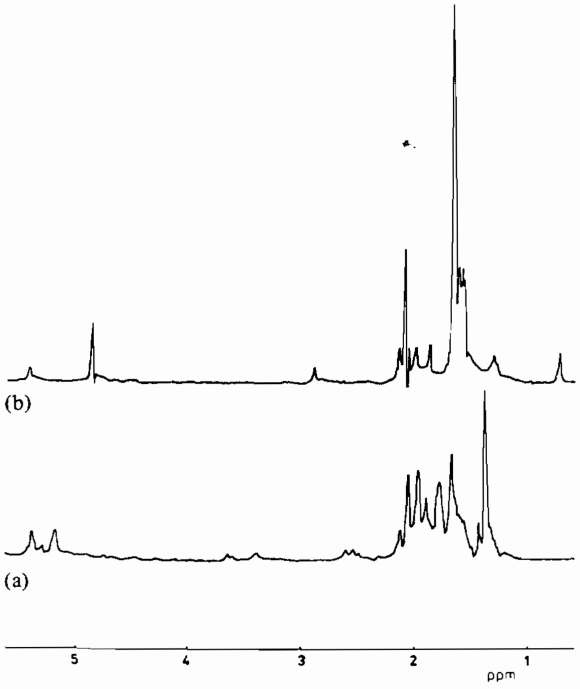

Fig. 1. $^1$H NMR spectra in $CDCl_3$ of complexes isolated in reactions: (a) Rh(acac)(CO)P(OPh)$_3$ + $CH_3J$; (b) Rh(acac)(CO)PPh$_3$ + $CH_3J$.

Moreover, since both the alkyl and acyl complexes can exist as couples of isomers, the observed complexity of a spectrum is not surprising.

After the complex with $CH_3J$ is dissolved in $CHCl_3$, the IR spectrum exhibits a very slow lowering of the band intensity at 1720 cm$^{-1}$ and the formation of a new band at 2006 cm$^{-1}$. It could indicate the reproduction of the initial complex Rh(acac)CO[P(OPh)$_3$], but the $^1$H NMR spectrum of the appropriate solution shows no clear lines at 1.65 and 1.99 ppm. Regardless of the structure of the compound obtained, it could be stated that the acyl complex produced the complex containing the terminal CO group. The broadened lines in the $^1$H NMR spectrum, whose intensity changed over time, indicate the dynamics of the spectra.

For comparison, we have also examined the product of the reaction Rh(acac)(CO)PPh$_3$ + $CH_3J$. This compound was synthesized following the method previously described [12]. It was found that its IR spectrum presents lines at 2045 and 1735 cm$^{-1}$. The $^1$H NMR spectrum of the product of the reaction Rh(acac)(CO)PPh$_3$ + $CH_3J$ (Fig. 1b) contained sharp, well-separated bands; the highest bands ($\delta$ = 1.75 and 2.18 ppm) derive most probably from $CH_3$ acetylacetone groups in the alkyl and acyl complexes.

The reaction of $CH_3J$ with Rh(acac)(CO)P, which is slow in $CHCl_3$, is much slower in $C_6H_6$. But when other alkyl iodides (e.g. $C_3H_7J$, $C_4H_9J$) were used instead of $CH_3J$, no products of the oxidative addition reaction were observed even after 24 h. The reaction of Rh(acac)(CO)P with allyl iodide is faster. The appropriate alkyl complex presents the $\nu$(CO) band at 2080 cm$^{-1}$, and the acyl one at 1680 and 1725 cm$^{-1}$.

## Experimental

Rh(acac)(CO)P was obtained by the reaction between Rh(acac)(CO)$_2$ [13] and P ([Rh]:[P] = 1:1) [14], or by the reaction of equimolar amounts of Rh(acac)P$_2$ [15] and Rh(acac)(CO)$_2$ [16]. Solutions of concentrations [Rh] = 0.16 mol l$^{-1}$ and $CH_3J$ = 0.16–1.6 mol l$^{-1}$ were used. Freshly distilled $CH_3J$ was always used. The product of the reaction of Rh(acac)(CO)P with $CH_3J$ was isolated in solid state by repeated crystallization of the oil, obtained by condensation of the solution containing Rh(acac)(CO)P and $CH_3J$ ([Rh]:[$CH_3J$] = 1:3) in $CHCl_3$, *in vacuo*. The compound is dark-brown. *Anal.* Calc. for $RhC_{25}H_{25}O_5PJ$: C, 44.0; H, 3.4. Found: C, 41.3; H, 2.1%. The $^1$H NMR spectra were recorded on a Tesla 80 MHz spectrometer and the IR spectra on a Specord 75 IR spectrometer.

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