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Reactions of *trans*-[IrCl(CO)(PPh$_3$)$_2$] and *trans*-[RhCl(CO)(PPh$_3$)$_2$] with Organic Tetrahalides – Oxidative Addition and Formation of Dihaloalkenes

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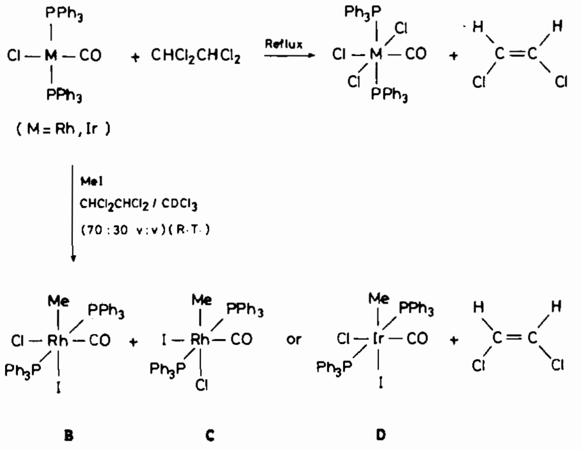
Oxidative addition reactions of the title compounds with 1,1,2,2-tetrachloroethane yield *trans*-[MCl$_3$(CO)(PPh$_3$)$_2$], (M = Rh(III), Ir(III)) and *cis*-1,2-dichloroethene. The stereochemistry of these complexes was assigned using IR and ^{31}P{^{1}H} NMR spectroscopy, and the addition is stereospecific and *trans* in this particular case. Tetrachloroethane is used as a solvent in many reactions. In view of the finding now that it takes part in the reaction, care must be excercised in the use of such a solvent in similar reactions. Addition of MeI to the title compounds in tetrachloroethane gives a *trans* addition product with the Ir complex, and *cis*, *trans*-addition products with the Rh complex.

The reduction of organic halides by metals is a well-known route to olefins and cycloalkanes [1–3]. The reduction of organic tetrahalides by a metal is still not known.

In view of our interest in biheterometallic and platinum complexes [4–6], we have investigated the reaction between *trans*-[RhCl(CO)(PPh$_3$)$_2$] and *cis*-[PtCl$_2$(PPh$_3$)$_2$] in the presence of 1,1,2,2-tetrachloroethane as a good solvent recommended for the preparation of binuclear platinum complexes of the type [Pt$_2$X$_4$(PR$_3$)$_2$] [7]. By examining the resulting solution of the reaction by IR and ^{31}P NMR spectroscopy, we found that, there is no change in the platinum complex spectrum but a dramatic change in the rhodium spectrum. However, the above reaction was repeated in the presence of RhCl(CO)(PPh$_3$)$_2$ and tetrachloroethane only, under N$_2$ and refluxing. The resulting solution was examined by IR, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The results confirm the formation of *mer*,*trans*-[RhCl$_3$(CO)(PPh$_3$)$_2$] and *cis*-dichloroethene, Scheme 1.



Scheme 1.

The complex *trans*-[RhCl(CO)(PPh$_3$)$_2$] (500 mg) was dissolved in tetrachloroethane (10 ml). The solution was stirred under nitrogen and refluxed for 1–2 h, and the solvent removed *in vacuo*. The yellow solids were dissolved in CDCl$_3$ and Et$_2$O was added to precipitate fine, yellow crystals (Et$_2$O may be added to the original solution to obtain yellow crystals). The vapours from the reaction were cooled through a condenser and then passed through cold CDCl$_3$ solution. The IR spectra of the yellow solid exhibit a strong band at 2100 cm^{-1}, assigned for the new ν(CO) group of the Rh(III) complex, and a weak band at 1960 cm^{-1}, assigned for ν(CO) of the starting Rh(I) complex (compare with the authentic sample). The IR band at 331 cm^{-1} assigned for ν(Rh–Cl) (*trans* to CO) and a strong band at 345 cm^{-1} assigned for RhCl$_2$ (*trans* Cl), asymmetric stretching vibration. The IR spectra of the new complex are in good agreement with the analogous rhodium complex *trans*-[RhCl$_3$(CO)(PMe$_3$)$_2$] [8]. Further strong evidence was obtained from the CDCl$_3$ solution of the new complex. The ^{31}P{^{1}H} NMR spectrum consists of a doublet at δ +8.9 and $^1J(^{103}\text{Rh}-^{31}\text{P})$, 78.1 Hz and small broad doublets appear at δ + 29.0 and $^1J(^{103}\text{Rh}-^{31}\text{P})$, 127.0 Hz assigned for the starting complex (compare with authentic sample). Coupling constant values are comparable to the values of $^1J(^{103}\text{Rh}-^{31}\text{P})$ obtained from *trans*-[RhCl$_3$(CO)(PMe$_3$)$_2$], ^1J, 72 Hz and for *trans*-[RhCl(CO)(PMe$_3$)$_2$], ^1J, 114 Hz [8]. The ^{1}H and ^{13}C NMR spectra of the CDCl$_3$ solution of the resulting condensed vapour showed a significant quantity of dichloroethene. The ^{1}H NMR spectrum showed a single peak which appears at δ 6.45 ppm and ^{13}C NMR spectra showed a signle peak at δ 116.6 ppm. These results are comparable to the authentic sample of *cis*- and *trans*-dichloroethene (^{1}H, δ 6.47, 6.36 and ^{13}C δ, 117.0, 120.0 for *cis* and *trans* respectively in CDCl$_3$ and also fit well with the reported values [9, 10]).

Accordingly, the olefinic product is more likely to be *cis*-1,2-dichloroethene. This probably is formed as a result of decomposition of Rh(III)-alkyl intermediates; similar intermediates were obtained in the Rh(I) macrocycle reaction with organic dihalides [11]. The above reaction does not work at room

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temperature. The case is different when Vaska's complex, *trans*-[IrCl(CO)(PPh$_3$)$_2$] (100 mg), is treated with tetrachloroethane (10 ml) at room temperature (the reaction was completed in 24 h) or refluxed under nitrogen for a few minutes. The fine yellow crystals, obtained as before, showed IR and ^{31}P NMR spectra for a new Ir(III) complex, *trans*-[IrCl$_3$(CO)(PPh$_3$)$_2$], and the formation of *cis*-1,2-dichloroethene. The ^{31}P{^{1}H} NMR spectrum showed a sharp single peak at δ −17.5 (no traces of the starting Ir(I) complex were observed). The ^{31}P NMR spectrum of the starting Ir(I) complex shows a broad peak at δ +23.8 (obtained separately). The IR spectrum of the newly Ir(III) complex, showed a strong peak at 2095 cm^{-1}, assigned for ν(CO), and a characteristic peak near 301 cm^{-1} assigned for Ir–Cl (*trans* to CO). As a result, reaction of either complex, Ir(I) or Rh(I), with tetrachloroethane gives only one isomer, thus the addition is stereospecific and *trans* in this particular case. The above reactions provide the first examples of the formation of Rh(III) and Ir(III) complexes and elimination of *cis*-1,2-dichloroethene.

We also investigated the reactions of MeI with the title compounds in tetrachloroethane, at room temperature. Examination of the ^{31}P{^{1}H} NMR spectrum of the new Rh(III) products (completed in 48 h in the presence of excess tetrachloroethane) clearly indicates the formation of two new complexes which appear as two doublets, at δ +23.6, $^1J(^{103}\text{Rh}-^{31}\text{P})$, 107.4 Hz, and at δ +12.3, $^1J(^{103}\text{Rh}-^{31}\text{P})$, 90.3 Hz, assigned for the *trans* and *cis* addition of MeI (B and C, Scheme 1). In the iridium(I) complex, only one species is formed, assigned for the *trans* addition species (D, Scheme 1); ^{31}P{^{1}H} NMR shows only one single peak at δ − 19.1. This behaviour is in contrast to the addition of MeI to the analogous *trans*-[IrCl(CO)(PPh$_2$Me)$_2$] complex in methanol which gives both *cis* and *trans* addition products (similar to B and C, Scheme 1) [12, 13].

All NMR spectra were measured on a JEOL JNM FX-100 spectrometer operating in the Fourier transform mode. Infrared spectra were measured on a Beckman 4240 spectrophotometer as KBr pellets.

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