# Hydroformylation of Propene Under Mild Conditions using $Rh_4(CO)_{12}$

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*Summary* Hydroformylation of propene using stoicheiometric amounts of $Rh_4(CO)_{12}$ and hydrogen, and direct synthesis of the first acyl cluster compounds are reported; catalytic synthesis in the presence of tertiary phosphines takes place together with decomposition of the phosphine.

Current interest in the hydroformylation of olefins *via* rhodium catalysts[1,2,3] prompted us to present some preliminary results with $Rh_4(CO)_{12}$[4] at room temperature and atmospheric pressure. Previously, $Rh_4(CO)_{12}$ has been used as an hydroformylation catalyst only at elevated pressure (50—100 atm) and temperature (75 °C).[5]

A solution of $Rh_4(CO)_{12}$ in toluene reacts rapidly with a mixture of propene and hydrogen (atmospheric pressure and room temperature) giving 90—95% yield of the aldehydes (*ca.* 1:1, n:iso) expected from equation (1). Under

$$3\ Rh_4(CO)_{12} + 4\ MeCH{:}CH_2 + 4\ H_2 \longrightarrow 2\ MeCH_2CH_2CHO + 2\ Me_2CH{\cdot}CHO + 2\ Rh_6(CO)_{16} \quad (1)$$

the same conditions there is no reaction with either hydrogen or propene in the absence of the other gas, only a slow formation of $Rh_6(CO)_{16}$ being observed, according to the known decomposition of $Rh_4(CO)_{12}$ in the absence of carbon monoxide.[6]

Reaction (1) is analogous to 'stoicheiometric' hydroformylation *via* $Co_2(CO)_8$ [equation (2)], but this requires

$$2Co_2(CO)_8 + 4\ \text{olefin} + 4H_2 \rightarrow 4\ \text{aldehyde} + Co_4(CO)_{12} \qquad (2)$$

high pressure (40—100 atm) at 31 °C.[7]

As for reaction (2), reaction (1) is inhibited by carbon monoxide: using a mixture of gases containing 10% of carbon monoxide, the time required for a 90—95% transformation is increased from 3 to *ca.* 40 h. The reaction stops when the temperature is lowered to 0 °C. This temperature dependence parallels the behaviour of $HCo(CO)_4$ towards olefins when using a carbon monoxide atmosphere.[8] Both the effect of the carbon monoxide partial pressure and the temperature on the reaction rate suggest that reaction (1) involves dissociation of the catalyst.

In more polar solvents such as methanol or acetone only traces of aldehydes are formed, the reaction products being $Rh_6(CO)_{16}$ and a brown solution from which, on addition of a tetra-alkylammonium salt, acyl derivatives of the type $[NR_4][Rh_6(CO)_{15}(COR)]$ are obtained. Using ethylene it was possible to isolate the salt $[NMe_4][Rh_6(CO)_{15}(COEt)]$ in 80% yield, while using propene, the salt $[NEt_4][Rh_6(CO)_{15}(COPr)]$ has been obtained. In both salts the presence of a weak i.r. absorption at 1655—1670 $cm^{-1}$ indicates the presence of an acyl group, while the i.r. bands at 2080w, 2040vs, 2020w, 1820w, 1785sh, 1775s, and 1725w $cm^{-1}$ are analogous to those found in the related anions $[Rh_6(CO)_{15}X_9]^-$ (X = Cl, Br, I, CN, SCN, $CO_2R$, CONHR and H) recently isolated in this laboratory.[9]

Further confirmation of the presence of an acyl group comes from the n.m.r. spectrum of $[NMe_4][Rh_6(CO)_{15}(COEt)]$ in which the ethyl ($\tau$ = 9·05; 6·92) and tetramethylammonium ($\tau$ = 6·48) signals are present in the expected ratio. Moreover decomposition of $[NEt_4][Rh_6(CO)_{15}(COPr)]$ with iodine in methanol gives the expected mixture of n- and iso-methylbutyrate (ratio *ca.* 2:1).

In the absence of propene, $Rh_4(CO)_{12}$ reacts with aqueous acetone according to equation (3). In the presence of

$$3Rh_4(CO)_{12} + H_2O \rightarrow 2(H.solv.)^+ + [Rh_{12}(CO)_{30}]^{2-} + CO_2 + 5\ CO \qquad (3)$$

olefin there is an analogous reaction [equation (4)].

$$3Rh_4(CO)_{12} + 2C_2H_4 + 2\ H_2O \longrightarrow 2(H.solv.)^+ + 2[Rh_6(CO)_{15}(COEt)]^- + 2\ CO_2 + 2\ CO \qquad (4)$$

In both cases slow separation of $Rh_6(CO)_{16}$ occurs. The presence of free acidity was shown by precipitation of the anion using a neutral tetra-alkylammonium salt followed by titration of the filtered solution, and observing that the i.r. spectrum of the original solution was coincident with the i.r. spectrum of the precipitated tetra-alkylammonium salt.

Reaction (4) involves formation of a dissociated acid; in fact $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_6(CO)_{15}I]^-$ have the $Rh_6(CO)_{16}$ type of structure,[10] in which there are no easily available co-ordination positions for the formation of an additional covalent bond.

Treatment of $Rh_4(CO)_{12}$ with $PPh_3$ gives, amongst others, $Rh_2(CO)_4(PPh_3)_4$,[2] which has been reported to be an efficient catalyst for the hydroformylation of olefins under mild conditions.[1,2] Therefore, the addition of a large excess of $PPh_3$ to $Rh_4(CO)_{12}$ should give directly an efficient hydroformylation catalyst.

Surprisingly, hydroformylation becomes catalytic with the addition of only 1—2 fold excess of $PPh_3$, or on starting from pure preformed $Rh_4(CO)_{10}(PPh_3)_2$. Under these mild conditions there is no hydrogenation to alcohol and there is increase of the normal aldehyde on increasing the amount of $PPh_3$.[1]

During the reaction, formation of the hydrocarbon corresponding to the radicals of the phosphine is observed (butane, benzene, cyclohexane), *e.g.* using a $PPh_3$:$Rh_4(CO)_{12}$ ratio of 2, about one mol. equiv. of benzene (g.l.c.) is found.† It seems probable that phosphido bridges are formed as has been reported in the reaction between $Os_3(CO)_{12}$ and $PPh_3$.[11] It is worth mentioning that related catalysts which contain a tertiary amine are reported to be active in mild conditions only with tribenzylamine,[3] an amine which readily undergoes internal *ortho*-metallation reactions.

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† In toluene at 25 °C and atmospheric pressure ($CO:H_2:C_3H_6 = 1:1:1$); in solution a similar reaction also takes place between $Rh_4(CO)_{12}$ and $PPh_3$ under nitrogen.

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