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Preliminary communication

New models for the formation of oxygenates in the Fischer–Tropsch reaction

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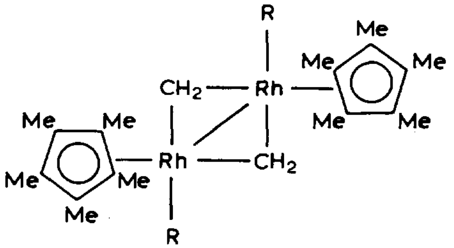
Abstract

Decomposition of the Fischer–Tropsch model complex $[(C_5Me_5Rh)_2(CH_3)_2(\mu\text{-}CH_2)_2]$ (**1a**) with $Na_2IrCl_6/PdCl_2$ or $FeCl_3/PdCl_2$ gave acetaldehyde and acetone. Analogously, $[(C_5Me_5Rh)_2(CD_3)_2(\mu\text{-}CH_2)_2]$ gave CD_2HCOCH_2D, derived from the C_1-ligands of the complex, and $[(C_5Me_5Rh)_2(n\text{-}C_3H_7)_2(\mu\text{-}CH_2)_2]$ gave pentan-2- and -3-one.

Although the synthesis by Fischer–Tropsch reactions (the catalysed condensation/polymerisation of carbon monoxide and hydrogen) of hydrocarbons for fuel is now probably of little economic significance [1], the selective production of oxygenates is still an important objective. In most cases, under both heterogenous and homogeneous conditions, the oxygen already present in the CO has been used to form the oxygenates [2,3]. We report here model studies to illustrate an alternative strategy, in which olefins are first made and then oxidised.

The complex $[(C_5Me_5Rh)_2(CH_3)_2(\mu\text{-}CH_2)_2]$ (**1a**) on pyrolysis or on reaction with one-electron oxidisers gives largely methane and propene, a little ethene, and a trace of ethane. The C_2 and C_3 hydrocarbons arise by coupling the methyl with methylene ligands [4].



(**1a** , R = CH_3 ;
1b , R = CD_3 ;
2 , R = $n\text{-}C_3H_7$)

When complex **1a** was decomposed with Na_2IrCl_6 and $PdCl_2$ or $FeCl_3$ and $PdCl_2$ in tetrahydrofuran/water (10/1 v/v; 15 h, 55 °C), acetaldehyde and acetone

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were formed, in essentially quantitative yields (based upon the amounts of ethene and propene produced in the absence of $PdCl_2$). Thus, oxidation of **1a** (56 μmol) with six equivalents each of $PdCl_2$ and Na_2IrCl_6 gave methane (41 μmol), acetone (32 μmol), and acetaldehyde (3 μmol), as well as methyl chloride (7 μmol), ethane (4 μmol) and propene (1 μmol). Oxidation of **1a** (37 μmol) with $FeCl_3/PdCl_2$ gave acetone (29 μmol), acetaldehyde (1 μmol), methane (21 μmol), and small amounts of C_2 and C_3 gases. The chief reaction of **1a** (> 60%) can therefore be represented as:

$$\underset{\textbf{(1a)}}{[(C_5Me_5Rh)_2(CH_3)_2(\mu\text{-}CH_2)_2]} - 4e + PdCl_2 + H_2O \rightarrow$$

$$CH_4 + CH_3COCH_3 + 2HCl + Pd^0 + 2[C_5Me_5Rh]^{2+}$$

Na_2PdCl_4 or even finely divided palladium metal in the presence of Na_2IrCl_6 also gave acetone and acetaldehyde, but their activities were not as great as that of $PdCl_2$. By contrast, no oxygenates were formed on reaction of **1** with only $FeCl_3$ or Na_2IrCl_6, and the reaction of **1a** in thf/water with $PdCl_2$ alone gave completely different products: methane (65%), ethane (34%) and methyl chloride (11%). Ethane is normally a very minor component of the decomposition products of **1**.

The propene from **1b** and Na_2IrCl_6 or $FeCl_3$ in moist solvents is very largely $CD_2{=}CHCDH_2$ [5]; reaction of **1b** with Na_2IrCl_6 and $PdCl_2$ in H_2O gave acetone which was shown by $^2H\{^1H\}$ NMR spectroscopy to be mainly CDH_2COCHD_2 (δ 1.931 ppm, CD_2H, and 1.948 ppm, CDH_2; relative intensity observed 1.8/1, expected 2/1). This was confirmed by the ^1H NMR spectrum which showed a 1/1/1 triplet (CDH_2, J(D–H) 2 Hz) and a quintet (CHD_2, J(D–H) 2 Hz). A small amount of acetone-CH_3 was also present, the proportion of which grew with time owing to exchange with H_2O solvent. The formation of CDH_2COCHD_2 is consistent with the acetone being derived from $CD_2{=}CHCDH_2$, and shows that this Wacker-type reaction [6] is also highly specific.

Ketones were also obtained from the higher alkyl homologues of **1**. Thus complex **2** (51 μmol), after reaction with $FeCl_3/PdCl_2$ in moist thf, gave a mixture which contained pentan-3-one (1 μmol) and pentan-2-one (0.7 μmol) * as the C_5 products, together with propyl chloride. The proportions of chloroalkanes formed in decomposition of the higher homologues of **1** increase with increasing Rh-alkyl chain length.

Oxygenate products from Fischer-Tropsch reactions have hitherto been derived directly from CO by a partial reduction [2,3]. This work opens up the possibility of a quite different type of process in which the oxygenates arise by oxidation of intermediately formed alkenes (or even alkanes),

$$CO + H_2 \rightarrow R^1CH{=}CHR^2 \xrightarrow{[O]} R^1COCHR^2$$

Palladium on lanthanide oxides has been shown to be a good catalyst for methanol production from syn-gas [7], and although CO plus hydrogen gave almost only methane over rhodium, the presence of an oxidising catalyst (Rh_2O_3) or

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* Complex **2** on oxidation (Na_2IrCl_6/thf/water) gave pent-1-ene (2%), pent-2-ene (7%), pentane (2%), as well as C_1–C_4 hydrocarbons and propyl chloride (35%). Oxidation ($PdCl_2$/thf/water) of pent-1-ene gave largely pentan-2-one while pent-2-ene gave a 1/1 mixture of pentan-2- and -3-ones [10].

promoter ($LaRhO_3$) caused the formation of oxygenates, in particular acetaldehyde and propionaldehyde [8]. A similar approach has been used for a direct synthesis of ethanol [9] *.

Clearly, by combination of iridium (or iron) electron-oxidisers with other reagents, it should be possible to make other organics from the combination of hydrocarbon ligand fragments in (1) and its analogues.

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* *Note added in proof.* Recent patents have disclosed the use of two-component catalyst systems containing Pd–Fe and either Rh–Mg–Li or Rh–Sc–Li on silica at 275–285 °C and 30 atm for the selective formation of C_2 oxygenates (ethanol, acetaldehyde, and acetic acid) from hydrogen–carbon monoxide mixtures (2.5/1). (T. Saito, N. Taniguchi, K. Mitarai, S. Arimitsu, K. Yanagi, and K. Takada, Jpn. Kokai Tokkyo Koho JP 61, 178, 938 and 61, 178, 942; Chem. Abstr., 106 (1987) 17880s and 17881t.)