Further Studies Relating to the Formation of Propene in the Fischer–Tropsch Reaction

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The Fischer–Tropsch model complexes [(C$_5$Me$_5$Rh)$_2$(Me)$_2$(μ-CH$_2$)$_2$] (Me = ^{13}CH$_3$, CD$_3$) react with Na$_2$IrCl$_6$ or FeCl$_3$ hydrate to give largely ^{13}CH$_2$=^{12}CH–^{12}CH$_3$ and CD$_2$=CH–CH$_2$D respectively; a mechanism is proposed and it is suggested that charged organometallic species may play a vital role also in C–C coupling reactions on surfaces.

The di-μ-methylene-dimethyl-dirhodium complex (1) is decomposed, either thermally (200—350 °C) or by the action of electrophiles or one-electron oxidants [*e.g.*, Na$_2$IrCl$_6$ in tetrahydrofuran (thf) or acetonitrile at 20—50 °C], to give largely methane and propene, some ethene, and a little ethane.[1] The decomposition processes are intramolecular. In the IrCl$_6^{2-}$ promoted reaction, the first two-electron step yields methane (by combination of a rhodium methyl and the hydrogen from a μ-methylene) and an unstable intermediate postulated to have the structure (A).

Further oxidation steps lead to the propene, derived from one rhodium methyl and two μ-methylenes, and to ethene, derived largely from the coupling of a rhodium methyl and a

μ-methylene. Complex (1) is therefore a useful model for the polymerisation step in the Fischer–Tropsch reaction.[2,3]
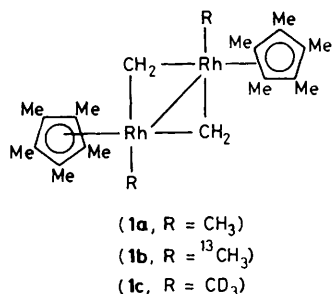
Further labelling studies have now elucidated the mode of formation of propene, the most interesting product. The ^{13}C n.m.r. spectrum of the solution obtained after decomposition of (1b, R = ^{13}CH$_3$) by Na$_2$IrCl$_6$ in MeCN or tetrahydrofuran showed the presence of [^{13}C$_1$]propene and of ^{13}CH$_4$ (δ −4.5). The propene was very largely ^{13}CH$_2$=^{12}CH–^{12}CH$_3$ (>85%, label at δ 116.1), rather than the anticipated isotopomer ^{12}CH$_2$=^{12}CH–^{13}CH$_3$ (label at δ 19.5).

Decomposition of (1c, R = CD$_3$) under the same conditions gave principally CD$_2$=CH–CDH$_2$. The ^{2}H{^{1}H} n.m.r. spectrum (Figure 1) showed three singlets [at δ 1.7 (methyl), 4.9

Table 1. Decomposition products of complex (**1a**).

Conditions	% Decomp.	CH$_4$	C$_2$H$_4$ (%^{a})	C$_2$H$_6$	C$_3$H$_6$
Pyrolysis (350 °C)	61	43	21	1	35
Na$_2$IrCl$_6$, aq. MeCN	77	26	10	5	60
Na$_2$IrCl$_6$, aq. thf	71	17	4	6	73
Na$_2$IrCl$_6$, aq. hexane	62	33	11	5	52
FeCl$_3$, aq. thf	75	32	10	5	54
FeCl$_3$, aq. hexane	80	24	5	3	68
Fe(NO$_3$)$_3$, aq. thf	69	26	27	14	34
Fe(NO$_3$)$_3$ aq. cyclohexane	32	30	24	20	26
AgBF$_4$, MeCN	61	28	9	55	9

^{a} The percentages are normalised to take account of the fact that methane, ethene, ethane, and propene take 1, 2, 2, and 3, respectively of the 4C$_1$ ligands available in (**1a**).
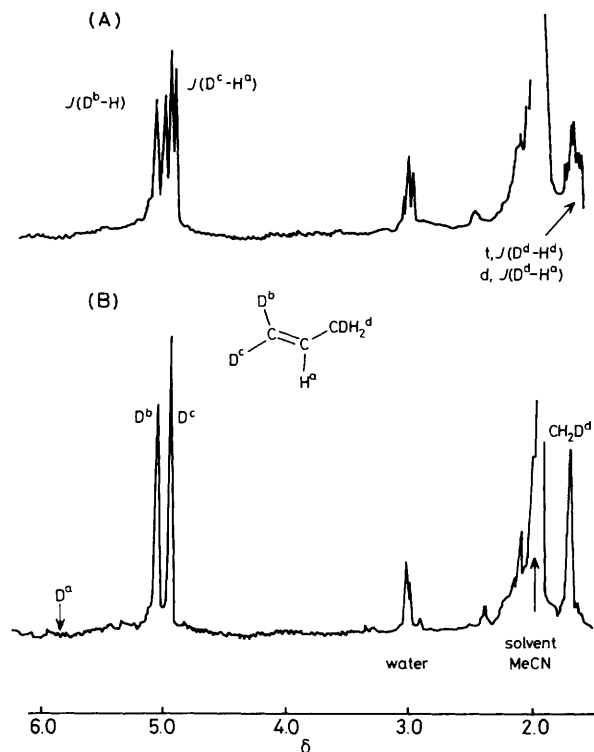

(**1a**, R = CH$_3$)

(**1b**, R = ^{13}CH$_3$)

(**1c**, R = CD$_3$)

Figure 1. N.m.r. spectra of the product from [(C$_5$Me$_5$Rh)$_2$(μ-CH$_2$)$_2$(CD$_3$)$_2$] + Na$_2$IrCl$_6$ in MeCN. (A) ^{2}H N.m.r. spectrum (^{1}H coupled); (B) ^{2}H{^{1}H} n.m.r. spectrum.

(D^c) and 5.1 (D^b)] of approximately the same intensity indicating that the same number of deuteriums were in each site. There was no peak at δ 5.9, indicating insigificant deuterium labelling at H^a. The ^{1}H coupled ^{2}H spectrum showed doublets for D^c [J(D^c–H^a) 1.5 Hz] and D^b [J(D^b–H^a) 2.8 Hz] arising from coupling to H^a only, and a triplet of doublets for the methyl [J(D-H$_{gem}$) 2; J(D–H^a) 1 Hz], showing the presence of –CDH$_2$ there. These results were confirmed by the ^{1}H n.m.r. spectrum [td at δ 1.675, J(H–D$_{gem}$) 2; J(H–H^a) 6.8 Hz], which also showed the virtual absence of protium at H^b and H^c.

Very similar results were obtained with other one-electron oxidisers, and in a variety of solvents (Table 1). A particularly effective and clean oxidant was hydrated ferric chloride; again the C$_1$+C$_2$+C$_3$ gases accounted for ca. 80% of the C$_1$ ligands present in the molecule, and propene was the major product.

Decomposition of the ^{13}C labelled complex (**1b**) with FeCl$_3$ hydrate in cyclohexane gave [^{13}C$_1$]propene, which was shown by ^{13}C n.m.r. spectroscopy to be 80—85% ^{13}CH$_2$=^{12}CH–^{12}CH$_3$ and 20—15% ^{12}CH$_2$=^{12}CH–^{13}CH$_3$. The ^{1}H and ^{2}H n.m.r. spectra of cyclohexane solutions of the products of decomposition of the deuterio-complex (**1c**) with FeCl$_3$ hydrate showed the presence of CD$_2$=CH–CH$_2$D and CH$_2$=CH–CD$_3$ in the ratio ca. 75 : 25. In neither case was there any significant amount of label at the central CH.

Since two very different oxidising systems (IrCl$_6$$^{2-}$ in tetrahydrofuran and FeCl$_3$ in moist cyclohexane) gave very comparable results, similar mechanisms for propene formation must be operating, involving direct electron transfers to the oxidant, and no intervention of organo-iridium (or organo-iron) species.

To accommodate the labelling observed, most (>70%) of the reaction must proceed by a highly specific transfer of one deuterium from CD$_3$ to the μ-methylene within the proposed
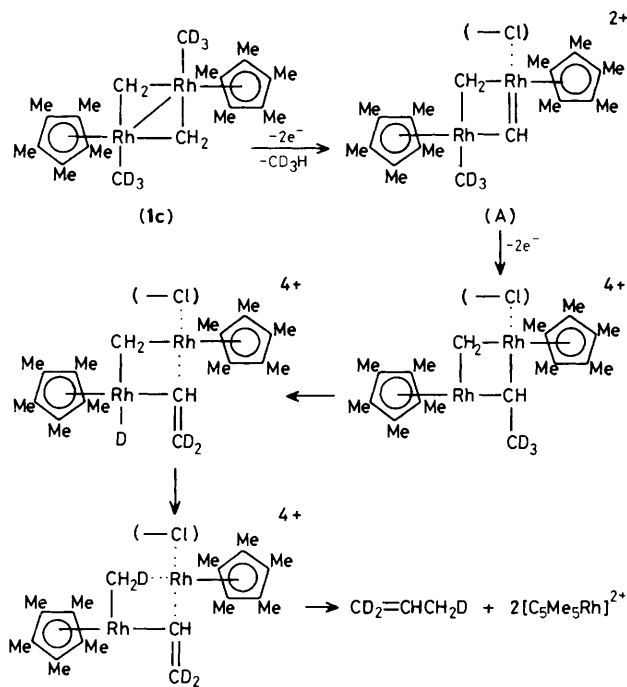
Scheme 1

intermediate (A). We suggest this occurs as shown (Scheme 1) and that the last step is a coupling of a σ-bonded vinyl and a methyl. The data also exclude mechanisms involving the

intermediacy of ethene[4] or of dimetallacyclopentanes[5] that have been suggested by workers for related systems.

Use of ferric nitrate in place of ferric chloride gave lower amounts of decomposition (both in moist cyclohexane and in tetrahydrofuran) and proportionately more ethene and ethane and less propene were formed. This may indicate that electron transfer is significantly promoted by chloride (probably *via* a chloride bridge), and that a chloride bridge also helps to stabilise an intermediate on the way to propene (Scheme 1).

The mechanisms of action of more electrophilic reagents on (1) may involve alkyl transfer from one metal to another. For example, in the Ag^+-promoted decomposition the amount of ethane is significantly higher; that could well arise from a silver-mediated coupling of two methyls originally attached to Rh.

These latest data suggest possible roles also for organo-metallic cations in the mechanisms of Fischer–Tropsch reactions on heterogeneous surfaces. In fact a related but intermolecular process (in which Me_2O^+- is transformed *via* $CH_3-O^+-CH_2^-$ into $CH_3CH_2-O<$) has been invoked to explain the formation of ethene from dimethyl ether on a zeolite.[6]

Previous studies have shown that the paths by which (1) decomposes thermally and under the influence of oxidants must be very similar.[1] Attempts to probe the finer details of the pyrolysis reactions more fully were frustrated by scrambling of ^{13}C and of deuterium labels; thus the propene from (1b) contained approximately equal amounts of $^{13}CH_2=CHCH_3$ and $CH_2=CH^{13}CH_3$ (but no $CH_2=^{13}CHCH_3$) by ^{13}C n.m.r. spectroscopy. Such scrambling under thermal conditions has long been known to occur.[7]

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