Synthesis of Alkan-2-ones by Dirhodium-mediated Four-carbon Coupling†

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Butan-2-one and pentan-2-one are obtained by C–C–C–C coupling of the *four* ligands in the dirhodium complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(CO)]^+$ **1b** (R = CH_3, $^{13}CH_3$ or CD_3) or **2b** (R = Et), which are readily generated from the acetonitrile complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(MeCN)]^+$ with CO. Complete decomposition of **1b** or **2b** occurred readily under mild conditions (CO, 1–12 atm, MeCN solvent, 25 °C, 12–48 h) to give RCH_2COMe and $[(C_5Me_5)Rh(CO)_2]$. Complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R_2]$ **3** (R = Me) or **4** (R = Et) reacted similarly with CO in MeCN (6 atm, 25 °C, 20 h) in the presence of $[Fe_4(OH)_2(SO_4)_5]$ or slowly, in its absence, under more forcing conditions (6 atm, 90 °C, 20 h). Analogous reactions occurred in methanol (or CD_3OD), but with the co-production of methyl acetate. When the complex **3c** (R = $^{13}CH_3$) was decomposed in the presence of $[Fe_4(OH)_2(SO_4)_5]$ in CD_3OD, labelling showed that the majority of the methyl acetate contained $^{13}CH_3CO_2CD_3$. A chief function of the iron salt is to cleave off R as RH; thus complex **3** yielded substantial amounts of methane and propene, in addition to butan-2-one. Analysis of RCH_2COMe from $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(MeCN)]^+$ **1a** (R = $^{13}CH_3$ or CD_3) and from **3** (R = $^{13}CH_3$ or CD_3) or **4** show that the R is derived from the rhodium alkyl, while both the CH_2 and the CH_3 are from the μ-CH_2 ligands. A crossover experiment in which equimolar amounts of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}^{13}CH_2)_2(^{13}CH_3)_2]$ (92% ^{13}C) were decomposed together gave labelled butan-2-one (largely $^{13}C_2H_5{}^{12}CO^{13}CH_3$) and only natural-abundance ^{13}C levels in the pentan-2-one; this shows the reaction to be intramolecular. Carbonylation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(CD_3CN)]^+$ in the presence of CD_3CN–D_2O gave $CH_3CH_2COCH_2D$; $^{13}CH_3CH_2COCH_2D$ was obtained from the carbonylation of **3c** (92% ^{13}C) in CD_3OD in the presence of $[Fe_4(OH)_2(SO_4)_5]$. A mechanism is proposed for the C–C–C–C coupling leading to ketone; it involves μ-ketene, -oxaallyl, and -enolate intermediates and terminates with a step which is formally a hydrolysis. The role of the dinuclear framework on which reaction occurs is to hold the reactants in place and to supply the electrons needed for the C–C–C–C coupling.

The di-μ-methylene-dirhodium complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(L)]^+$ **1** offer a very good framework on which mechanisms about the joining together of several organic ligands can be investigated. Such processes are also of interest since they can give insight into the detailed steps of the Fischer–Tropsch polymerization process. A currently popular mechanism for this invokes the joining of methylenes and methyls on a surface. Previous publications from our laboratory have dealt with the generation of C_2 and C_3 hydrocarbons, and have developed an alternative view of the polymerization process.[1]

There are now quite a number of different dinuclear (and even polynuclear) systems which can act as models to allow the investigation of the C–C coupling processes.[2] However, the products of the coupling often remain ligated to the framework and are not readily released. The advantage of complex **1a** (L = MeCN) and its analogues is that the free organics are readily released, and usually under mild conditions. Thus scrambling of label is normally only a minor side-reaction, and both ^{13}C and deuterium labelling experiments can be analysed for meaningful information on the course of the reactions. For example, labelling studies of the C–C–C coupling of three ligands (two μ-CH_2 and one terminal methyl) to give propene from methyl-di-μ-methylene-dirhodium complexes, such as **1a**, have elucidated the reaction path in some detail.[1]

The present paper reports on the extension of this research to the incorporation of CO into the polymerization process, where the combination of *four* ligands (one alkyl, R, two μ-CH_2, and CO) by C–C–C–C coupling leads quite efficiently to alkan-2-ones (RCH_2COCH_3) under simple conditions in homogeneous phase. A part of the work has been communicated.[3]

Results

Reactions with CO *in* MeCN.—(i) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(L)]PF_6$, **1**. When complex **1a**[4] (100 μmol) was treated with CO (6 atm) in acetonitrile solution (Scheme 1, 25 °C, 20 h) the main organic product was butan-2-one (52 μmol). In addition, ethene (23 μmol), methane (12 μmol), ethane and propene (4 μmol each) were formed (Table 1, reaction 1). The metal complex was recovered as $[(C_5Me_5)Rh(CO)_2]$ [75%; IR, ν(CO) 1950 and 2018 cm^{-1}; ^1H NMR, δ 2.03(s)]; evidence was obtained for the presence of a second, minor, metal carbonyl product (*ca.* 25%) [IR, ν(CO) 1841, 2001, 2023, 2065 and 2110 cm^{-1}; ^1H NMR δ 1.74(s)], the structure of which is under investigation.

The yield of butan-2-one at 6 atm CO was 52% of the theoretical maximum; despite some gas loss during work-up, most (78%) of the remaining C_1 ligands (CH_3 and CH_2) are accounted for as C_1–C_3 gases. The yield of butan-2-one depended on the CO pressure and was 27% at 1 atm (Table 1, reaction 2); the amounts of propene increased somewhat at lower pressure, while those of methane and ethene remained constant within the limits of the experiment. Based on these data, further increases in the yield of butan-2-one may be anticipated if the reactions are carried out at high CO pressures.

Reaction with hydrogen (6 atm) and CO (6 atm) under the standard conditions had little effect on the products (reaction 4); the amount of ethene went up slightly and that of butan-2-one dropped a little. No aldehydes were detected.

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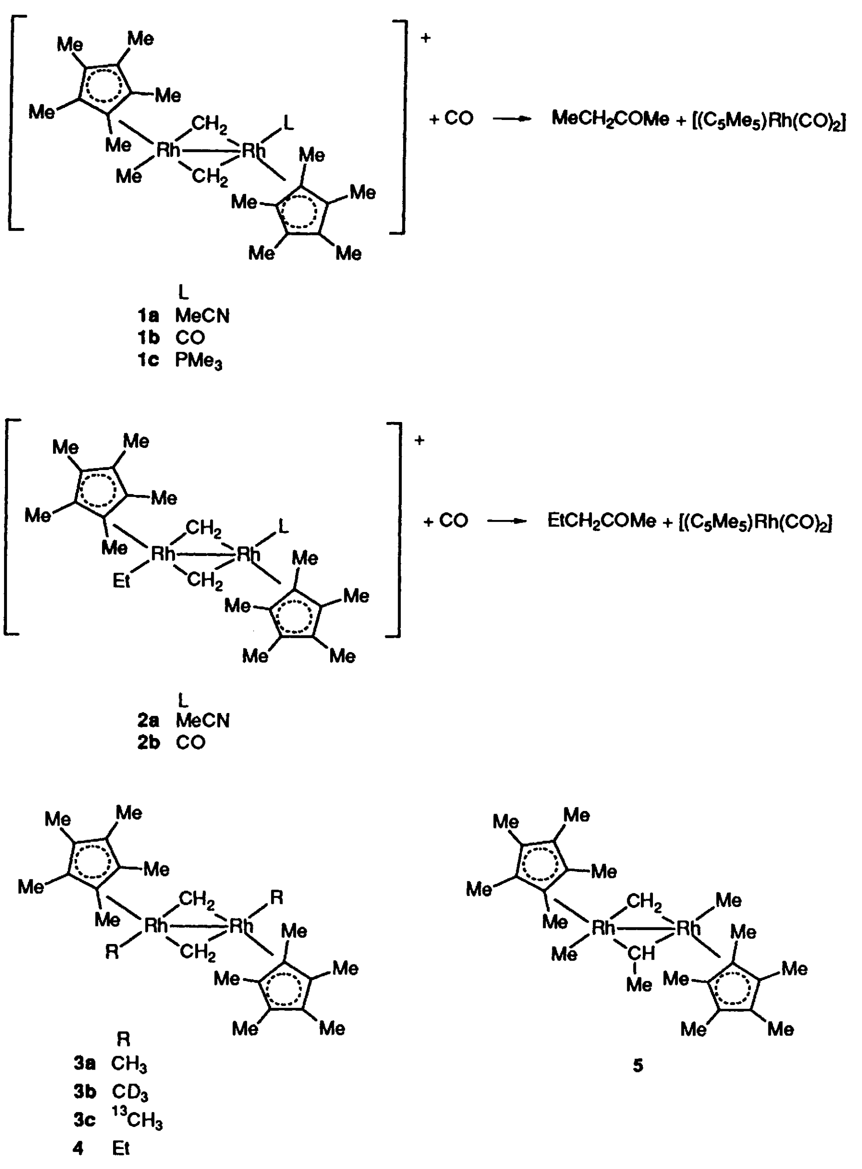
† *Non-SI unit employed:* atm = 101 325 Pa.



Scheme 1

Table 1 Products (μmol) obtained from the carbonylation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(L)]PF_6$ **1** or of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ in the presence of $[Fe_4(OH)_2(SO_4)_5]$ in acetonitrile[a]

			Products (μmol)							
Reaction	Starting complex	p_{CO}/atm	MeCOEt	$MeCO_2H$	CH_4	C_2H_4	C_2H_6	C_3H_6	Total
1	**1a**	6	52	*b*	12	23	4	4	95
2	**1a**	1	27	*b*	18	22	*b*	10	77
3	**1a**[c]	1	30	—	22	28	*b*	12	92
4	**1a**	12[d]	45	*b*	13	34	4	4	100
5	**1c**	6	43	*b*	4	22	*b*	4	73
6	**3b**[e]	1	37	11	117	4	1	43	213

[a] Using 100 μmol of complex; for details see Experimental section. Analyses for hydrocarbon gases of the reactions run under pressure (1, 4 and 5) represent minimum values and are approximate. [b] Trace. [c] Using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(MeCN)]$. [d] p_{CO} = 6 atm, p_{H_2} = 6 atm. [e] With the addition of $[Fe_4(OH)_2(SO_4)_5]$ (0.320 g, 434 mmol).

As has been reported before, when the acetonitrile complex, **1a**, is treated with CO under very mild conditions (3.5 atm, 0 °C, 5 min), the carbonyl complex **1b** is obtained in high yield.[4] Thus it may be presumed that all carbonylation reactions of **1a** proceed *via* primary formation of **1b**; this is confirmed by the reactions of **1b** in methanol (see below). The trimethylphosphine complex, **1c**, was also found to undergo the same carbonylation reaction to give butan-2-one, again in similar yield (reaction 5). Here too the reaction must proceed *via* **1b**.

The ^1H NMR spectrum of butan-2-one from reaction of $^{13}CH_3$ labelled complex **1a** (Rh–Me contains 92% ^{13}C) with CO (6 atm, CD_3CN, 20 h, 25 °C) showed the presence of 90% $^{13}CH_3{}^{12}CH_2{}^{12}CO^{12}CH_3$ [δ 0.95 dt, *J*(CH) 64, *J*(HH) 7 Hz] and 10% $^{12}CH_3{}^{12}CH_2{}^{12}CO^{12}CH_3$. When the reaction was repeated using complex **1a** (R = CD_3, 99% D), only $CD_3CH_2COCH_3$ could be detected by ^1H NMR spectroscopy. Thus, we can conclude that essentially all the 4-methyl in the butan-2-one arises from a rhodium methyl.

When the reaction of protio **1a** (R = CH_3) was carried out in CD_3CN wetted with D_2O, the ^1H NMR spectrum of the butan-2-one showed a 1:1:1 triplet at δ 2.03 [J(DH) 2 Hz] due to the presence of CH_2DCO–; no other deuterium above natural abundance was present. This is consistent with a protonolysis (deuteriolysis) step at a key point in the reaction. There was also a substantial amount of $CH_3COCH_2CH_3$ (*ca.* 50%), which may have arisen from exchange with some H_2O, condensed during work-up.

(ii) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et(MeCN)]PF_6$ **2a**. The related cationic ethyl complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et(MeCN)]PF_6$[4] **2a** (100 μmol) reacted similarly (6 atm, 25 °C, 20 h, MeCN solvent) to give pentan-2-one, $EtCH_2COMe$ (32 μmol, 32%). This is again consistent with the terminal *ethyl* of the pentan-2-one being derived from the rhodium ethyl. A very small amount of butan-2-one (1 μmol) was found, but no pentan-3-one was formed in this reaction, showing the very high specificity of the coupling. The corresponding carbonyl $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et(CO)]^+$ **2b** is the probable intermediate here too.

(iii) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ **3** *in the absence and in the presence of iron*(III). Rather similar results to those for **1** were obtained from the decomposition of the dimethyl complex **3a** under CO. There was no reaction at 25 °C (6 atm, 20 h, MeCN solution) but the formation of a small amount of butan-2-one (4%) and $[(C_5Me_5)Rh(CO)_2]$ occurred on heating (6 atm, 90 °C, 20 h, MeCN).

Complex **3** reacted much more easily (CO, 1 atm, 25 °C, 20 h, MeCN solution) to give a much higher yield of butan-2-one, on addition of a promoter, the best being the rather insoluble iron hydroxo sulfate $[Fe_4(OH)_2(SO_4)_5]$. Much methane was also formed. Labelling experiments showed that the methane (117 μmol) obtained on decomposition of **3b** (R = CD_3; 100 μmol) was 90% CD_3H; propene (43 μmol) was also formed (reaction 6), but only minor amounts of ethene were obtained, in contrast to the reactions 1–5. The major oxygenate was again butan-2-one (37 μmol, 37%), and acetic acid (11 μmol) was also formed. The butan-2-one was exclusively $CD_3CH_2COCH_3$; the origin of the *ethyl methyl* was confirmed by the formation of only $^{13}CH_3CH_2COCH_3$ when **1c** (R = 99% $^{13}CH_3$) was reacted.

The co-production of acetic acid is facilitated by the addition of $[Fe_4(OH)_2(SO_4)_5]$; the product from the labelled complex **3c** (92% ^{13}C) was $^{13}CH_3CO_2H$ (70%) and $^{12}CH_3CO_2H$ (30%), thus it largely derives from the rhodium methyl. It may also be noted that when the iron(III) salt was added to complex **1a** under CO (6 atm) acetic acid (53 μmol) as well as butan-2-one (47 μmol, 47%) were formed.

(iv) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** *in the presence of iron*(III). When it was decomposed under CO in the presence of $[Fe_4(OH)_2(SO_4)_5]$, the diethyl complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** (100 μmol) underwent an exactly analogous reaction to **3**, to yield pentan-2-one (62 μmol) as the main oxygenate, together with a small amount of butan-2-one (2 μmol). In this case propionic acid (16 μmol) as well as acetic acid (17 μmol) were also formed.

(v) *Crossover experiment using* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}^{13}CH_2)_2(^{13}CH_3)_2]$ **3d** *and* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** *in the presence of iron*(III). To test whether the reactions to give the ketones were intramolecular, a crossover experiment was carried out. Equimolar amounts (20 μmol each) of complex **3d**, where all the C_1 ligands (methyls and methylenes) were labelled with 92% ^{13}C, and of the diethyl complex **4**, were decomposed with $[Fe_4(OH)_2(SO_4)_5]$ under CO in MeCN. The products, butan-2-one (10 μmol), pentan-2-one (13 μmol), acetic acid (19 μmol) and propionic acid (13 μmol), suggested that each complex had reacted on its own. A GC–MS analysis showed that (*i*) the pentan-2-one contained only the amount of ^{13}C to be expected for natural abundance, and (*ii*) the distribution of isotopomers in the butan-2-one was that expected (within instrumental uncertainty) if the methyl and methylene carbons only come from the labelled carbons of **3d**. Based upon 92% ^{13}C enrichment the expected values in brackets can be compared with the actual values, $^{13}C_3H_8{}^{12}CO$, 69 (78%); $^{13}C_2{}^{12}CH_8{}^{12}CO$, 15 (20%); $^{13}C^{12}C_2H_8{}^{12}CO$, 7 (2%); and $^{12}C_3H_8{}^{12}CO$, 8 (< 1%).

The small amount of butan-2-one also found to arise in the decomposition of the diethyl complex **4** (see above) accounts for the higher than expected abundance of both unlabelled $^{12}C_3H_8{}^{12}CO$ and singly labelled $^{13}C^{12}C_2H_8{}^{12}CO$, and the lower than expected amounts of $^{13}C_3H_8{}^{12}CO$ and $^{13}C_2{}^{12}CH_8{}^{12}CO$. In addition, the acetic acid was 70% $^{13}CH_3{}^{12}CO_2H$; this is consistent with the majority (*ca.* 76%) of the acetic acid arising from one labelled methyl (or methylene) and (unlabelled) CO. This agrees well with the result from decomposition of labelled **3c** (see above), which also showed that the label derived from an Rh–Me. Analysis of the propionic acid from the crossover experiment showed that most (80%) contained ^{13}C at natural abundance level, and therefore came from the diethyl complex **4**. However *ca.* 20% was $^{13}C_2H_5CO_2H$, which must therefore arise as a minor side-product from decomposition of the dimethyl complex, where it is detected in trace amount.

(vi) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Me_2]$ **5** *in the presence of iron*(III). The recently described μ-ethylidene-μ-methylene complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Me_2]$ **5**[5] (100 μmol) was also decomposed on reaction with CO and $[Fe_4(OH)_2(SO_4)_5]$ in MeCN. Ketones were formed, though in rather low yield, the main product being acetic acid. Three ketones were found, the expected pentan-3-one (6 μmol), and 3-methylbutan-2-one (7 μmol) as well as a small amount of butan-2-one (2 μmol).

Reactions with CO *in Methanol*.—(i) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(CO)]PF_6$ **1b**. The carbonylation reactions of these complexes have also been examined in methanol to allow a comparison between a protic and an aprotic medium to be made. The results are collected in Table 2.

Reaction of the carbonyl complex **1b** in methanol (reaction 7, CO, 6 atm, 25 °C, 20 h; paralleling that of the acetonitrile complex **1a**, Table 1, reaction 1) again gave butan-2-one (42 μmol, 42%). In this case however methyl acetate was also formed (33 μmol), together with small amounts of acetone, methyl acrylate and methyl propionate, which presumably arise from side-reactions. Rather more butan-2-one (52, 53μmol; 52, 53%) and more methyl acetate (47, 48 μmol) were formed when the carbonylation in methanol was carried out in the presence of $[Fe_4(OH)_2(SO_4)_5]$ (reactions 8 and 9).

A labelling experiment, in which $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(CO)]PF_6$ (100 μmol; 99% ^{13}C) was carbonylated in CD_3OD, was carried out to obtain more information on the origin of the methyl acetate. Proton NMR spectroscopy showed that it contained *ca.* 10% $^{13}CH/D_3CO_2CD_3$ and 90% $^{12}CH/D_3CO_2CD_3$; the spectrum showed the presence of considerable deuterium incorporation in the acetate methyl, but this could not be quantified. Thus it appears that the methyl acetate is derived from three sources, the solvent (by a rhodium-catalysed carbonylation of CD_3OD), from the μ-methylenes, and from the rhodium methyl (*ca.* 10%) of the complex.

Very similar results were obtained when the chloro complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(Cl)]$ **6** was carbonylated in place of **1b** (reaction 10). As expected, however, when the reaction was run (reaction 11) under a lower pressure of CO (1 atm, to allow the gaseous products to be evaluated), the yields both of butan-2-one and of methyl acetate decreased (to 33 and 38 μmol respectively). The main gaseous products were CH_4, 2, C_2H_4, 25 and C_3H_6, 2 μmol.

(ii) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ **3a**. Rather similar results were obtained (reaction 12) when the dimethyl

Table 2 Products from the carbonylation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(CO)]^+$ **1b** and related complexes in methanol[a]

			Oxygenate products (μmol)					
Reaction	Starting complex	p_{CO}/atm	MeCOEt	Me_2CO	$MeCO_2Me$	$CH_2{=}CHCO_2Me$	$MeCH_2CO_2Me$	Total
7	**1b**	6	42	4	33	2	1	83
8	**1b**[b]	6	52	9	47	2	3	113
9	**1b**[b]	6	53	5	48	3	2	111
10	**6**[b,c]	6	58	2	48	1	3	112
11	**1b**[b,d]	1	33	4	38	8	*e*	83
12	**3a**[b,f]	1	14	11	30	1	0	56

[a] Using 100 μmol of dirhodium complex; for details, see Experimental section. Runs 8 and 9 are identical and were used to check the reproducibility of the procedure. The gases CH_4, C_2H_4, C_2H_6 and C_3H_6 were not estimated for reactions 7–10. [b] With the addition of $[Fe_4(OH)_2(SO_4)_5]$ (0.320 g, 434 μmol). [c] Using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(Cl)]$ (**6**, 100 μmol). [d] Using **1b** (100 μmol) in methanol (2 cm^3) and CO (1 atm, 50 °C, 2.5 h). Hydrocarbon gases were also analysed, using a Poropak QS GC column: CH_4, 2; C_2H_4, 25; C_2H_6, trace; and C_3H_6, 2 μmol. [e] Trace. [f] Using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ (**3a**, 0.055 g, 100 μmol) and $[Fe_4(OH)_2(SO_4)_5]$ (0.320 g, 434 μmol) in methanol (2 cm^3) under CO (1 atm, 25 °C, 20 h). Hydrocarbon gases were also analysed, using a Poropak QS GC column: CH_4, 55; C_2H_4, 19; C_2H_6, 9; and C_3H_6, 27 μmol.

complex **3a** was carbonylated in methanol under 1 atm of CO. In this case no reaction at all was detectable in the absence of $[Fe_4(OH)_2(SO_4)_5]$; in its presence, butan-2-one was substantially reduced (by comparison with reaction 11, using **1c**), while much greater amounts of methane (55 μmol) and of propene (27 μmol) were formed.

In this case too, a labelling experiment was carried out, using complex **3c** (using 92% ^{13}C) and $[Fe_4(OH)_2(SO_4)_5]$ in CD_3OD (CO 1 atm; 25 °C, 20 h). Proton NMR spectroscopy of the product solution showed the presence of $CDH_2COCH_2{}^{13}CH_3$ (65% D; 87% ^{13}C) in the butan-2-one, and that the methyl acetate contained *ca.* 70% $^{13}CH_3CO_2CD_3$. The acetone was 71% $(^{13}CH_3)_2CO$. Thus we can say with confidence that, under these conditions, the methyls which end up in the ethyl of the butan-2-one, in the acetate, and in acetone very largely originate from Rh–Me in the original complex **3**.

(iii) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(PMe_3)]PF_6$ **1c**. In addition, the reactions of the trimethylphosphine complex **1c** were also briefly examined under the same conditions (MeOH; CO, 6 atm; 25 °C). Butan-2-one and methyl acetate were again the major products; the former increased with time (21, 30 and 36 μmol respectively after 20, 72, and 100 h), the latter a little less so (29, 35 and 38 μmol).

(iv) *Reaction of* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4**. A further set of experiments were conducted with the diethyl complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ (100 μmol), in methanol in the presence of $[Fe_4(OH)_2(SO_4)_5]$, under CO (6 atm, 25 °C, 20 h). In this case the main product was pentan-2-one (45 μmol, 45%), together with equal amounts of both methyl acetate and methyl propionate (23 μmol each), and a little butan-2-one (4 μmol). The same reaction at 1 atm CO gave less pentan-2-one (11 μmol, 11%), methyl acetate (8 μmol), and methyl propionate (5 μmol), but propene (21 μmol) and a mixture of C_4 hydrocarbons (3 μmol) were formed.

Discussion

Reactions to form the Alkan-2-ones in Acetonitrile Solution.—The complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(MeCN)]^+$ **1a** (R = Me) and **2a** (R = Et) decompose easily under remarkably mild carbonylation conditions (25 °C, 1–6 atm CO, MeCN solution), *via* the carbonyl cations, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(CO)]^+$, **1b** or **2b**, to give RCH_2COMe and $[(C_5Me_5)Rh(CO)_2]$.

Yields of the ketones are surprisingly high (>50% at 6 atm CO; Tables 1 and 2) considering that the reaction represents the coupling of *four* C_1 ligands. Propene is also formed from **1** and there is an approximately inverse relation between the amount of butan-2-one and that of propene, the former being favoured at higher p_{CO}. The other significant by-product from these reactions was ethene. Since propene is the major product from the decomposition of **1a** in the absence of CO, this implies the coexistence of two paths, with the 'normal' decomposition path[1] taking over when the p_{CO} is too low.

Formation of butan-2-one also occurs when the dimethyl complex **3** is decomposed under CO at higher temperature or when the decomposition is promoted by the addition of $[Fe_4(OH)_2(SO_4)_5]$. The overall effect of adding the iron(III) salt to **3** is to provide a source of H^+ which cleaves a Rh–Me. Thus, when **3b** was so decomposed, methane (90% CD_3H) was formed in addition to $CD_3CH_2COCH_3$. These reactions therefore also proceed *via* the cationic carbonyl complexes [equation (1)].

$$\underset{\textbf{3b}}{[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CD_3)_2]} + H^+ + CO \longrightarrow$$

$$\underset{\textbf{1b}}{[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CD_3)(CO)]^+} + CD_3H \qquad (1)$$

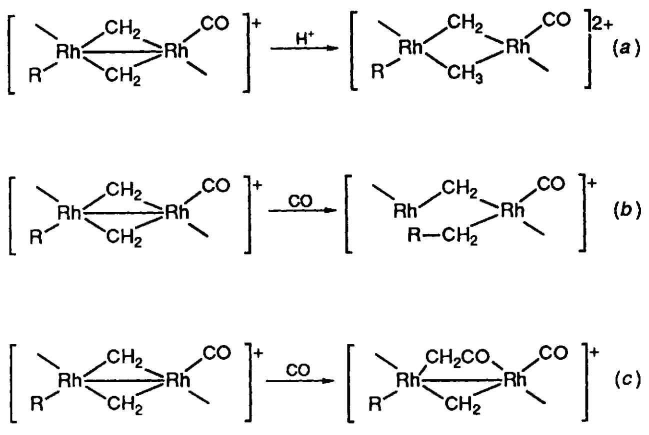
The yields of butan-2-one from reactions 2, 3 and 6 (Table 1) are similar; this indicates a close similarity in mechanism, namely that complex **3** reacts *via* **1**.

The formation of pentan-2-one (from **2a** and, even better, in 62% yield from the diethyl complex **4**) shows that the C–C–C–C coupling reaction is general, and is not adversely affected by a larger terminal alkyl. By contrast, although the bridge-branched μ-ethylidene-μ-methylene complex **5** was also carbonylated in MeCN in the presence of $[Fe_4(OH)_2(SO_4)_5]$ to give ketones (in this case $Me_2CHCOMe$ and Et_2CO) by a four-ligand coupling, the yields were low. This suggests that branching at the methylene adversely affects the reaction, and that the coupling of the bridge CHR is in the rate-determining step.

As reaction 4 (Table 1) shows, a pressure of 6 atm of hydrogen had no effect on the carbonylative decomposition of complex **1a**, and no aldehydes were observed.[6]

Labelling experiments unambiguously show that the methyl ketones, $MeCOCH_2R$, are built up from the ligands, R, CH_2, CO and CH_2, derived from a single dirhodium framework, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(CO)]^+$, in a very selective process. The formation of pentan-2-one from decomposition of the ethyl complex **2a**, and of the butan-2-one isotopomers ($^{13}CH_3CH_2COCH_3$ and $CD_3CH_2COCH_3$, respectively) arising from the labelled **1a** (R = $^{13}CH_3$ and CD_3) show that the alkyl R in the complex ends up only as RCH_2COMe in the ketone.

The ketone formation is intramolecular. Thus in the crossover experiment in which $[\{(C_5Me_5)Rh\}_2(\mu\text{-}^{13}CH_2)_2(^{13}CH_3)_2]$ **3d** and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** were decomposed together there was no significant incorporation of $\mu\text{-}^{12}CH_2$ into the butan-2-one ($^{13}CH_3{}^{13}CH_2CO^{13}CH_3$) derived from **3d** and, equally, no incorporation of $\mu\text{-}^{13}CH_2$ from the other molecule, **3d**, into the pentan-2-one derived from **4**.



Scheme 2 Possible alternative first steps (*a–c*) in the conversion of $[\{(C_5Me_5)Rh\}(\mu\text{-}CH_2)_2R(CO)]^+$ into RCH_2COCH_3 (C_5Me_5 rings omitted for clarity)

It was found that the butan-2-one from reaction of **1a** with CO in MeCN wetted with D_2O contained very substantial amounts of deuterium, as $CH_3CH_2COCH_2D$. Thus the site of attack of the water is the ketonic methyl.

The other main products from reactions of **1a** without additives are ethene, methane and propene, and the dicarbonyl, $[(C_5Me_5)Rh(CO)_2]$ (75%) as the main metal complex. This leads to an overall reaction sequence which can largely be described by equation (2).

$$2[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(CO)]^+ + 9\,CO + D_2O \longrightarrow 2\,RCH_2COCH_2D + 4\,[(C_5Me_5)Rh(CO)_2] + 2\,H^+ + CO_2 \quad (2)$$

Other Ketone Formation Reactions.—Quite a number of reactions of organometallic carbonyls have been reported to give ketones.[7] The most common route to such molecules is *via* intermediate formation of alkylmetal acyls, which then reductively eliminate [equation (3)] and it has been commented that

$$L_nM(COR^1)R^2 \longrightarrow L_nM + R^1COR^2 \quad (3)$$

this is a 'favourable' reductive elimination, which probably occurs most easily at a single metal centre.[8]

CO-Based coupling reactions occur to give ketones [equation (4)] by carbonylation of alkyl halides in the presence of a suitable halide acceptor, such as nickel or iron;[9] rhodium has

$$2\,R\text{–}X + CO \longrightarrow R\text{–}CO\text{–}R \quad (4)$$

also been utilised.[10] In addition, catalytic syntheses, especially of pentan-3-one (from ethene) occur during hydroformylation reactions catalysed by rhodium complexes.[9]

Four-carbon coupling reactions are extremely rare, and the type of reaction reported here appears to be without precedent. The closest analogies to the processes described here appear to be the nickel-promoted carbonylative couplings described by Chiusoli and Salerno,[11] for example, the co-reaction of iodobenzene and acetylene [equation (5)].

$$PhI + HC{\equiv}CH + CO + MeOH \longrightarrow PhCOCH_2CH_2CO_2Me \quad (5)$$

Possible Mechanisms for the C–C–C–C *Coupling leading to Alkan-2-one Formation.*—Although the source of each atom of the alkan-2-one is known, and rather little scrambling occurs, several alternative precise sequences of events can be postulated to account for the labelling observed. In the simplest case, the reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2R(CO)]^+$ to RCH_2COMe under CO in MeCN, with no additives, three possible first steps can be considered: (*a*)–(*c*), Scheme 2. Step (*a*) involves initial attack by H^+ at a μ-CH_2 to give a μ-CH_3 intermediate, while in step (*b*) the migration of R onto the μ-CH_2 takes place to give a μ-ethyl intermediate, and in (*c*) the CO and a μ-CH_2 first combine to give a μ-ketene intermediate. For each case three or more further reaction alternatives then present themselves.

The possibilities may however be simplified and reduced by the following considerations. Initial protonation at a μ-CH_2, (*a*), is unlikely since it is known from extensive studies of the protonation of alkyl di-μ-methylene dirhodium complexes that the terminal alkyls are cleaved first. The μ-methylenes are only cleaved later under much more stringent conditions. For example, the product of the protonation of **1a** in MeCN is the di-μ-methylene dication, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(MeCN)_2]^{2+}$. Thus (*a*) can be discounted as a viable mechanistic suggestion.

The formation of propene by the non-carbonylative decomposition of **1b** has been shown to involve, as first step, the loss of H^+ from a μ-CH_2 consequent upon one-electron oxidation. Facile coupling of a terminal methyl and the resultant μ-methyne then takes place to give a μ-ethylidene intermediate which must rapidly β-eliminate H from the CH_3 to give a vinyl. We deduce from this sequence that migration of methyl (R) onto μ-CH_2 is not favoured; this is supported by the stability of complexes such as **3** and its analogues. Thus there is no evidence to favour route (*b*).

By contrast, a number of reactions are known in which μ-CH_2 ligands and CO couple readily, in some cases to give a μ-ketene intermediate bridging two metals.[12] The observation that substitution at a μ-methylene (as in the reactions of the μ-ethylidene complex **5**) substantially reduces ketone formation supports the view that a coupling of the methylene and CO is involved in a key step. Thus, on present information (*c*) appears the most likely first step.

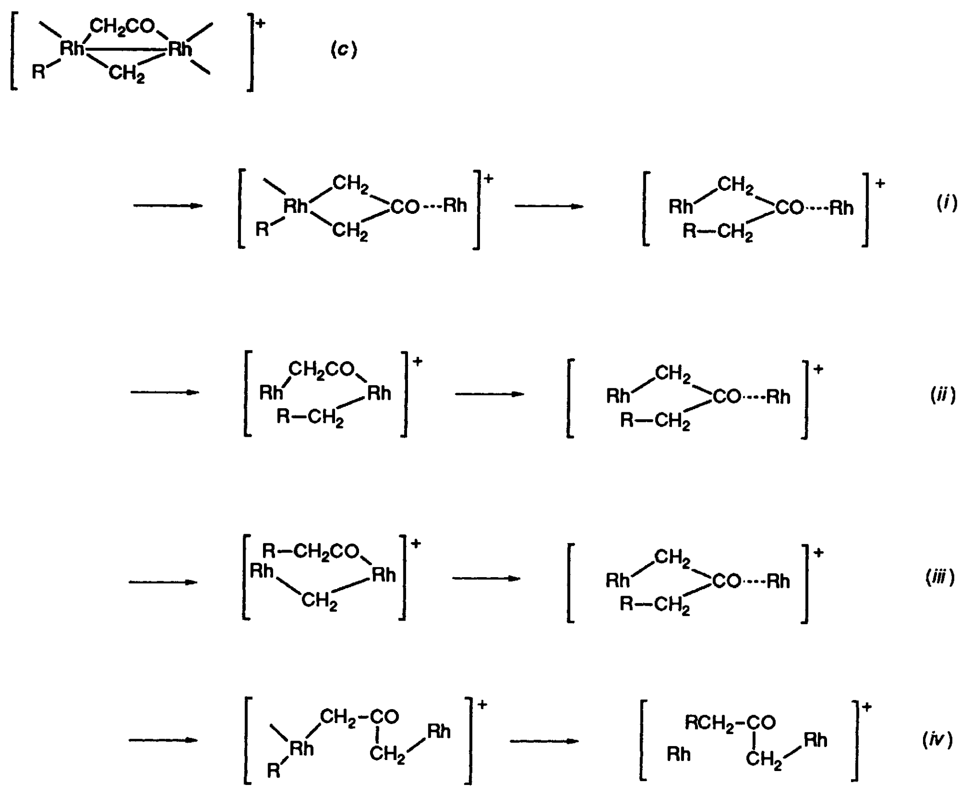
Four subsequent reaction sequences can then be defined starting from (*c*); they are (*i*)–(*iv*) in Scheme 3. Again, the chief difference between them is the order of the steps; in (*i*) and (*iv*) a second coupling of the μ-ketene with the μ-CH_2 takes place to give either a metallocyclobutanone $[(C_5Me_5)Rh(CH_2COCH_2)R]$ in a higher oxidation state, or a linear dinuclear species. The first step in both is a reductive elimination involving one sp^3 and one sp^2 carbon, and in both cases the sequence ends with reductive elimination of R and the linked CH_2–(sp^3–sp^3) to give RCH_2COCH_2Rh, and hence the anion (enolate) of butan-2-one.

In paths (*ii*) or (*iii*) the first step is the coupling of R with either the μ-CH_2 or the carbon of the μ-ketene. Both involve the reductive elimination of two rhodium–alkyl, sp^3 carbons. The reactions continue by coupling the ketene with the ethyl, for (*ii*), or of the acyl with the μ-methylene, for (*iii*), both sp^2–sp^3 couplings.

Since it is generally agreed that sp^3–sp^3 reductive elimination is more difficult than the alternative of sp^2–sp^3 coupling, the sequences (*ii*) and (*iii*), where the sp^3–sp^3 coupling must precede the sp^2–sp^3 coupling, represent less likely reaction paths than (*i*) or (*iv*) where they come afterwards. Thus, on the evidence available, paths (*c–i*) or (*c–iv*) appear the more probable.

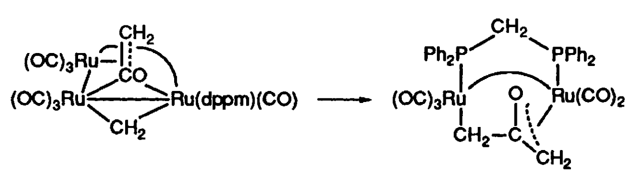
In support of this, Holmgren *et al.*[13] recently found that carbonylation of the $[Ru_3(CO)_7\{\eta^3\text{-}(C,C,O),\mu_3\text{-}COCH_2\}(\mu\text{-}CH_2)(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) complex **7** gave a diruthenium complex with a bridging oxaallyl (CH_2COCH_2) ligand, identified as $[Ru_2(CO)_5\{(\eta^4\text{-}C,C,C,O),\mu\text{-}CH_2COCH_2\}(dppm)]$ **8** by a single crystal X-ray structure determination. Thus the μ-oxaallyl structure and its formation from such reactions is securely established. A similar process can be envisaged for the reactions on dirhodium along the lines indicated by path (*c–iv*).

The initial complexes **1** are all 34-electron species; the first coupling intermediate given by (*c*) is then a 32 electron species, unless the vacant site is already occupied by another CO. If the oxaallyl is assumed to function as a four-electron ligand in the



$$[\{(C_5Me_5)Rh\}_2(RCH_2COCH_2)]^+ + D_2O + 5\,CO \longrightarrow 2\,[(C_5Me_5)Rh(CO)_2] + RCH_2COCH_2D + D^+ + CO_2$$

Scheme 3 Possible alternative second and third steps (*i*–*iv*) in the formation of alkan-2-one, and the redox hydrolysis which releases the products (C_5Me_5 rings omitted for clarity)



7 **8**

intermediate from reaction (*iv*), this also becomes a 32-electron species, or 34 again if a vacant site is occupied by CO.

The overall reaction is completed by cleavage of the Rh–CH_2COEt bond assisted by water, *via* hydrolysis of the enolate anion, $CH_2{=}C(O^-)Et$, which should be easily released by the rhodium. It is quite instructive to compare this reaction sequence to the very detailed scheme devised by Bergman[14] to account for the formation of acetone from the decomposition of $[(cp)_2Co_2(\mu\text{-}CO)_2Me_2]$ ($cp = C_5H_5$). There, cleavage and carbonylation are postulated to yield two mononuclear species, $[(cp)CoMe(CO)]$ and $[(cp)CoMe_2(CO)]$ which combine and disproportionate to give $[(cp)Co(CO)_2]$ and $[(cp)CoMe_2(CO)]$, the latter yielding $[(cp)Co(COMe)Me(CO)]$, the direct precursor to Me_2CO. Since the dirhodium system does not easily lend itself to detailed kinetic studies, and no intermediates have been detected, our suggestions must remain tentative.

Reactions to form the Alkan-2-ones in Methanol.—The chief point to note from a comparison of the data in Tables 1 and 2 is the essential qualitative similarity between reactions in the two solvents. This also applies to the labelling studies. Quantitative differences are seen in the carbonylation (1 atm) of the dimethyl complex **3a** in the presence of $[Fe_4(OH)_2(SO_4)_5]$, which gives 37 μmol butan-2-one and 11 μmol acetic acid in acetonitrile (reaction 6), but gives much less butan-2-one (14 μmol), together with acetone (11 μmol), and a lot of methyl acetate (30 μmol) in methanol (reaction 12). This difference may be due in part to solubility differences, both of the complexes and of CO in the two solvents.

Thus we suggest that the overall mechanistic scheme proposed for ketone formation in the acetonitrile reaction is largely valid also for the methanol solutions.

Reactions to form Acetic Acid or Methyl Acetate.—The major difference between the acetonitrile and the methanol reactions is that methyl acetate is a major product in the latter while acetic acid is normally only present in small amounts in the former; in both cases the yield is markedly increased in the presence of $[Fe_4(OH)_2(SO_4)_5]$. Labelling studies indicate that CH_3CO– in the acetic acid stems largely from a rhodium–methyl, while the opposite appears to be true for the methanol reactions giving methyl acetate. Further investigations are needed to clarify this point.

Conclusion

This work has shown that a dirhodium frame will hold an alkyl (R) and two μ-methylenes and allow them to react with a CO to give the alkan-2-one $MeCOCH_2CH_2R$ in quite good yield. Labelling studies have shown the origin of each fragment of the alkan-2-one, and a mechanism for the process has been proposed.

Our aim in this work has been to model Fischer–Tropsch polymerisation reactions on rhodium surfaces. Although rhodium, especially when promoted with a rare-earth-metal oxide,[15] is a good catalyst for the production of oxygenates from syngas ($CO + 2H_2$), ketones have not normally been claimed as products. However alcohols are formed and it is generally agreed that they arise by hydrogenation of intermediate carbonyl species. Thus the reaction illustrated by the formation of RCH_2COCH_3 may serve to illustrate one part of this process.

Experimental

Complexes were prepared as described in the literature and were characterised. The isotopic abundances, where appropriate, were checked by ^1H NMR spectroscopy. Analyses of organic products were carried out by ^1H NMR (Bruker AC-250), IR (PE 1600 FT-IR), GC (Perkin-Elmer 8700) and GC–MS (Hewlett-Packard HP5971A mass-selective detector interfaced to a HP5890 Series II gas chromatograph and for earlier measurements, a Kratos MS-9 interfaced to a Carlo Erba gas chromatograph). Gas chromatography analysis for oxygenates used a 50 m CPSil5 column (with cyclohexane or methyl propionate as internal standard) or, for hydrocarbons, a Poropak QS column (using methane as external standard). Gas and solution phases were analysed separately by GC (Tables 1 and 2). NMR spectra were measured directly on the product solutions for reactions of complex **1**; however, those solutions to which $[Fe_4(OH)_2(SO_4)_5]$ [BDH, basic iron(III) sulfate] had been added required preliminary separation from iron residues before estimation. Some typical experiments are detailed below. The CD_3 labelled complexes were made from $Mg(CD_3)I$ which was in turn made from CD_3I (99% D; Aldrich); the $^{13}CH_3$ labelled complexes were made similarly using $^{13}CH_3I$ (92% ^{13}C, Service des Molécules Marquées, France, or 99%, Fluorochem). Acetonitrile (May and Baker or Fisons) was distilled from CaH_2; it always contained some propionitrile, which was allowed for.

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(MeCN)]PF_6$, **1a**, *with* CO (6 *atm*).—The complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(MeCN)]PF_6$ (0.071 g, 100 μmol) was placed in a Fisher-Porter tube under CO and acetonitrile (6 cm^3, CO saturated) was added. The tube was charged with CO (6 atm) and the solution stirred (25 °C, 20 h) to give a deep red solution. The tube was then cooled in a carbon tetrachloride bath (−15 °C) and the CO pressure slowly released. A GC analysis of the solution phase showed the presence of the following products (μmol): CH_4 (12), C_2H_4 (23), C_2H_6 (4), C_3H_6 (4), MeCOEt (52) and $MeCO_2H$ (trace).

Spectroscopy of the solution showed the major organometallic product (*ca.* 75%) to be $[(C_5Me_5)Rh(CO)_2]$, IR ν(CO) 1950 and 2018 cm^{-1} (vs); ^1H NMR δ 2.03. Small amounts of another carbonyl containing species were also formed, IR ν(CO) 1854, 2064 and 2095 cm^{-1} (weak), ^1H NMR δ 1.74.

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(MeCN)]PF_6$ *with* CO (1 *atm*).—Acetonitrile (1 cm^3, CO saturated) was added to $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(MeCN)]PF_6$ (0.036 g, 50 μmol; 99% ^{13}C) in a 5 cm^3 graduated flask under CO (1 atm). The flask was then sealed (with a suba seal and wire) and the solution stirred (25 °C, 72 h) to give a deep red solution. A GC analysis of the solution and gas phase showed the following products (total, μmol): CH_4 (11), C_2H_4 (14), C_3H_6 (6) and MeCOEt (15). All the butan-2-one and most of the hydrocarbons were in the solution phase.

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(MeCN)]PF_6$ **1a** *with* CO *and* H_2.—Acetonitrile (6 cm^3, CO saturated) was added to $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(MeCN)]PF_6$ (0.071 g, 100 μmol) in a Fisher-Porter tube under CO. The tube was charged with CO (6 atm) and H_2 (6 atm) and the solution stirred (25 °C, 20 h) to give a deep red solution. The tube was then cooled in an ice–salt bath and the CO pressure slowly released. A GC analysis (solution phase) showed the presence of the following products (μmol): CH_4 (13), C_2H_4 (34), C_2H_6 (4), C_3H_6 (4), MeCOEt (45) and $MeCO_2H$ (trace).

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(MeCN)]PF_6$ **1a** *with* CO; Analysis by NMR Spectroscopy.—The complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(^{13}CH_3)(MeCN)]PF_6$ (0.071 g, 100 μmol; 92% ^{13}C) was carbonylated (6 atm) as described above in CD_3CN (3 cm^3, CO saturated; 25 °C, 20 h). After cooling and release of the pressure, the volatiles were then distilled *in vacuo* and collected at −196 °C. The ^1H NMR spectrum of this solution showed signals at: δ 2.05 (s, $CH_3COCH_2CH_3$), 2.42 (m, $CH_3COCH_2CH_3$); 0.95 [t, *J*(HH) 7; $CH_3COCH_2{}^{12}CH_3$]; 0.95 [dt, *J*(CH) 63.5, *J*(HH) 7 Hz; $CH_3COCH_2{}^{13}CH_3$]. Integration of the signal at δ 0.95 and its ^{13}C satellites showed the butan-2-one to be 90% $CH_3COCH_2{}^{13}CH_3$ and 10% $CH_3COCH_2{}^{12}CH_3$.

The ^1H NMR spectrum of the distilled solution from an analogous experiment using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CD_3)(MeCN)]PF_6$ (0.071 g, 100 μmol; 99.5% D; CO, 6 atm; CD_3CN, 25 °C, 20 h) showed the butan-2-one to be $CH_3COCH_2CD_3$, 99.5%.

A further similar experiment was carried out using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CH_3)(MeCN)]PF_6$ (0.071 g, 100 μmol) in CD_3CN (3 cm^3, distilled under N_2 from $CaCl_2$; CO saturated) and D_2O (0.25 cm^3) under CO (6 atm; 25 °C, 20 h). The ^1H NMR spectrum of the distilled solution showed signals at: δ 2.05 (s, $CH_3COCH_2CH_3$); 2.42 [q; *J*(HH) 7; $CH_3COCH_2CH_3$]; 2.03 [1:1:1 t, *J*(DH) 2; $CDH_2COCH_2CH_3$]; 0.94 [t, *J*(HH) 7; $CH_3COCH_2CH_3$]. Integration of the signals at δ 2.03 and 2.05 showed the butan-2-one to be 50% $CDH_2COCH_2CH_3$ and 50% $CH_3COCH_2CH_3$. (Even though the CD_3CN had been carefully dried, some contamination by adventitious H_2O during the handling of the solutions clearly occurred.)

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et(MeCN)]PF_6$ **2a** *with* CO.—The complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et(MeCN)]PF_6$ (0.072 g, 100 μmol) in acetonitrile (6 cm^3, CO saturated) was carbonylated (CO 6 atm; 25 °C, 20 h) as above. A GC analysis of the solution phase showed the presence of butan-2-one (1 μmol) and pentan-2-one (32 μmol) as well as propene and ethene, which were not quantified.

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CD_3)_2]$ **3b** *with* $[Fe_4(OH)_2(SO_4)_5]$ *under* CO (1 *atm*).—The complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CD_3)_2]$ (0.055 g, 100 μmol; 99.5% D) and $[Fe_4(OH)_2(SO_4)_5]$ (0.320 g, 434 μmol) were dissolved in acetonitrile (2 cm^3, CO saturated), and stirred under CO (1 atm; 25 °C, 72 h) to give an orange-red solution plus an off-white precipitate. A GC analysis of the solution and gas phases showed the presence of (total, μmol): CH_4 (117), C_2H_4 (4), C_2H_6 (1), C_3H_6 (43), MeCOEt (37) and $MeCO_2H$ (11). GC–MS showed that the methane is largely CD_3H (90%), and that the butan-2-one is exclusively $CD_3CH_2COCH_3$ (*m/z* 75; fragmentation pattern in agreement with this isotopomer). Analysis of a similar reaction carried out on $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ under pressure (CO, 6 atm, 25 °C, 20 h) showed the presence of (μmol): MeCOEt (47), $MeCO_2H$ (53) and $EtCO_2H$ (<5).

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** *with* $[Fe_4(OH)_2(SO_4)_5]$ *under* CO.—An analogous reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ (0.056 g, 100 μmol) and $[Fe_4(OH)_2(SO_4)_5]$ (0.160 g, 217 μmol) was carried out in acetonitrile (5 cm^3, CO saturated; CO, 6 atm; 25 °C, 20 h). A GC analysis showed the presence of the following oxygenates (μmol): MeCOEt (2), $MeCOPr^n$ (62), $MeCO_2H$ (17) and $MeCH_2CO_2H$ (16).

Crossover Experiment: Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ **4** *and* $[\{(C_5Me_5)Rh\}_2(^{13}CH_2)_2(^{13}CH_3)_2]$ **3d** *with*

$[Fe_4(OH)_2(SO_4)_5]$ *under* CO.—The complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ (0.011 g, 20 μmol), $[\{(C_5Me_5)Rh\}_2(\mu\text{-}{}^{13}CH_2)_2({}^{13}CH_3)_2]$ (0.011 g, 20 μmol; 92% ^{13}C) and $[Fe_4(OH)_2(SO_4)_5]$ (0.064 g, 87 μmol) in acetonitrile (2 cm^3, CO saturated) were stirred under CO (6 atm, 25 °C, 20 h). A GC analysis showed the presence of the following products (μmol): MeCOEt (10), $MeCOPr^n$ (13), $MeCO_2H$ (19) and $MeCH_2CO_2H$ (13). GC–MS analysis showed that the pentan-2-one contained only ^{13}C of natural abundance by comparison with pentan-2-one formed in a control experiment using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CH_3)_2]$ and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ containing ^{13}C only in natural abundance. The distribution of isotopomers of butan-2-one was (found, expected), $^{13}C_3H_8CO$ (69, 78%), $^{13}C_2{}^{12}C_1H_8CO$ (15, 20%), $^{13}C_1{}^{12}C_2H_8CO$ (7, 2%) and $^{12}C_3H_8CO$ (8, $\leqslant$1%); some of the butan-2-one comes from carbonylation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Et_2]$ (see experiment above), accounting for the higher than expected amount of unlabelled $^{12}C_3H_8CO$ and $^{13}C_1{}^{12}C_2H_8CO$. The fragmentation pattern of $^{13}C_3H_8{}^{12}CO$ was consistent with $^{13}CH_3{}^{13}CH_2{}^{12}CO\text{-}{}^{13}CH_3$, while that of the acetic acid was consistent with the presence of $^{13}CH_3{}^{12}CO_2H$ (70%) and $^{12}CH_3{}^{12}CO_2H$ (30%). The propanoic acid was largely $^{12}C_2H_5{}^{12}CO_2H$, but *ca.* 20% was $^{13}CH_3{}^{13}CH_2{}^{12}CO_2H$, and 5% was $^{13}CH_3{}^{12}CH_2{}^{12}CO_2H$; carbonylation of the dimethyl complex and $[Fe_4(OH)_2(SO_4)_5]$ often yields small amounts of propanoic acid.

Reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CHMe)(\mu\text{-}CH_2)Me_2]$ **5** *with* $[Fe_4(OH)_2(SO_4)_5]$ *under* CO.—The complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)(\mu\text{-}CHMe)Me_2]$ (0.056 g, 100 μmol) in the presence of $[Fe_4(OH)_2(SO_4)_5]$ (0.160 g, 434 μmol) in acetonitrile (5 cm^3, CO saturated) was carbonylated (CO, 12 atm; 25 °C, 20 h). A GC analysis showed the formation of (μmol): MeCOEt (2), $MeCO_2H$ (63), $MeCOPr^i$ (7) and EtCOEt (6).

Carbonylation Reactions in Methanol.—These were carried out in a similar manner to those in acetonitrile; the results are summarized in Table 2. Typical conditions were as follows. For reaction 7 $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(CO)]PF_6$ (0.070 g, 100 μmol) was carbonylated in a Fisher-Porter tube in methanol (3 cm^3, CO saturated); the solution was stirred under CO (6 atm; 25 °C; 20 h) to give a deep red solution. After the usual work-up, GC analysis (column CPSil5, cyclohexane internal standard) of the solution phase showed the presence of the oxygenates. Reactions 8 and 9 (identical to check the reproducibility of the procedure) were carried out as for 7 but with the addition of $[Fe_4(OH)_2(SO_4)_5]$ (0.320 g, 434 μmol). Reaction 10 used the complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(Cl)]$ (**6**, 100 μmol) and $[Fe_4(OH)_2(SO_4)_5]$ (0.320 g, 434 μmol). Reactions 11 and 12 were carried out using $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me(CO)]PF_6$ (0.070 g, 100 μmol) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ (0.055 g, 100 μmol) respectively, in methanol (2 cm^3) and CO (1 atm, 50 °C, 2.5 h); here the gases were also analysed, using a Poropak QS GC column.

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