Synthesis of Alkan-2-ones by Dirhodium-mediated Four Carbon Coupling

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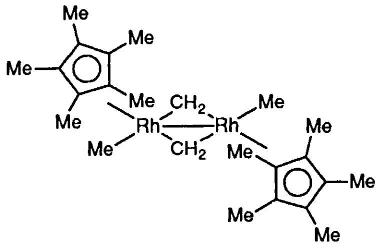
Alkan-2-ones (RCH_2COCH_3) are obtained by C–C–C–C coupling of the *four* ligands in the dirhodium complexes, $[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(R)(CO)]^+$ ($R = CH_3$, $^{13}CH_3$, CD_3, C_2H_5); the reaction is intramolecular.

We have previously described the synthesis of hydrocarbons by C–C–C coupling of three ligands (two μ-CH_2 and one terminal alkyl) in dialkyl-di-μ-methylene-dirhodium complexes; for example, propene is obtained from **1**.[1] The recent claim that **1** on silica is a precursor to a species active in carbonylation[2] leads us to disclose data on some simple reactions in homogeneous phase in which the efficient combination of four ligands (one alkyl, R, two μ-CH_2, and CO) by C–C–C–C coupling leads to n-alkan-2-ones (RCH_2COCH_3).



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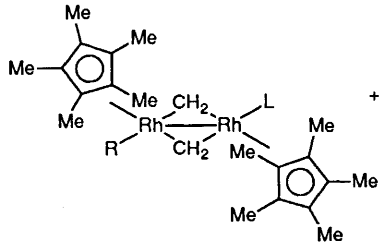
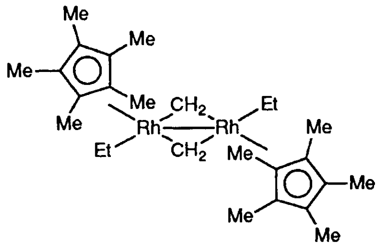


2a; R = Me, L = MeCN
b; R = Me, L = CO
c; R = Et, L = MeCN



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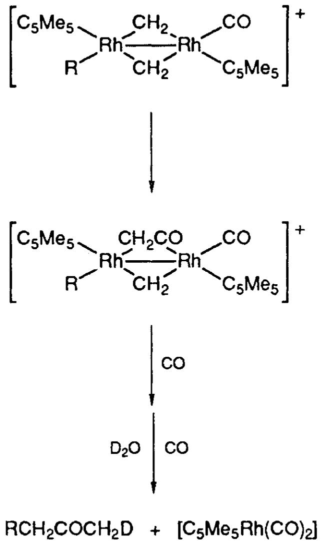
Complex **2a**[3] (100 μmol) reacted easily with CO (standard conditions: 6 atm, 25 °C, 20 h, MeCN solvent) to give methyl ethyl ketone (MEK, 52 μmol), together with ethene (23 μmol), methane (12 μmol), ethane and propene (4 μmol each). The metal complex was recovered as $[C_5Me_5Rh(CO)_2]$ [IR ν(CO) 1950, 2018 cm^{-1}]. The yield of MEK depends on the CO pressure and was 27 μmol at 1 atm; higher yields can presumably be achieved at high pressures. Addition of hydrogen to the CO (6 atm each) under the standard conditions had little effect on MEK formation, and no aldehyde was detected.

The MEK from reaction of $^{13}CH_3$ labelled complex **2a** [containing 92% ^{13}C, prepared from **1** (Me = $^{13}CH_3$)] with CO showed the presence of only $^{13}CH_3{}^{12}CH_2{}^{12}CO^{12}CH_3$ (90%, by ^1H NMR spectroscopy). Further, only $CD_3CH_2COCH_3$ could be detected (by ^1H NMR) when complex **2a**, (R = CD_3, 99%D) was carbonylated. When the reaction of protio **2b** was carried out in CD_3CN wetted with D_2O, the ^1H NMR of the product ketone showed a 1 : 1 : 1 triplet at δ 2.03 [J_{H-D} 2 Hz] due to the presence of CH_2DCO–. This suggests that the reaction ends by cleavage of Rh–CH_2COEt by $H_2O(D_2O)$.

The related cationic ethyl complex **2c** (100 μmol) reacted similarly (6 atm, 25 °C, 20 h, MeCN solvent) to give n-propyl methyl ketone (n-PMK, $EtCH_2COCH_3$, 32 μmol). No diethyl ketone was formed in this reaction, showing the very high specificity of the coupling.

All the reactions proceed *via* the cationic carbonyl complex, and **2b**, for example, is conveniently prepared by saturating an acetone solution of **2a** with CO at 0 °C.[3] However, that complex is unstable and better yields are obtained when it is slowly generated *in situ*, from **2a**.



Scheme 1

Addition of ferric oxysulphate, $[Fe_4(OH)_2(SO_4)_5]$, Monsel's salt, to the carbonylation of **2a** had little effect on MEK yield (57 μmol). However, the neutral complex **1** only reacted directly with CO in the presence of promoters such as $[Fe_4(OH)_2(SO_4)_5]$. The (insoluble) ferric sulphate appears to act by slowly releasing small amounts of H^+, which cleave one methyl, giving **2b**. This is confirmed by the formation of CD_3H (≈ 90%) as the main volatile product, in addition to $CD_3CH_2COCH_3$, on decomposition of **1** (Me = CD_3) [CO 1 atm, 72 h, 25 °C, CH_3CN, $Fe_4(OH)_2(SO_4)_5$] [eqn. (1)].

$$[(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CD_3)_2] + H^+ + CO \rightarrow [(C_5Me_5Rh)_2(\mu\text{-}CH_2)_2(CD_3)(CO)]^+ + CD_3H \quad (1)$$

Carbonylation of the diethyl-di-μ-methylene complex **3** in the presence of $Fe_4(OH)_2(SO_4)_5$ in MeCN gave n-PMK, while an equimolar mixture of $[(C_5Me_5Rh)_2(\mu\text{-}^{13}CH_3)_2(^{13}CH_3)_2]$ **1** ($^{13}C_4$) and complex **3** [MeCN, 25 °C, 6 atm, 24 h, $Fe_4(OH)_2(SO_4)_5$] gave a mixture of MEK and n-PMK. Analysis showed that the MEK was largely $^{13}C_2H_5CO^{13}CH_3$, and that there was no significant incorporation of ^{13}C into the n-PMK. This crossover experiment indicates the ketone formation reaction to be intramolecular.

These data indicate that the reaction proceeds by a sequential coupling of R, μ-CH_2, CO and μ-CH_2, and two metal atoms are needed to accommodate the four C_1 ligands involved. However, since the labelled methyl and the CO are on different rhodiums in **2** and since the label in MEK is not on the methyl adjacent to the CO, we suggest that the first step is a CH_2–CO migratory insertion giving a bridging ketene intermediate[4] (Scheme 1). The precise order of the further steps is not yet clear; since alkyl–acyl coupling occurs more readily than alkyl–alkyl coupling,[5] one might anticipate a methylene–ketene coupling, followed by a reductive elimination of $Rh(R)(CH_2CO\cdot\cdot)$.

CO-based coupling reactions to give ketones are still quite unusual. Furthermore, although rhodium, especially when promoted with a rare earth oxide,[6] is a good catalyst for the production of oxygenates from syn-gas (CO + $2H_2$), ketones have not generally 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 serves to illustrate one part of this process.

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