Easy Coupling of μ-Methylene Groups in Di-(μ-methylene)-dicobalt Complexes: Model Reactions for the Fischer–Tropsch Synthesis

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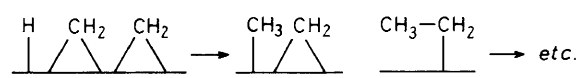
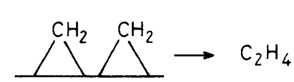
Carbon–carbon coupling reactions occur at room temperature in reactions of $[Co_2(CO)_4(\mu\text{-}CH_2)_2(\mu\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$) with alkynes to give ethene and $[Co_2(CO)_4(\mu\text{-}RCCR)(\mu\text{-dppm})]$, with ethene to give propene, and, at higher temperature, with hydrogen to give ethane.

We report the first example of hydrogenolysis of a di-(μ-methylene) transition metal complex to give ethane and some remarkably easy methylene coupling reactions to give ethene. The reactions are significant as models for the proposed steps in the Fischer–Tropsch synthesis using transition metal catalysts such as cobalt shown in equation (1), and with respect to the related reaction of equation (2).[1]



(1)



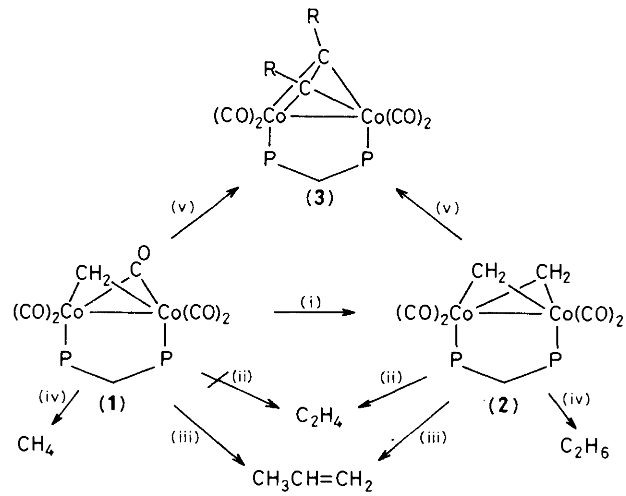
(2)

Some of the new reactions are shown in Scheme 1, and are based on the recently reported μ-methylene-dicobalt complexes (**1**) and (**2**).[2] Pyrolysis of (**2**) occurred readily at 80—90 °C in decalin to give ethene, identified by g.c., and (**2**) also reacted slowly at room temperature with the alkynes RCCR (R = CF_3 or Ph) to give (**3**)[3],† with evolution of ethene. No other hydrocarbon products were observed. We have not yet proved that this methylene coupling reaction is intramolecular, but the observation that the complexes (**1**) and $[Co_2(CO)_4(\mu\text{-}CH_2)(\mu\text{-}CHCO_2Et)(\mu\text{-dppm})]$ fail to give ethene on pyrolysis strongly indicates an intramolecular coupling reaction. Coupling of substituted alkylidene groups to give $Me_2C{=}CHMe$ has been observed on pyrolysis of a complex containing the $Ru_2(\mu\text{-}CMe_2)(\mu\text{-}CHMe)$ unit at 200 °C,[1,4] but only one previous example of the room-temperature coupling of simple methylene units to give ethene is known.[5] Reaction of (**1**) or (**2**) under ethene (*ca.* 1 atmosphere) at room temperature gave propene and unidentified cobalt-containing products;[6—8] no butenes were detected in either case, showing that ethene couples with only one μ-methylene group of (**2**).

Most interesting is the pyrolysis of (**2**) in decalin under hydrogen (1 atmosphere) at 85 °C when only traces of ethene were formed, the major hydrocarbon product being ethane.‡ We suggest that ethane is formed by oxidative addition of hydrogen to (**2**), followed by the reactions of equation (1) and

† Complex (**3**; R = CF_3) has not been reported. It was characterized by elemental analysis, mass spectrometry (*m/z* 776), and i.r. and ^{1}H, ^{19}F, and ^{31}P n.m.r. spectroscopy: $\delta(CH_2P_2)$ 3.45 [t, ^2J(PH) 11 Hz]; $\delta(^{19}F)$ −50.5 p.p.m. from $CFCl_3$ [t, ^4J(PF) 4 Hz]; $\delta(^{31}P)$ 73.3 p.p.m. from $PO(OMe)_3$. It can also be prepared by reaction of $CF_3C{\equiv}CCF_3$ with $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-dppm})]$. The reaction of (**2**) with $CF_3C{\equiv}CCF_3$ took *ca.* 2 days for completion.

‡ Yields: C_2H_4, 0.4%; C_2H_6, 54.9%, based on (**2**). No attempt was made to optimise yields.



Scheme 1. P⌒P = $Ph_2PCH_2PPh_2$ (dppm). *Reagents*: (i) CH_2N_2, (ii) heat at 80—90 °C, (iii) C_2H_4, (iv) H_2 at 80—90 °C, (v) RC≡CR (R = CF_3 or Ph).

$$[Co_2(CO)_4(\mu\text{-CHMe})_2(\mu\text{-dppm})]$$
(4)

$$[Co_2(CO)_4(\mu\text{-CH}_2)(\mu\text{-CHMe})(\mu\text{-dppm})]$$
(5)

reductive elimination of ethane. Note that pyrolysis of (**1**) under hydrogen gives methane but no ethane,[7] again suggesting an intramolecular C–C coupling reaction for (**2**). In addition, pyrolysis in decalin of $[Co_2(CO)_4(\mu\text{-CHMe})_2(\mu\text{-dppm})]$ (**4**)§ or $[Co_2(CO)_4(\mu\text{-CH}_2)(\mu\text{-CHMe})(\mu\text{-dppm})]$ (**5**)§ gave ethene only [complex (**4**)] or ethene and propene [complex (**5**)] with the ethene presumably being formed by β-elimination from the μ-CHMe group. Under hydrogen, both (**4**) and (**5**) gave considerably higher ethene : ethane ratios than did (**2**).¶ Since the pyrolysis products from (**2**), (**4**), and (**5**) are apparently the same (green insoluble solids), a mechanism of ethane formation from (**2**) by catalytic hydrogenation of initially formed ethene is very improbable. This system therefore gives a useful model for the first and second steps of the proposed catalytic reaction of equation (1).[1] An excellent model for the second and subsequent steps has been developed by Maitlis and co-workers.[9]

We thank N.S.E.R.C. (Canada) and Imperial Oil Ltd. for financial support.

Received, 21st September 1983; Com. 1248

§ Complex (**4**) was prepared by reaction of excess of diazoethane with $[Co_2(CO)_4(\mu\text{-CO})_2(\mu\text{-dppm})]$ and was fully characterized by elemental analysis and ^1H and ^{13}C n.m.r. spectroscopy. Complex (**5**) was prepared by reaction of diazoethane with (**1**).

¶ Complex (**4**) under H_2 gave C_2H_4 (9%) and C_2H_6 (36%). Complex (**5**) under H_2 gave C_2H_4 (10%), C_2H_6 (53%), $CH_3CH{=}CH_2$ (20%), and C_3H_8 (4%). No attempts were made to optimise yields.

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