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Formation of Ketenes from μ-Alkylidenedicobalt Complexes: Model Reactions for the Fischer–Tropsch Synthesis

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The coupling of μ-methylene groups on pyrolysis of $[Co_2(\mu\text{-}CH_2)_2(CO)_4(\mu\text{-dppm})]$, dppm = $Ph_2PCH_2PPh_2$, and related complexes to give ethylene has been reported [1]. In view of the significance of cobalt catalysis of the Fischer–Tropsch synthesis and of current interest in coupling of coordinated alkylidene and carbonyl ligands to give ketene derivatives as models for proposed steps in formation of oxygenated products during such catalysis [2, 3], we now report the easy coupling of μ-alkylidene groups with CO in μ-alkylidenedicobalt complexes. Yields of both cobalt-containing and organic products were determined by carrying out the reactions at room temperature in sealed NMR tubes and integrating signals due to each product against an internal reference. Ketenes were trapped by reaction with CD_3OD to give the corresponding ester (eqn. (1)) since the probable ketene complex intermediates could not be detected. The possibility that CD_3OD attacks coordinated rather than free ketene cannot be ruled out though free ketene could be detected by GC when reactions were carried out in the absence of alcohol.

$$RCH{=}C{=}O + CD_3OD \longrightarrow RCHDCO_2CD_3 \qquad (1)$$

1a, R = H
1b, R = Me
1c, R = CO_2Et

Yields of products from reactions carried out under CO atmosphere are given in Table I. They show that the alkylidene–CO coupling reaction is not limited to μ-CH_2 groups but also occurs in high yield for μ-CHMe and μ-$CHCO_2Et$ groups. Under these conditions, the coupling of two μ-alkylidene groups to give alkenes [1] is not competitive with the alkylidene–CO coupling.

TABLE I. Products (yields, %) from Reactions of $[Co_2(\mu\text{-}R)(\mu\text{-}R^1)(CO)_4(\mu\text{-dppm})]$ under CO to give $[Co_2(\mu\text{-}CO)_2(CO)_4(\mu\text{-dppm})]$, **2**, and **1**[a]

Reagent		Products (%)			
R	R^1	**2**	**1a**	**1b**	**1c**
CH_2	CO	70	90	–	–
CH_2	CH_2	80	95	–	–
CHMe	CHMe	80	–	85	–
CH_2	CHMe	70	85	80	–
$CHCO_2Et$	CO	70	–	–	85
CH_2	$CHCO_2Et$	90	95	–	90
CH_2	SO_2	35[a]	65	–	–

[a] $[Co_2(\mu\text{-}CO)(\mu\text{-}SO_2)(CO)_4(\mu\text{-dppm})]$ was also detected in 25% yield.

TABLE II. Products (yields, %) from Reactions of $[Co_2(\mu\text{-}R)(\mu\text{-}R^1)(CO)_4(\mu\text{-dppm})]$ with SO_2 or R^2CCR^2 to give $[Co_2(\mu\text{-}SO_2)_2(CO)_4(\mu\text{-dppm})]$, **3**, or $[Co_2(\mu\text{-}CF_3CCCF_3)(CO)_4(\mu\text{-dppm})]$, **4**, and **1**

Reagents			Products			
R	R^1	SO_2	**3**	**1a**	**1b**	**1c**
CH_2	CO		15	65	–	–
CH_2	CH_2		35	90	–	–
CHMe	CHMe		25	–	30	–
CH_2	CHMe		15	25	25	–
$CHCO_2Et$	CO		15	–	–	55
CH_2	$CHCO_2Et$		10	60	–	50
CH_2	SO_2		30	60	–	–
R	R^1	CF_3CCCF_3	**4**	**1a**	**1b**	**1c**
CH_2	CO		>40	85	–	–
CH_2	CH_2		>25	80	–	–
CHMe	CHMe		25	–	45	–
CH_2	CHMe		25	35	50	–
$CHCO_2Et$	CO		>40	–	–	75
CH_2	$CHCO_2Et$		>25	95	–	95
CH_2	SO_2		45	50	–	–

Reaction of $[Co_2(\mu\text{-}CH_2)_2(CO)_4(\mu\text{-dppm})]$ with SO_2 occurred according to eqn. (2), to give new $Co_2(\mu\text{-}SO_2)$ complexes**.

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**NMR data for new complexes $[Co_2(\mu\text{-}R)(\mu\text{-}R^1)(CO)_4(dppm)]$: R = R^1 = SO_2; 4.01 [$\underline{t}$, $^2J(PH)$ = 14, $C\underline{H}_2P_2$]; 32.9 [$\underline{s}$, ^{31}P]. R = SO_2, R^1 = CH_2; 5.18 [$\underline{m}$, $^2J(H^aH^b)$ = 4, $Co_2C\underline{H}^aH^b$]; 4.28 [$\underline{m}$, $^2J(PH)$ = 20, $Co_2CH^a\underline{H}^b$); 4.19 [$\underline{m}$, $^2J(H^cH^d)$ = 14, $C\underline{H}^cH^dP_2$]; 2.93 [$\underline{m}$, $CH^c\underline{H}^dP_2$]; 60.2 [$\underline{s}$, ^{31}P]. R = SO_2, R^1 = $CHCO_2Et$; 4.56 [$\underline{t}$, $^3J(PH)$ = 22, Co_2CH]; 1.20 [$\underline{t}$, $^3J(HH)$ = 7, CH_3]; 4.01 [$\underline{q}$, $C\underline{H}_2O$]; 3.40 [$\underline{m}$, $CH^aH^bP_2$]; 2.66 [$\underline{m}$, $CH^a\underline{H}^bP_2$]; 54.6 [$\underline{s}$, ^{31}P]. R = SO_2, R^1 = CO; 3.25 [$\underline{t}$, $^2J(PH)$ = 10, CH_2P_2].

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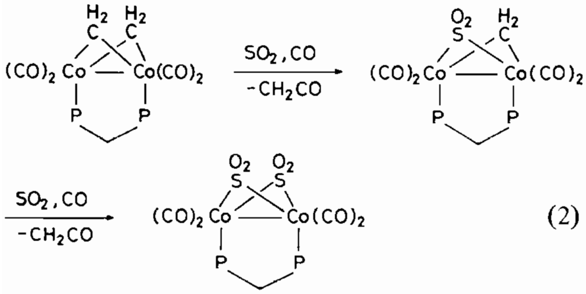

(2)

The yields of products after extended reaction periods are given in Table II. The yields of cobalt-containing products are low, which can partially be rationalized since the extra CO needed according to eqn. (2) must be formed by general decomposition of some cobalt carbonyl derivative. Only for the $Co_2(\mu\text{-}CH_2)_2$ derivative was some C_2H_4 detected and in no case was sulfene, the expected product of insertion of SO_2 into the $Co_2(\mu\text{-}CH_2)$ group, observed as its methanol-d$_4$ derivative $CH_2DSO_3CD_3$. Thus the CHR–CO coupling to give ketene occurs more readily than CHR–SO_2 coupling to give sulfene in these complexes. In contrast, $[Rh_2(\mu\text{-}CH_2)(CO)_2(C_5Me_5)_2]$ reacts with SO_2 to give a sulfene complex [4].

Some information on relative reactivities of different μ-alkylidene groups was obtained from these experiments. Thus reaction of $[Co_2(\mu\text{-}CH_2)(\mu\text{-}CHCO_2Et)(CO)_4(\mu\text{-dppm})]$ with SO_2 gave at intermediate stages **1a** and $[Co_2(\mu\text{-}CHCO_2Et)(\mu\text{-}SO_2)(CO)_4(\mu\text{-dppm})]$ *, indicating greater reactivity of the μ-CH_2 group compared to the μ-$CHCO_2Et$ group towards coupling with CO.

Similar results were obtained on reaction of the μ-alkylidene complexes with hexafluorobut-2-yne as shown in Table II. Again coupling of μ-CHR and CO groups to give ketene derivatives accounts for the majority of the organic products formed in these reactions [1], but the yields are generally lower than for the reactions carried out under CO. The combined results of Tables I and II suggest that coupling of μ-CHR and CO groups is a reasonable step during catalysis of the Fischer–Tropsch synthesis by cobalt catalysts.

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