Applications of Homogeneous Water-gas Shift Reaction. IV. Hydrocarbonylation and Dimerization of Methyl Acrylate with CO and H_2O

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Hydrocarbonylation of methyl acrylate with CO and H_2O forms dimethyl 4-oxopimelate in 94% yield based on H_2O, the $Co_2(CO)_8$-1,2-bis(diphenylphosphino)ethane (diphos) catalyst system being used as in the case of ethylene or propylene. Increasing temperature tends to promote the dimerization and/or hydrodimerization of methyl acrylate to give 1,3-bis(methoxycarbonyl)-1-butene and/or dimethyl 2-methylglutarate. Effects of CO pressure and H_2O concentration on the hydrocarbonylation and dimerization were examined at 135 and 165 °C. Catalytically active intermediates for the hydrocarbonylation take part in the dimerization of methyl acrylate.

In connection with the synthesis of dialkyl 4-oxopimelate under oxo conditions using transition metal catalyst,[1] only one case is known, where a cobalt-catalyzed hydroesterification of methyl acrylate in the presence of pyridine produces the ketone as a minor product.[2]

Recently, we have described a homogeneous catalysis of hydrocarbonylation of ethylene or propylene with CO and H_2O where the $Co_2(CO)_8$–phosphine system is a catalyst precursor and symmetrical ketones are selectively produced.[3,4]

In the present paper, the applicability of this method to selective synthesis of dimethyl 4-oxopimelate from methyl acrylate is first tested, then an unexpected dimerization of the olefin under identical conditions is described, and finally a possible scheme effective for both hydrocarbonylation and dimerization is discussed in connection with catalytically active intermediates.

Experimental

Materials. Methyl acrylate, acrylonitrile, and H_2O were distilled before use. 1,2-Bis(diphenylphosphino)ethane (diphos) and the solvent were used without further purification. $Co_2(CO)_8$ was prepared by the conventional method.

Reaction Procedure. The hydrocarbonylation (dimerization) reaction was carried out in a 300 cm³ stainless-steel autoclave. A reaction vessel containing $Co_2(CO)_8$, diphos, H_2O, substrate, and solvent was placed in the autoclave, and after sealing, CO was introduced. The vessel was kept heated with stirring at a reaction temperature for a certain period and then cooled down to room temperature. Liquid products formed were analyzed at 180 °C with a gas chromatograph equipped with an FID using a 4-m squalane column.

Results and Discussion

Typical Examples of Hydrocarbonylation with CO and H_2O. As shown in Table 1, dimethyl 4-oxopimelate[5] was formed in 94% yield based on H_2O when the reaction was carried out in dioxane with an initial CO pressure of 100 kg/cm² at 135 °C (Run 6). However, the yield drastically decreased as the methyl acrylate (MA) : $Co_2(CO)_8$ ratio was decreased (Runs 4—6). The effectiveness of polar ether solvents for increasing the yield is in the order dioxane>1,2-dimethoxyethane>THF (Runs 1—3). The use of H_2 as hydrogen donor resulted also in decrease in the yield and methyl 4-oxobutyrate was predominantly produced (Runs 7 and 8). These features of catalytic behavior are similar to those observed for the hydrocarbonylation of ethylene[3] or propylene.[4] No detectable amounts of other isomers (n-to-iso or iso-to-iso ketone) were formed under these condition. Hydrogenation of MA to methyl propionate occurred (see Table 1, last column). Thus, the $Co_2(CO)_8$–diphos complex, which is effective for the hydrocarbonylation of ethylene or propylene, was also found to be an active and selective catalyst for the reaction of MA with CO and H_2O to give dimethyl 4-oxopimelate.

$$2CH_2{=}CH\text{-}COOMe + 2CO + H_2O \longrightarrow CO(CH_2CH_2COOMe)_2 + CO_2 \quad (1)$$

$$CH_2{=}CH\text{-}COOMe + 2CO + H_2O \longrightarrow OHC\text{-}CH_2CH_2COOMe + CO_2 \quad (2)$$

$$CH_2{=}CH\text{-}COOMe + CO + H_2O \longrightarrow CH_3CH_2COOMe + CO_2 \quad (3)$$

It has been found that under the conditions employed, dimerization and/or hydrodimerization[6] of MA occur to give 1,3-bis(methoxycarbonyl)-1-butene (unsaturated head-to-tail dimer, UD) and dimethyl 2-methylglutarate (saturated dimer, SD) as identified by ^{13}C NMR and IR spectal analysis,[7] whereas no trace of dimethyl adipate (saturated head-to-head dimer) is formed; thus this is the first example of cobalt-catalyzed dimerization of MA with CO and H_2O.

$$2CH_2{=}CHCOOMe \longrightarrow CH_3CH(COOMe)CH{=}CHCOOMe \quad (4)$$

$$2CH_2{=}CHCOOMe + CO + H_2O \longrightarrow CH_3CH(COOMe)CH_2CH_2COOMe + CO_2 \quad (5)$$

Effect of Temperature. Effects of reaction parameters on product yields were examined by allowing the reaction of MA with $Co_2(CO)_8$ in a 100:2 molar ratio to proceed in dioxane for 4 h using the $Co_2(CO)_8$–diphos catalyst system.

Temperature dependence at 100 kg/cm² CO pressure is illustrated in Fig. 1. The yield of dimethyl 4-oxopimelate increased with an increase in tempera-

TABLE 1. HYDROCARBONYLATION OF METHYL ACRYLATE USING CO AND H_2O CATALYZED BY $Co_2(CO)_8$-DIPHOS SYSTEM

$Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, solvent 50 ml, temp 135 °C, time 10 h, and H_2O 35 mmol.

Run	MA (mmol)	Solvent	P_{CO}/kg cm^{-2}	Yield/mmol[a]				
				DP/%[b]	UD	SD	AD	MP
1	100	THF	70	22.6 (64.5)	1.44	0.1	0.15	—
2	100	1.2-Dimethoxy-ethane	70	24.9 (71.2)	1.71	0.12	0.23	—
3	100	Dioxane	70	29.6 (84.6)	1.1	0.16	0.08	<0.1
4	60	Dioxane	100	12.4 (35.4)	1.0	0.18	0.1	—
5	100	Dioxane	100	31.5 (90.0)	1.2	0.18	0.15	<0.1
6	150	Dioxane	100	32.7 (93.5)	1.3	0.20	0.20	0.15
7[c]	100	Dioxane	70	7.3 (20.8)	0.62	1.1	4.7	—
8[c]	100	Dioxane	70	7.7 (22.0)	—	0.9	10.6	—

a) Abbreviations DP, UD, SD, AD, and MP stand for dimethyl 4-oxopimelate, 1,3-bis(methoxycarbonyl)-1-butene, dimethyl 2-methylglutarate, methyl 4-oxobutyrate, and methyl propionate, respectively. b) Based on H_2O (35 mmol). c) H_2 35 mmol, time 4 h, temp 135 °C (Run 7), and 120 °C (Run 8).

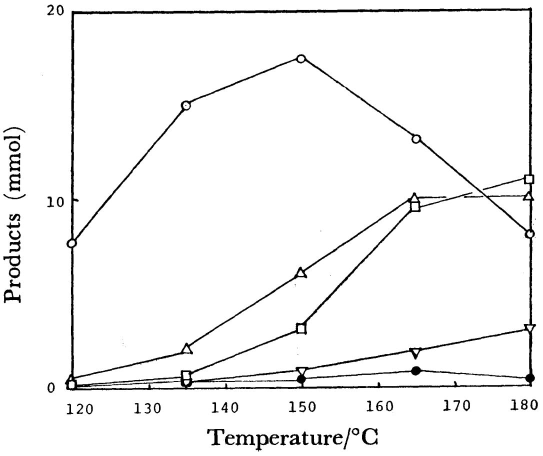


Fig. 1. Effect of temperature.

$Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, H_2O 35 mmol, dioxane 50 ml, CO 100 kg/cm^2 (initial), methyl acrylate 100 mmol, time 4 h. —○—: Dimethyl 4-oxopimelate, —△—: 1,3-bis(methoxycarbonyl)-1-butene, —▽—: methyl 2-methylglutarate, —□—: methyl propionate, —●—: methyl 4-oxobutyrate.

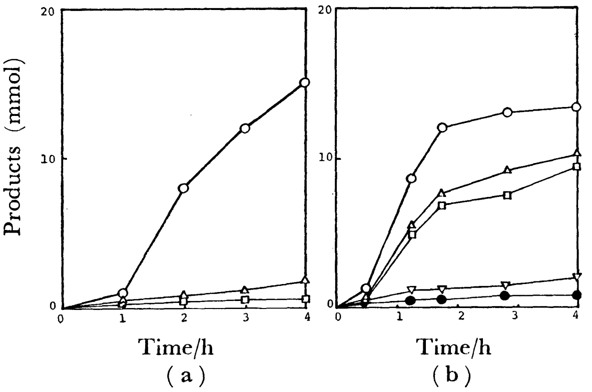


Fig. 2. Cobalt catalyzed hydrocarbonylation and dimerization as a function of time.

(a): 135 °C, (b): 165 °C. $Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, H_2O 35 mmol, dioxane 50 ml, CO 70 kg/cm^2, methyl acrylate 100 mmol. Marks (○, △, ▽, □, ●): See footnote of Fig. 1.

ture between 120 and 150 °C but decreased thereafter. Considerable amounts of dimers UD and SD as well as methyl propionate were formed at high reaction temperature. In order to examine catalytic properties of dimerization as well as hydrocarbonylation, two reaction temperatures 135 and 165 °C were adopted for varying parameters such as time course, P_{CO}, and P_{H_2O} in the experiments to be described below.

Time Course of Product Formation. As shown in Fig. 2, there was an induction period, similar in trend to those observed for the hydrocarbonylation of ethylene[3] and propylene.[4] Two dimers UD and SD were also formed with the same induction period with the ketone.

Effect of CO Pressure. As illustrated in Fig. 3a (135 °C), the yield of dimethyl 4-oxopimelate is slightyl dependent on CO pressure over the range from 50 to 130 kg/cm^2. Lowering the pressure reduces the yield because it induces partial decomposition of $Co_2(CO)_8$. At 165 °C, the yield incerased with the increase in CO pressure (Fig. 3b). On the contrary, yields of the two dimers UD and SD as well as methyl propionate decreased with the increase in CO pressure (Fig. 3b).

Effect of H_2O Concentration. The results are shown in Fig. 4a; the yield of the ketone increased with increasing H_2O concentration in the range 30—180 mmol but leveled off thereafter. At 165 °C, the yield increased initially as the H_2O concentration increased from 10 to 60 mmol, but a further increase in H_2O concentration resulted in decrease in the yield (Fig. 4b). The formation of dimer UD showed a H_2O dependence similar to that of the ketone formation, while the formation of dimer SD was steadily accelerated with increase in H_2O concentration. The hydrogenation of MA to methyl propionate was favored at higher H_2O concentrations.

Catalytically Active Intermediates and a Possible Reaction Scheme. Since the hydrocarbonylation of MA with CO and H_2O selectively produces dimethyl 4-oxopimelate (Table 1), catalytically active intermediates responsible for this reaction may be $HCo(CO)_m(diphos)_n$, as in the case of ethylene[3] and propylene.[4] In fact, induction period was observed for the reaction (Fig. 2) and their catalytic characteristics are similar, especially at 135 °C (Figs. 1a, 3a, and 4a).

Dimerization and/or hydrodimerization, by which dimers UD and/or SD were produced from MA, occurred under the conditions described above (Table 1). It seems likely that the intermediates $HCo(CO)_m$-$(diphos)_n$ catalyze the hydrocarbonylation as well as the dimerization. In fact, there was an induction period for the formation of two dimers UD and SD (Fig. 2). Also, a support for the contention was furnished by an experiment in which a catalyst solution, consisting of $Co_2(CO)_8$, diphos, H_2O, and dioxane, and active in the water-gas shift reaction, was prepared at 165 °C[8] and, in the absence of gaseous CO, a stoichiometric reaction of the solution with MA occurred even at room temperature to give both dimethyl 4-oxopimelate and the two dimers UD and

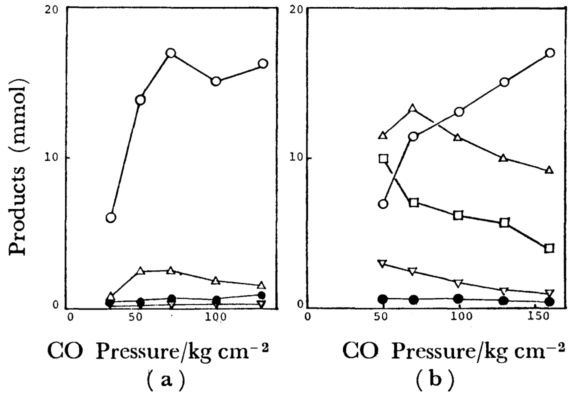


Fig. 3. Effect of CO pressure.
(a): 135 °C, (b): 165 °C. $Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, H_2O 35 mmol, dioxane 50 ml, methyl acrylate 100 mmol, time 4 h. Marks: See footnote of Fig. 1.

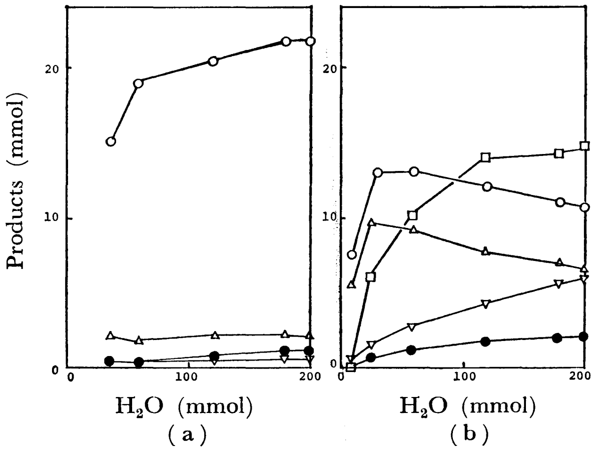
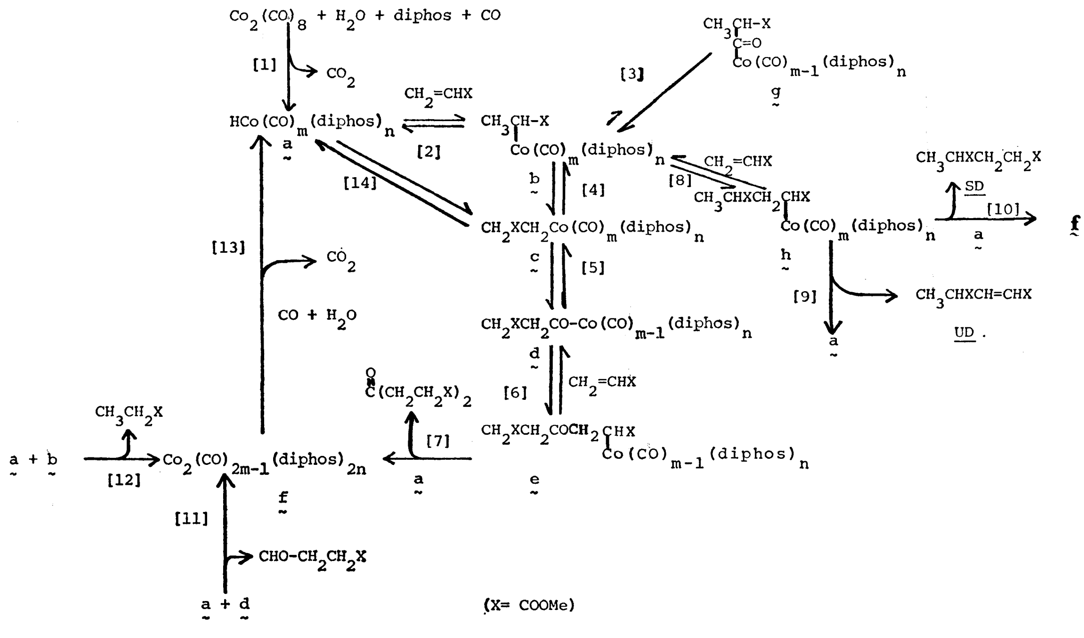


Fig. 4. Effect of H_2O concentration.
(a): 135 °C, (b): 165 °C. $Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, CO 70 kg/cm^2 (initial), dioxane 50 ml, methyl acrylate 100 mmol, time 4 h. Marks: See footnote of Fig. 1.



Scheme 1. A possible reaction scheme of the hydrocarbonylation and dimerization of methyl acrylate with CO and H_2O.

TABLE 2. HYDROCARBONYLATION OF ACRYLONITRILE BY $Co_2(CO)_8$-DIPHOS COMPLEX
$Co_2(CO)_8$ 2 mmol, diphos 1.5 mmol, CO 100 kg/cm^2(initial), acrylonitrile 100 mmol, H_2O 35 mmol, and time 5 h.

Run	Temp	Ketone[a] (mmol)			Propionitrile (mmol)	Aldehyde[b] (mmol)	
	°C	n-to-n	n-to-iso	iso-to-iso		n	iso
1	135	0.77	2.5	1.2	28.1	—	0.20
2	165	0.70	3.7	0.30	27.8	—	0.30

a) 4-Oxopimelonitrile (n-to-n), 2-methyl 3-oxoadiponitrile (n-to-iso), and 2,4-dimethyl 3-oxoglutaronitrile (iso-to-iso). b) 4-Oxobutyronitrile (n) and 2-methyl-3-oxopropionitrile (iso).

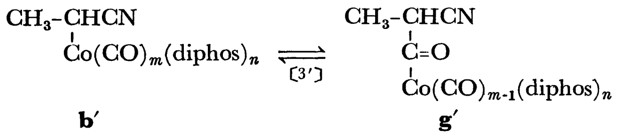
SD.[9,10)]

Considering the scheme previously mentioned for the hydrocarbonylation of ethylene,[3)] a possible scheme is proposed as Scheme 1, where [2- and 1-(methoxycarbonyl)ethyl]cobalt complexes **c** and **b**,[11)] formed by the reaction of $HCo(CO)_m(diphos)_n$ with MA followed by hydride addition, are assumed to be other key imtermediates for the production of the ketone and two dimers; unlike the hydrocarbonylation of ethylene, CO insertion into **b** to yield [2-(methoxycarbonyl)-propionyl]cobalt complex, **g**, would occur very slightly because **g** is a β-dicarbonyl-type complex which is thermally unstable.[12)] This is in agreement with the absence of n-to-iso or iso-to-iso ketone as well as methyl 2-methyl-3-oxopropionate (Table 1). At low reaction temperatures, a direct formation of **c** (step [14]) would predominantly occur because the higher selectivity for the ketone is achieved in 135 °C reactions (Table 1);[13)] rapid CO insertion followed by MA addition to **d** gives complex **e** and the reaction of **a** with **e** forms dimethyl 4-oxopimelate (Table 1).[14)]

Further addition of MA to [1-(methoxycarbonyl)-ethyl]cobalt complex **b** gives [1,3-bis(methoxycarbonyl)butyl]cobalt complex **h**, which undergoes β-elimination to yield 1,3-bis(methoxycarbonyl)-1-butene (dimer UD) and cobalt hydride complex **a**. The reaction of complex **h** with **a** affords dimethyl 2-methylglutarate (dimer SD) and dimeric cobalt complex **f**. Since there was no detectable amount of dimethyl adipate, CO insertion into [2-(methoxycarbonyl)ethyl]-cobalt complex **c** would be rapid and smooth.[15)]

Steps [11] and [12] account for the formation of methyl 4-oxo butyrate and methyl propionate, respectively. The resulting complex **f** is converted into **a** by the water-gas shift reaction pathway [13] again, as described in the preceding paper.[3)]

To obtain additional information about the catalytically active intermediate **b**, hydrocarbonylation of acrylonitrile was carried out under the same conditions with MA.



$$\underset{\mathbf{b}'}{\begin{array}{l}CH_3\text{-}CHCN\\ \;\;|\\ Co(CO)_m(diphos)_n\end{array}} \underset{[3']}{\rightleftharpoons} \underset{\mathbf{g}'}{\begin{array}{l}CH_3\text{-}CHCN\\ \;\;|\\ \;\;C{=}O\\ \;\;|\\ Co(CO)_{m-1}(diphos)_n\end{array}}$$

In this case, we expect that CO insertion into (1-cyanoethyl)cobalt complex **b**′ (step [3′]) can occur to give (2-cyanopropionyl)cobalt complex **g**′ and successively give n-to-iso and/or iso-to-iso ketones as well as n-to-n ketone. Satisfactory data are shown in Table 2, through a considerable amount of propionitrile was formed. It is worth noting that there were no detectable amounts of such dimers as 1,3-dicyano-1-butene and 2-methyl glutaronitrile.

Some attempts were tried in vain to isolate complexes **b** and **c** and identify them spectroscopically. Therefore, Scheme 1 needs to be considered as one of some probable schemes for the hydrocarbonylation and dimerization of methyl acrylate with CO and H_2O.

References

1) I. Wender and P. Pino, "Organic Synthesis *via* Metal Carbonyl," Wiley, New York (1977), Vol. 2; J. Falbe, "New Syntheses with Carbon Monoxide," Springer, New York (1980).

2) A. Matsuda, *Bull. Chem. Soc. Jpn.*, **42**, 571 (1969).

3) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 2089 (1981).

4) K. Murata and A. Matsuda, *Bull. Chem. Soc. Jpn.*, **54**, 245 (1981); *Chem. Lett.*, **1980**, 11.

5) Satisfactory spectral data were obtained.

6) H. Kanai and K. Ishii, *Bull. Chem. Soc. Jpn.*, **54**, 1015 (1981).

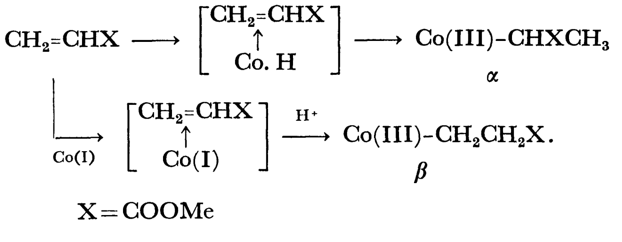
7) Spectral data were as follows. UD: ^{13}C NMR (C_6D_6) δ=12.5, 33.8, 51.5, 51.6, 130.5, 133.4, 167.5, and 170.5; IR 1650 (C=C), 1715 and 1740 cm^{-1} (C=O); SD: ^{13}C NMR (C_6D_6) δ=16.8, 28.8, 31.6, 38.7, 51.1, 173, and 175.9; IR 1730 cm^{-1} (C=O).

8) The preparation was described in detail in the preceding paper.[3)]

9) A trace amount of methyl 4-oxobutyrate was also detected.

10) No dimerization occurred in the presence of diphos without $Co_2(CO)_8$.

11) It has already been reported that a hydride $HCo(dmg)_2P(n\text{-}C_4H_9)_3$ (dmg=dimethylglyoximato) reacts with MA to yield [1-(methoxycarbonyl)ethyl]cobaloxime derivatives,[a)] while the 2-(methoxycarbonyl)ethyl isomers are formed the protonation of the cobaloxime(I)–olefin π-complex.[b)] a) G. N. Schrauzer and R. J. Holland, *J. Am. Chem. Soc.*, **93**, 1505 (1971); b) G. N. Schrauzer, *Angew. Chem.*, **88**, 465 (1976); G. N. Schrauzer, J. H. Weber, and T. M. Beckham, *J. Am. Chem. Soc.*, **92**, 7078 (1970):



$$CH_2{=}CHX \longrightarrow \begin{bmatrix} CH_2{=}CHX \\ \uparrow \\ Co.H \end{bmatrix} \longrightarrow \underset{\alpha}{Co(III)\text{-}CHXCH_3}$$

$$\xrightarrow[Co(I)]{} \begin{bmatrix} CH_2{=}CHX \\ \uparrow \\ Co(I) \end{bmatrix} \xrightarrow{H^+} \underset{\beta}{Co(III)\text{-}CH_2CH_2X.}$$

X=COOMe

12) I. Ogata and T. Asakawa, *Kogyo Kagaku Zasshi*, **74**, 1640 (1971).

13) The isomerization of **c** to **b** ([4]) and the successive MA addition ([8]) would considerably occur as temperature rises; this may be responsible partially for the fact that higher temperatures favor the formation of two dimers UD and SD (Fig. 1).

14) There is an alternative route: acyl complex **d** reacts with alkyl complex **c** to yield the ketone and dimeric cobalt complex **f**.

15) MA addition to **c** to give [1,4-bis(methoxycarbonyl)-butyl]cobalt complex **h′** may not be ruled out:

$$\underset{\mathbf{c}}{\mathrm{CH_2XCH_2Co(CO)}_m\mathrm{(diphos)}_n} \xrightleftharpoons[\mathrm{CH_2{=}CHX}]{} \underset{\mathbf{h}'}{\mathrm{CH_2XCH_2CH_2CHXCo(CO)}_m\mathrm{(diphos)}_n}.$$

However, this step would occur to a lesser extent, because no traces of 1,4-bis(methoxycarbonyl)-1-butene or dimethyl adipate were detected.