Mechanism of the Pyridine-Modified Cobalt-Catalyzed Hydromethoxycarbonylation of 1,3-Butadiene

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*Summary: The pyridine-modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene (**1**) starts by the disproportionation of $Co_2(CO)_8$ to $[CoPy_6][Co(CO)_4]_2$ followed by the formation of $HCo(CO)_4$ (**3**). The addition of **3** to **1** leads to $CH_3CH{=}CHCH_2Co(CO)_4$ (**4**), which, depending on the conditions, can undergo facile CO insertion to yield $CH_3CH{=}CHCH_2COCo(CO)_4$ (**5**) or reversible decarbonylation to form η^3-$C_4H_7Co(CO)_3$ (**7**). Pyridine accelerates the conversion of **7** to methyl-3-pentenoate (**2**) and the methanolysis of **5**.*

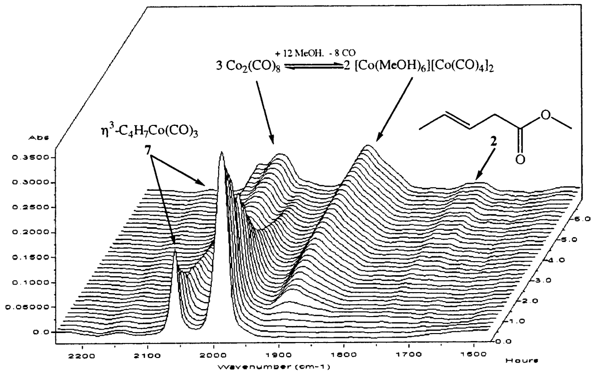

Figure 1. Reaction of 18.08 mmol of η^3-$C_4H_7Co(CO)_3$ (**7**) with CO (75 bar) and MeOH (55 mL) at 140 °C.

The hydromethoxycarbonylation of 1,3-butadiene (**1**) to methyl 3-pentenoate (**2**) could be the first step in the green production of adipic acid or ϵ-caprolactam, which are key intermediates in nylon manufacture.[1,2] $Co_2(CO)_8$ in the presence of pyridine (Py) represents one of the few known catalyst systems which is suitable for this reaction.[3] Although several different mechanisms have been proposed for this system,[4−7] no intermediates have been isolated and characterized under reaction conditions. One of the proposed mechanisms is based on the catalytic cycle of cobalt-catalyzed hydroesterification of olefins.[4c] Thus, the reaction starts by the addition of $HCo(CO)_4$ (**3**) to **1**, resulting in $CH_3CH{=}CHCH_2Co(CO)_4$ (**4**), which can undergo CO insertion to yield $CH_3CH{=}CHCH_2COCo(CO)_4$ (**5**). Imyanitov has suggested that the reaction of **5** with pyridine could lead to $[CH_3CH{=}CHCH_2COPy]^+[Co(CO)_4]^-$, which in turn could react with MeOH to give **2** and regenerate **3**.[4] In contrast, Milstein has suggested the formation of the coordinatively unsaturated species $\{MeOCOCo(CO)_3\}$ by the reaction of $[Co(CO)_4Py]^+[Co(CO)_4]^-$ and MeOH.[5] The addition of **1** to $\{MeOCOCo(CO)_3\}$ leads to the allyl complex $(\eta^3$-$CH_2CHCHCH_2COOMe)Co(CO)_3$ (**6**),[6] which reacts with **3** to give **2** and the coordinatively unsaturated $\{Co_2(CO)_7\}$. These species have not been observed under catalytic conditions, however. We report here our high-pressure IR and NMR study on the pyridine-modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene (**1**), which has led to the characterization of several key intermediates and the catalytic cycle.

First we have investigated the addition of **1** to the equilibrium mixture[7] of $Co_2(CO)_8$ and $[Co(MeOH)_6][Co(CO)_4]_2$ under 75 bar of CO at 100 °C in MeOH.[8] The quantitative formation of η^3-$C_4H_7Co(CO)_3$ (**7**)[9] was observed (the first spectrum in Figure 1.). Since no further reaction could be detected after several hours, the temperature was increased to 140 °C. During the next 6.5 h, **7** disappeared and the formation of **2**[8d] and the equilibrium mixture of $Co_2(CO)_8$ and $[Co(MeOH)_6][Co(CO)_4]_2^-$ was observed (Figure 1). Compound **6**, which could be readily isolated in THF is apparently absent in the reaction mixture.[5a,6] The formation of **7**, instead of **6**, was confirmed in a similar experiment by using high-pressure NMR.[10]

When the reaction was performed in pyridine, $[CoPy_6][Co(CO)_4]_2$ was the only cobalt species detectable by IR[8e] even at 100 °C under 75 bar of CO (the first spectrum

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[†] Eötvös University.

[‡] This paper is dedicated to the memory of Mr. Zoltán Pusztai, a cherished colleague whose untimely death prematurely ended a brilliant career.

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[1] Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpainter, C. W. *J. Mol. Catal. A* **1995**, *104*, 17−85.

[2] Dahlhoff, G.; Niederer, J. P. M.; Hoelderich, W. E. *Catal. Rev.* **2001**, *43(4)*, 381−441.

[3] Matsuda, A. *Bull. Chem. Soc. Jpn.* **1972**, *46*, 524−530.

[4] (a) Imyanitov, N. S.; Bogoradovskaya, N. M.; Semenova, T. A. *Kinet. Katal.* **1978**, *19*, 573. (b) Imyanitov, N. S. *Kinet. Katal.* **1999**, *40*, 71. (c) Forster, D.; Hersman, A.; Morris, D. E. *Catal. Rev. Sci. Eng.* **1981**, *23*, 89.

[5] (a) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6150−6152. (b) Milstein, D. *Acc. Chem. Res.* **1988**, *21*, 428−434.

[6] Since no spectroscopic data were reported for **6**,[5a] we have characterized it by both IR and NMR. IR (ν(CO), *n*-pentane, cm^{-1}): 2067 (vs), 1999 (vs), 1751 (w). ^{13}C NMR in d_4-MeOH (ppm): syn isomer, 36.8 (CH_2), 48.0 (CH_2), 51.2 (CH_3), 66.6 (CH), 83.3 (CH), 171.7 (C=O), 202.9 (C≡O); anti isomer, 36.8 (CH_2), 48.0 (CH_2), 51.0 (CH_3), 67.2 (CH), 82.2 (CH), 171.7 (C=O), 202.9 (C≡O).

[7] Mirbach, M. F.; Mirbach, M. J. *J. Mol. Catal.* **1985**, *32*, 59−75.

[8] Characteristic IR bands (ν(CO), MeOH, cm^{-1}): (a) $Co_2(CO)_8$, 2070 (s), 2041 (s), 2026 (s), 1858 (m); (b) $[Co(MeOH)_6][Co(CO)_4]_2$, 1903 (vs); (c) **7**, 2057 (s), 1988 (vs); (d) **2**, 1739 (vw); (e) $[CoPy_6][Co(CO)_4]_2$, 1889 (vs).

[9] (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097−1102. (b) Bertrand, J. A.; Jonassen, H. B.; Moore, D. W. *Inorg. Chem.* **1963**, *2*, 601−604.

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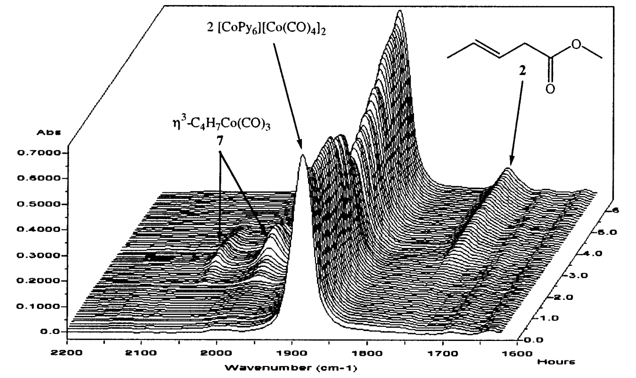


Figure 2. Reaction of 11.3 mmol of $Co_2(CO)_8$ with 28,2 mmol of 1,3-butadiene (**1**) and 39.5 mmol of MeOH in pyridine (55 mL) under 75 bar of CO at 140 °C.

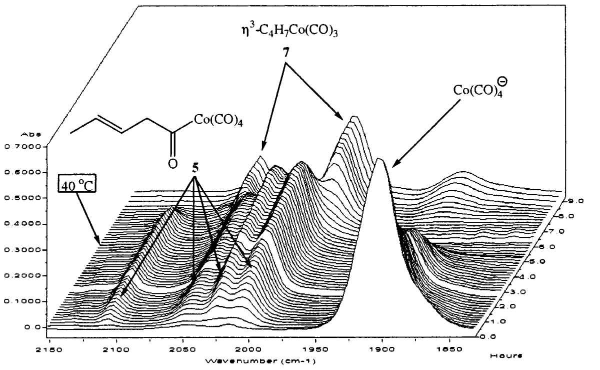


Figure 3. Reaction of 19.22 mmol of $NaCo(CO)_4$ with 19.43 mmol of crotyl bromide in MeOH (55 mL) under 70 bar of CO: formation of **5** at −40 °C and **7** above 40 °C.

in Figure 2). After the temperature was increased to 140 °C, the concentration of $[CoPy_6][Co(CO)_4]_2$ decreased and the formation of **7** and **2** was observed. Upon further stirring the formation of **2** continued and **7** was converted to $[CoPy_6][Co(CO)_4]_2$. It should be noted that the conversion of **7** to **2** is about 4 times faster in pyridine than in MeOH.

Since no intermediates could be observed under catalytic conditions, we have tried to prepare and characterize **4** and **5**. The reaction of $NaCo(CO)_4$ with crotyl bromide in MeOH at −40 °C under N_2 leads to the slow formation of **4**.[11a] This complex is very unstable and can be readily converted to **5**,[11b] by purging the reaction mixture with CO,[12] or to **7**, by raising the reaction temperature to room temperature. The reproduction of this experiment at −40 °C under 70 bar of CO resulted in the quantitative formation of **5** (Figure 3). While this complex is stable under 70 bar of CO even at 0 °C, at higher temperatures (>40 °C) it is readily converted to **7** and a small amount of $[Co(MeOH)_6][Co(CO)_4]_2$. The structure of **5** was unambiguously established also by in situ NMR experiments in d_4-MeOH.[13]

Since the accelerating effect of bases on the methanolysis of acyl cobalt carbonyls is well established,[14] we have investigated the role of pyridine on the methanolysis of **5**. The addition of pyridine to the solution of **5** under 82 bar of CO resulted in the rapid disappearance of **5** and the formation of **2** and $[CoPy_6][Co(CO)_4]_2$ (Figure 4), as expected. Thus, the formation of **2** can take place via the pyridine-assisted methanolysis of the acyl cobalt species $CH_3CH{=}CHCH_2COCo(CO)_4$ (**5**).

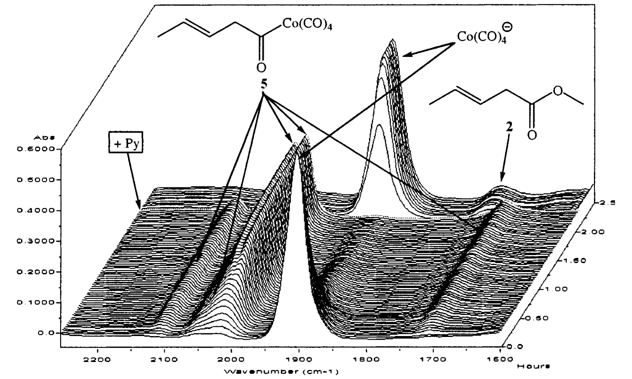
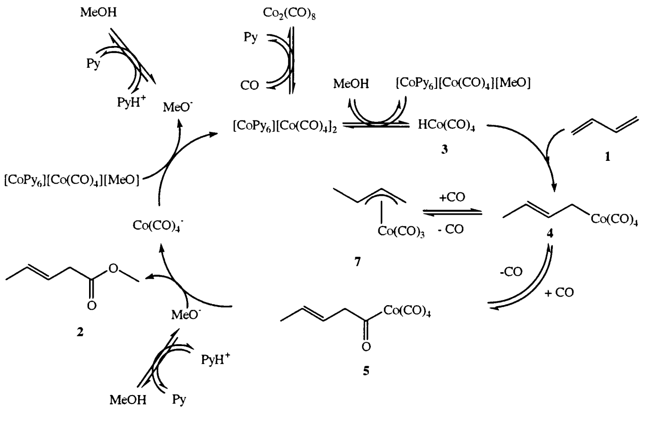


Figure 4. Reaction of 17.2 mmol of $NaCo(CO)_4$ with 18 mmol of crotyl bromide at 0 °C under 72 bar of CO in MeOH (55 mL) followed by the addition of 62 mmol of pyridine to the formed **5** at 0 °C under 82 bar of CO.

Scheme 1. Proposed Catalytic Cycle of the Hydromethoxycarbonylation of 1,3-Butadiene (1) by Pyridine-Modified Cobalt Catalysts



The proposed catalytic cycle is depicted in Scheme 1. The first step is the well-established disproportionation of $Co_2(CO)_8$, leading to $[CoPy_6][Co(CO)_4]_2$.[15] The formation of $HCo(CO)_4$ (**3**) can be explained by the reaction of MeOH with $[CoPy_6][Co(CO)_4]_2$. This is in accordance

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(10) All high-pressure NMR experiments were performed in 10 mm sapphire tubes, using a 250 MHz Bruker spectrometer. Preparation and detection of **7** was done under an N_2 atmosphere as follows: 0.16 g (2.96 mmol) of **1** was introduced into the high-pressure NMR tube at −80 °C. In the meantime 0.289 g (0.84 mmol) $Co_2(CO)_8$ was dissolved in 1.5 mL of d_4-MeOH in a Schlenk bottle at 0 °C and then added to **1** at −80 °C and pressurized with 50 bar of CO. Over the next 6 h the NMR tube was heated to 100 °C and the solution changed from brown to orange. NMR measurements of this solution were performed at room temperature. Besides the signals of **1**, compound **7** could be detected. ^{13}C NMR of **7** (ppm): 19.2 (CH_3), 45.8 (CH_2), 71.8 (CH), 84.0 (CH).

(11) Characteristic IR bands (ν(CO), MeOH, cm^{-1}): (a) **4**, 2099 (w), 2028 (m, sh), 2011 (s), 2005 (s, sh); (b) **5**, 2108 (w), 2047 (m), 2026 (s), 2007 (s), 1710 (w).

(12) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499−2502.

(13) Preparation of **5** was done under an N_2 atmosphere in a high-pressure NMR tube. A 1.5 mL solution of $NaCo(CO)_4$ (1.61 mmol) in d_4-MeOH was introduced into the NMR tube at 0 °C, which was then cooled to −80 °C. At this temperature 0.165 mL (1.62 mmol) of crotyl bromide was added dropwise, and then the tube was pressurized with 30 bar of CO. The reaction was conducted for 2 h at 0 °C, and the NMR measurements were performed at the same temperature. ^{13}C NMR (ppm): 17.2 (CH_3), 66.4 (CH_2), 123.6 (CH), 130.1 (CH), 196.8 ($C{=}O$), 227.0 ($C{=}O$).

(14) (a) Sóvágó, J.; Sisak, A.; Ungváry, F.; Markó, L. *Inorg. Chim. Acta* **1994**, *227*, 297−300. (b) Kovács, I.; Ungváry, F. *Coord. Chem. Rev.* **1997**, *161*, 1−32.

(15) Mirbach, M. F.; Mirbach, M. J. *J. Mol. Catal.* **1985**, *33*, 23−35.

with the fact that no accelerating effect was observed by the addition of H_2 on the hydromethoxycarbonylation of 1,3-butadiene (**1**).[3] The reaction of $HCo(CO)_4$ (**3**) with **1**[16] leads to the formation of the alkyl cobalt species $CH_3CH{=}CHCH_2Co(CO)_4$ (**4**). Depending on the conditions, this species can undergo CO insertion to yield $CH_3CH{=}CHCH_2COCo(CO)_4$ (**5**) or decarbonylation to form η^3-$C_4H_7Co(CO)_3$ (**7**). Similar steps have been demonstrated for the reaction of **3** and 2,3-dimethyl-1,3-butadiene.[17] It appears that the formation of η^3-$C_4H_7Co(CO)_3$ (**7**) is a reversible side reaction during the hydromethoxycarbonylation of 1,3-butadiene (**1**).

Our results indicate that the presence of pyridine leads to the formation of $[CoPy_6][Co(CO)_4]_2$ and $[HPy][Co(CO)_4]$, both of them being highly stable under reaction conditions (see Figure 2). The net result is a significantly lower concentration of the catalytically active cobalt species. On the other hand, pyridine accelerates the conversion of $C_4H_7Co(CO)_3$ (**7**) to **2** and the methanolysis of $CH_3CH{=}CHCH_2COCo(CO)_4$ (**5**) by providing a much higher concentration of [HPy][MeO].

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[16] (a) Jonassen, H. B.; Stearns, R. I.; Kenttämaa, J.; Moore, D. W.; Whittaker, A. G. *J. Am. Chem. Soc.* **1958**, *80*, 2586. (b) Rupilius, W.; Orchin, M. *J. Org. Chem.* **1971**, *36*, 3604.

[17] Ungváry, F.; Markó, L. *Organometallics* **1984**, *3*, 1466−1470.