Organometallics **1994,** *13,* 1927-1933 1927

Kinetics and Mechanism of the β-Hydride Elimination Reaction of (1,2-Bis(methoxycarbonyl)ethyl)cobalt Tetracarbonyl[1]

István Kovács,[†] Ferenc Ungváry,[*,‡] and László Markó[†]

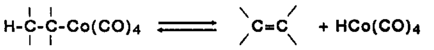
Research Group for Petrochemistry of the Hungarian Academy of Sciences and Institute of Organic Chemistry, University of Veszprém, P.O. Box 158, H-8201 Veszprém, Hungary

Received October 5, 1993[⊛]

The title complex, $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$ (1), was found to decompose in alkanes or chlorinated hydrocarbons as solvents quantitatively to $Co_2(CO)_8$ and a 1:1 mixture of dimethyl fumarate and dimethyl succinate at room temperature under 1 atm of CO. $HCo(CO)_4$ was trapped in this process either by 1-heptene or Proton Sponge in the form of *n*-octanoylcobalt tetracarbonyl or a $[BH]^+[Co(CO)_4]^-$ salt, respectively. As model reactions confirmed, the decomposition of 1 consists of two distinct steps such as (1) β-hydride elimination and (2) subsequent fast consumption of $HCo(CO)_4$ in its reaction with 1. Comparative ^1H NMR experiments on deuterium labeled $MeO_2CCHDCH(CO_2Me)Co(CO)_4$ (2) proved that the β-elimination reaction is stereospecific and *syn*. Consistent with kinetic studies, a modified mechanism of β-elimination is suggested, which includes a pre-equilibrium CO dissociation from 1, a fast intramolecular transformation of the resulting intermediate into a tricarbonylhydridoolefincobalt species, which may transfer a hydrogen atom to $Co(CO)_4$ radicals (formed by the homolytic dissociation of $Co_2(CO)_8$) in a rate-determining step to yield $HCo(CO)_4$. Together with earlier mechanistic studies on the formation of 1, we showed for alkylcobalt carbonyls for the first time the reversibility of the β-elimination reaction on a molecular level. $\Delta H^{\ddagger} = 25.1$ ($\pm$0.9) kcal mol^{-1} and $\Delta S^{\ddagger} = 5.3$ ($\pm$0.3) eu were obtained as overall activation parameters. The mechanism of CO dissociation was investigated by kinetic measurements of the ^{13}CO exchange reaction of 1. These studies provided the activation parametes $\Delta H^{\ddagger} = 7.7$ ($\pm$0.6) kcal mol^{-1} and $\Delta S^{\ddagger} = -44.2$ ($\pm$0.1) eu, which could be best explained by an intramolecular associative pathway. Accordingly, the gain in energy and the considerably more structured transition state resulting from the weak coordination of a carboxylic oxygen to cobalt to form a five-membered metallacycle may account for the particularly low values of activation enthalpy and entropy, respectively.

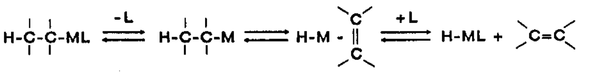
Introduction

The β-hydride elimination reaction is regarded as one of the main thermal reaction pathways (besides CO insertion into, and homolytic dissociation of the carbon–metal bond) of alkylcobalt carbonyl complexes having a hydrogen atom in the β-position to cobalt.[2,3] As shown in eq 1, it is the reverse of the well-known addition of $HCo(CO)_4$ to olefins.[4,5] This equilibrium is believed to play a key role in the olefin isomerization process occurring in the hydroformylation and related cobalt-catalyzed reactions. Unfortunately, the extreme instability of such complexes frustrated until recently the isolation of a model compound in pure form, and thus precluded mechanistic studies of the β-elimination on the catalytically important cobalt alkyls.



$$\text{H-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-Co(CO)}_4 \rightleftharpoons \;\rangle C{=}C\langle\; + \text{HCo(CO)}_4 \qquad (1)$$

Certainly, a mechanism of β-elimination had been established for stable alkylmetal carbonyl complexes.[6] This widely accepted scheme, outlined in eq 2, which involves a coordinatively unsaturated key intermediate, was generally applied for the decomposition of alkylcobalt carbonyls, as well.



$$\text{H-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-ML} \underset{}{\overset{-L}{\rightleftharpoons}} \text{H-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-M} \rightleftharpoons \text{H-M}\cdot\overset{C}{\underset{C}{\|}} \overset{+L}{\rightleftharpoons} \text{H-ML} + \;\rangle C{=}C\langle \qquad (2)$$

On the basis of some recently reported kinetic results, however, we find that the mechanism of β-elimination of seemingly similar alkylmetal carbonyls cannot be generalized. Halpern et al. showed that β-hydride elimination also can take place *via* a geminate radical pair formed by homolysis of the carbon–metal bond, like in the case of $PhCH(CH_3)M(CO)_nCp$ type (M = Fe, Ru, $n = 2$; M = Mo, W, $n = 3$) complexes. In this case, β-hydride elimination

---

[†] Hungarian Academy of Sciences.

[‡] Institute of Organic Chemistry.

[⊛] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) Kovács, I.; Ungváry, F. Presented at the XXVIIIth International Conference on Coordination Chemistry (ICCC), Gera, Germany, Aug 13–18, 1990 (Proceedings 1, pp 3–35) and at the 12th Summer School on Coordination Chemistry, Karpacz, Poland, June 6–12, 1993 (Abstracts p 83).

(2) Kemmitt, R. D. W.; Russel, D. R. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 5, pp 47–67.

(3) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* **1984,** *59,* 203.

(4) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961,** *83,* 4023.

(5) (a) Csizmadia, J.; Ungváry, F.; Markó, L. *Trans. Met. Chem.* **1976,** *1,* 170. (b) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1981,** *219,* 397. (c) Ungváry, F. *Acta Chim. Acad. Sci. Hung.* **1982,** *111,* 117. (d) Ungváry, F.; Markó, L.; Bockman, T. M.; Garst, J. F.; King, R. B. *Isr. J. Chem.* **1986,** *27,* 262. (e) Ungváry, F.; Markó, L. *Organometallics* **1986,** *5,* 2341. (f) Ungváry, F.; Sisak, A.; Markó, L. In *Homogeneous Transition Metal Catalyzed Reactions;* Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry Series 230; American Chemical Society: Washington, DC, 1992; p 297. (g) Roth, J. A.; Grega, K.; Orchin, M. *J. Organomet. Chem.* **1988,** *342,* 129.

(6) Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976,** *98,* 2789.

0276-7333/94/2313-1927$04.50/0

is accompanied by radical escape as a competitive pathway, which leads to the formation of saturated products.[7]

Recently, we reported the preparation and characterization of tractable new alkylcobalt carbonyls containing β-hydrogens, $\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4}$[5f,8] and $\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3}$.[8] These complexes are likely intermediates of the cobalt-catalyzed isomerization,[5e,9] hydrogenation,[5e,9] and/or hydroformylation[10] of fumarates and maleates. Since $\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4}$ was found to decompose in solution under ambient conditions *via* β-elimination, it can serve as an excellent model for kinetic and mechanistic studies. In addition, the kinetics and mechanism of its formation from $\mathrm{HCo(CO)_4}$ and dimethyl fumarate have been investigated;[5a,f] thus a direct comparison of the mechanisms of its formation and decomposition is possible for the first time. Since the previous studies revealed a radical-promoted addition mechanism, this suggests a similar—consequently new—mechanism of β-elimination of alkylcobalt tetracarbonyls on the basis of microscopic reversibility. Now we give an account of our mechanistic investigations of the β-hydride elimination reaction of $\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4}$.

Results

Stability and Decomposition of Complexes 1 and 2. Under 1 atm of CO and at a low temperature, $\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4}$ (**1**) and $\mathrm{MeO_2CCHDCH(CO_2Me)Co(CO)_4}$ (**2**), prepared by the addition of $\mathrm{HCo(CO)_4}$ and $\mathrm{DCo(CO)_4}$, respectively, to dimethyl fumarate, show considerable stability in crystalline form. For instance, both complexes were stored at −79 °C for several months without detectable degradation. In cold solutions and in the presence of CO, **1** and **2** form an equilibrium mixture with the corresponding acyl derivatives.[11] At room temperature, this equilibrium is shifted completely to the side of the alkyl complexes, but they begin to decompose irreversibly, as indicated by a color change from light yellow to dark brown. IR, NMR, and GC experiments on the decomposition of **1** proved the quantitative formation of $\mathrm{Co_2(CO)_8}$ and a 1:1 mixture of dimethyl fumarate and dimethyl succinate (eq 3). Practically no dimethyl formylsuccinate could be detected. Starting from **2**, a similar reaction took place, resulting in the formation of a 1:1 mixture of *d,l*-$\mathrm{MeO_2CCHDCHDCO_2Me}$ and dimethyl fumarate. The normal 3:1 ratio of the methyl and methine protons of dimethyl fumarate in the ^{1}H NMR spectra indicated the absence of deuterium on carbon-2.

$$2\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4} \xrightarrow{r_3} \mathrm{Co_2(CO)_8} + trans\text{-}\mathrm{MeO_2CCH{=}CHCO_2Me} + \mathrm{MeO_2CCH_2CH_2CO_2Me} \quad (3)$$

The product distribution of reaction 3 could be obtained according to two different decomposition pathways.

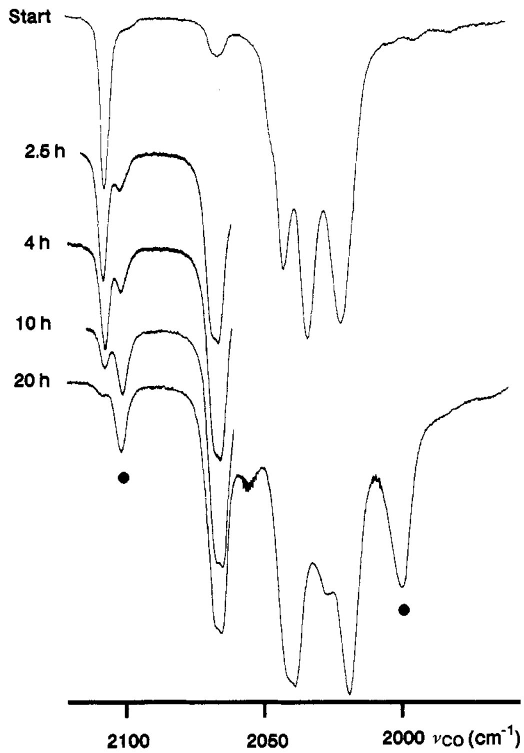


Figure 1. Formation of *n*-octanoylcobalt tetracarbonyl (●) during the decomposition of **1** in the presence of 1-heptene (*n*-octane, 25 °C, $[1]_0 = 0.01$ M, $[\text{1-heptene}]_0 = 0.39$ M, [CO] = 0.011 M).

Obviously, one is a β-elimination reaction (eq 4) where

$$\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4} \overset{r_4}{\rightleftharpoons} \mathrm{HCo(CO)_4} + trans\text{-}\mathrm{MeO_2CCH{=}CHCO_2Me} \quad (4)$$

$$\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4} + \mathrm{HCo(CO)_4} \xrightarrow{r_5} \mathrm{Co_2(CO)_8} + \mathrm{MeO_2CCH_2CH_2CO_2Me} \quad (5)$$

$\mathrm{HCo(CO)_4}$ could be consumed in a consecutive reaction with **1** (eq 5). In fact, there is precedent for cleavage of the carbon–cobalt bond of alkylcobalt tetracarbonyls by $\mathrm{HCo(CO)_4}$, leading to $\mathrm{Co_2(CO)_8}$ and RH.[12] The other possibility would be a radical disproportionation reaction *via* homolytic dissociation of the carbon–cobalt bond of **1** (eq 6). The key difference between these pathways is the formation of $\mathrm{HCo(CO)_4}$ in eq 4.

$$2\mathrm{MeO_2CCH_2CH(CO_2Me)Co(CO)_4} \rightarrow 2{}^\bullet\mathrm{Co(CO)_4} + 2\mathrm{MeO_2CCH_2CH^\bullet CO_2Me} \rightarrow \mathrm{Co_2(CO)_8} + trans\text{-}\mathrm{MeO_2CCH{=}CHCO_2Me} + \mathrm{MeO_2CCH_2CH_2CO_2Me} \quad (6)$$

Since $\mathrm{HCo(CO)_4}$ is well-known to produce acylcobalt tetracarbonyls with various olefins under CO, **1** was allowed to decompose in the presence of a ca. 40-fold excess of 1-heptene to trap the hydride if formed. Figure 1 illustrates that following the reaction by IR spectroscopy in the terminal carbonyl frequency range the four bands of **1** at 2111, 2046, 2036, and 2026 cm^{-1} were gradually

---

[7] Mancuso, C.; Halpern, J. *J. Organomet. Chem.* **1992**, *428*, C8.

[8] Ungváry, F.; Kovács, I.; Hammerschmitt, B.; Cordier, G. *Organometallics* **1993**, *12*, 2849.

[9] Taylor, P.; Orchin, M. *J. Organomet. Chem.* **1971**, *26*, 389.

[10] (a) Stolle, M.; Bolle, P. *Helv. Chim. Acta* **1938**, *21*, 1551. (b) Hagemeyer, H. J.; Hull, D. C., Jr. U.S. Pat. 2 610 203; *Chem. Abstr.* **1953**, *47*, 5960. (c) Falbe, J.; Huppes, N.; Korte, F. *Chem. Ber.* **1964**, *97*, 863.

[11] Ca. 10% of **1** was present as $\mathrm{MeO_2CCH_2CH(CO_2Me)C({=}O)Co(CO)_4}$ at −20 °C under 1 atm of CO in $\mathrm{CDCl_3}$ solution, as shown by ^{1}H NMR spectroscopy. Kovács, I.; Szalontai, G.; Ungváry, F. Manuscript in preparation.

[12] (a) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183. (b) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* **1985**, *107*, 666. (c) Kovács, I.; Hoff, C. D.; Ungváry, F.; Markó, L. *Organometallics* **1985**, *4*, 1347.

Table 1. Kinetic Data for the Decomposition of $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$ (1) in *n*-Octane Solution

T^a (°C)	10^2[**1**] (M)	$10^3[Co_2(CO)_8]$ (M)	$10^2[CO]^b$ (M)	$10^7 r_4{}^c$ (M s^{-1})
16	0.58	1.02	1.10	0.53
16	0.79	1.02	0.44	1.89
16	0.81	1.02	0.27	3.04
20	1.00	1.02	1.10	1.67
25	0.76	2.30	3.85	0.80
25	0.84	3.36	2.56	1.75
25	0.65	2.30	1.70	1.65
25	0.69	2.30	1.10	2.61 (5.23)
25	0.97	2.30	1.10	(6.16)^d
25	0.65	2.30	1.01	2.80
25	1.00	3.13	1.10	4.48
25	1.44	6.67	1.13	8.87
25	1.07	19.9	1.10	12.6
25	1.21	37.6	1.10	19.4
25	1.24	71.3	1.10	26.0
30	0.87	1.44	1.17	6.71
35	0.82	1.44	1.20	13.5
40	1.06	2.12	1.22	35.0 (70.0)
40	1.11	2.12	1.22	(445)^e
50	1.33	2.70	1.24	215

^{a} Accurate within ±0.05 °C. ^{b} Calculated from p_{CO} and the solubility of CO in *n*-octane. ^{c} Calculated rate of the β-elimination reaction in eq 4 (measured initial rates for the decomposition of **1**, r_3 in eq 3, appear in parentheses). ^{d} In the presence of 1-heptane (0.39 M). ^{e} In the presence of 1,8-bis(dimethylamino)naphthalene (0.025 M).

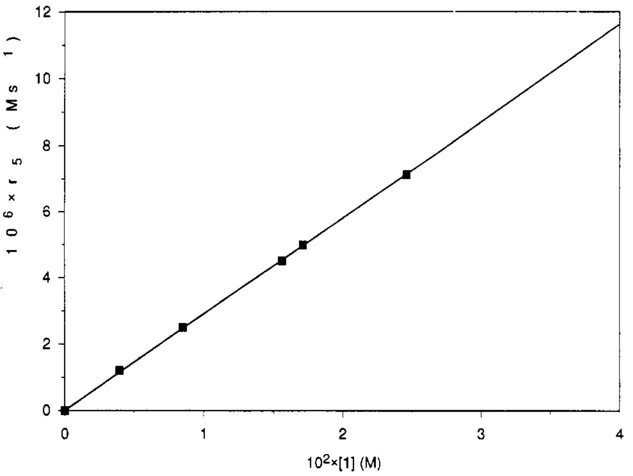


Figure 2. Initial rates of reaction 5 as a function of the concentration of 1 (*n*-octane, 20 °C, [CO] = 0.011 M, $[HCo(CO)_4]_o$ = 0.012 M).

replaced by a complex system including absorbances characteristic both for *n*-octanoylcobalt tetracarbonyl[13] and for $Co_2(CO)_8$.[14] By the time 1 has completely disappeared (ca. 20 h), two of the four bands of *n*-octanoylcobalt tetracarbonyl, well separated from those of $Co_2(CO)_8$, clearly evolved at 2103 and 2003 cm^{-1}, providing indirect evidence for the intermediacy of $HCo(CO)_4$ in reaction 3.[15] The rate of decomposition was only slightly influenced by the added olefin (Table 1).

The intermediate $HCo(CO)_4$ was also identified as a $[BH]^+[Co(CO)_4]^-$ salt.[16] When 1 decomposed in octane in the presence of a stoichiometric amount of the strong base 1,8-bis(dimethylamino)naphthalene (Proton Sponge), a yellow precipitate was formed according to the stoichiometry of eq 7. In this case, however, the rate of decomposition was found to be about 1 order of magnitude faster than that measured in the absence of base (Table 1). This experiment was repeated with 2, and pure crystalline dimethyl fumarate (containing no deuterium) and $[BD]^+[Co(CO)_4]^-$ as a yellow powder[17] were isolated quantitatively.

$$MeO_2CCH_2CH(CO_2Me)Co(CO)_4 + B \rightarrow [BH]^+[Co(CO)_4]^- + trans\text{-}MeO_2CCH{=}CHCO_2Me \qquad (7)$$

The reaction of $HCo(CO)_4$ with 1 was modeled subsequently and was found to take place as expressed in eq 5. According to the measured rates shown in Figure 2 the reaction rate (r_5) at a 0.01 M initial concentration of 1 is already comparable to that of β-elimination (r_4) if the concentration of $HCo(CO)_4$ is as low as 6 × 10^{-4} M.[18] Since the IR bands of 1, $Co_2(CO)_8$, and $HCo(CO)_4$ overlap to a significant extent, $HCo(CO)_4$ present in concentrations below 10^{-3} M cannot be detected in such reaction mixtures. This supports the assumption that $HCo(CO)_4$ formed in the β-elimination step is consumed by 1 fast enough not to accumulate in spectroscopically detectable concentrations.

The substitution of one CO ligand in 1 by PPh_3 resulted in a dramatic stabilization against β-elimination. $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ underwent no change in 1,2-dichloroethane solution at least up to 70 °C even in an argon atmosphere. An excess of Proton Sponge did not influence its stability at all. Its decomposition was not further studied.

Kinetics of the β-Elimination Reaction of 1. The rate of the thermal decomposition of 1 (r_3 of reaction 3) was determined by IR spectroscopy following the decrease of the concentration of 1 in *n*-octane at different concentrations of 1, CO, and $Co_2(CO)_8$ and in the temperature range 16–50 °C. The rate of the β-hydride elimination step (r_4 of reaction 4) was calculated as half of the measured rate of reaction 3, based on the well-established stoichiometries and relative rates of its individual reactions 4 and 5.

As shown in Figure 3, a correct pseudo-first-order rate plot was obtained for at least 2 half-lives of 1. Furthermore, the data in Table 1 illustrate half-order and inverse first-order dependences on the initial concentrations of $Co_2(CO)_8$ and CO, respectively. This kinetic behavior can be expressed by the rate law given in eq 8. The temperature

$$r_4 = k_{obs}[1][Co_2(CO)_8]^{0.5}[CO]^{-1} \qquad (8)$$

---

(13) IR for $n\text{-}C_7H_{15}C({=}O)Co(CO)_4$ (hexane): ν_{CO} 2103 (w), 2044 (m s), 2022 (vs), 2003 (vs) cm^{-1}. Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* **1963**, *44*, 184.

(14) IR for $Co_2(CO)_8$ (hexane): ν_{CO} 2112 (vw), 2107 (vw), 2071 (s), 2069 (vs), 2059 (m), 2044 (vs), 2042 (vs), 2031 (m s), 2023 (vs) cm^{-1}. (a) Noack, K. *Spectrochim. Acta* **1963**, *19*, 1925. (b) Bor, G. *Spectrochim. Acta* **1963**, *19*, 2065.

(15) Although the radical mechanism proposed by Halpern[7] also affords a hydride intermediate as a byproduct, the lifetime of $HCo(CO)_4$ in the presence of radicals is expected to be too short to be trapped by an olefin. Thus, from our point of view, Halpern's mechanism also can be expressed by eq 6.

(16) Data for $[BH]^+[Co(CO)_4]^-$ (B = 1,8-bis(dimethylamino)naphthalene) are as follows: IR (CH_2Cl_2) ν_{CO} 1888 (vs, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 19.1 (s, 1H, *H*$^+$), 7.98–7.24 (m, 6H, aromatic protons), 3.2 (s, 12H, CH_3) ppm; ^{59}Co NMR ($CDCl_3$) δ −3288 (line width = 200 Hz) ppm. The complex is identical to an authentic sample prepared from "proton sponge" and $HCo(CO)_4$.

(17) Data for $[BD]^+[Co(CO)_4]^-$ are as follows: ^{2}H NMR (CH_2Cl_2) δ 18.6 (s) ppm. All the other spectral data are identical to those of the perprotio derivative.[16]

(18) This calculation is based on the mechanism of the cleavage of $EtO_2CCH_2Co(CO)_4$ by $HCo(CO)_4$.[12b,c]

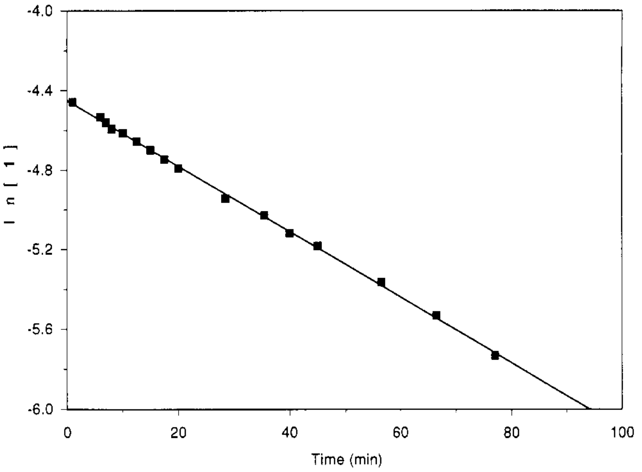


Figure 3. Pseudo-first-order rate plot for the thermal decomposition of 1 (n-octane, 25 °C, $[1]_o = 0.012$ M, $[Co_2(CO)_8]_o = 0.055$ M, [CO] = 0.011 M).

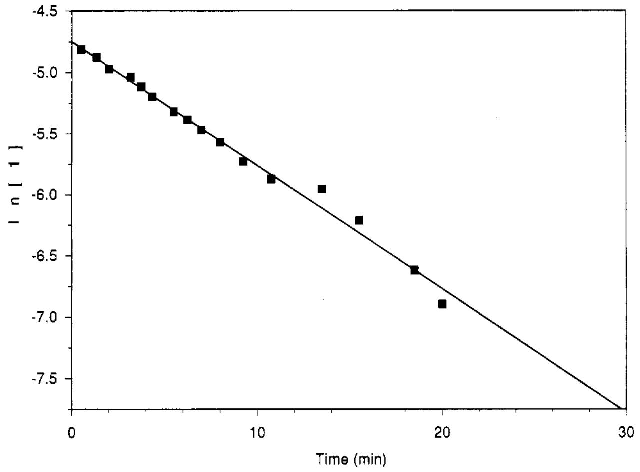


Figure 4. Rate plot for the ^{13}CO exchange reaction of 1 through 3 half-life times (n-octane, 11 °C, $[1]_o = 0.009$ M, $[^{13}CO] = 0.011$ M).

dependence of k_{obs} allowed us to determine the activation parameters of reaction 4 as $E_a = 26.3$ (±0.9) kcal mol^{-1}, $\Delta H^{\ddagger} = 25.1$ (±0.9) kcal mol^{-1}, and $\Delta S^{\ddagger} = 5.3$ (±0.3) eu.

Kinetics of the ^{13}CO Exchange Reaction of 1. The exchange of CO ligands with ^{13}CO in 1 takes place readily under 1 atm of ^{13}CO pressure and in solution. The kinetics of this process could be studied in the −9.5 to +15 °C temperature range by IR spectroscopy. After one molecule of ^{13}CO was incorporated (eq 9), a step-by-step exchange

$$MeO_2CCH_2CH(CO_2Me)Co(CO)_4 + {}^{13}CO \xrightarrow{r_9} MeO_2CCH_2CH(CO_2Me)Co(CO)_3({}^{13}CO) + CO \quad (9)$$

of the other three CO ligands occurred. Figure 4 shows first-order kinetics, as expected. The calculated half-life times and first-order rate constants, as functions of the temperature, are compiled in Table 2. The activation parameters for this reaction are as follows: $E_a = 8.2$ (±0.6) kcal mol^{-1}, $\Delta H^{\ddagger} = 7.7$ (±0.6) kcal mol^{-1}, and $\Delta S^{\ddagger} = -44.2$ (±0.1) eu. The ^{13}CO exchange of $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ was found to occur about 2 orders of magnitude slower than that of 1 (Table 2).

Discussion

Stereochemistry of the β-Elimination Reaction of 1. Some earlier reports dealing with the hydrogenation of diethyl fumarate[5a] and the isomerization of dimethyl maleate to dimethyl fumarate[9] by $HCo(CO)_4$ suggested that both the addition and elimination of the hydride to these olefins and from a hypothetic alkyl complex, respectively, must be stereospecific, namely *cis*. Deuterium labeling experiments supported this conclusion. On the basis of the structures of the complexes studied here, we can confirm these suggestions.

Table 2. First-Order Rate Constants for the ^{13}CO Exchange Reaction of $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$ (1) at Different Temperatures in n-Octane Solution[a]

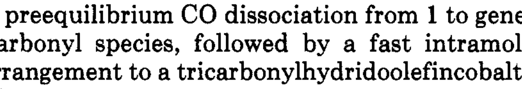
T^b (°C)	$\tau_{1/2}$ (min)	10^4k (s^{-1})
−9.5	19.4	5.95
1	12.0	9.60
6	8.90	13.0
11	6.75	17.1
15	5.00	23.1
25	3.29	35.1[c]
40	1.71	67.4[c]
40	340	0.340[d]

[a] $[^{13}CO] = 0.011$ M, $[1]_o$ was varied between 0.005 and 0.01 M. [b] Accurate within ±0.05 °C. [c] Extrapolated value. [d] Exchange rate constant for $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ in 1,2-dichloroethane.

According to ^1H NMR investigations, complex 1 shows three resonance-band systems (doublets of doublets), attributable to the protons of the substituted ethyl fragment $-CH_2CH-Co$, at 3.33 (CH), 3.11, and 2.56 (CH_2) ppm.[8] These resonances form an ABX spin system with coupling constants $J_{ax} = 12.45$ Hz, $J_{bx} = 3$ Hz, and $J_{ab} = 17.2$ Hz, where H^a and H^b label the methylene protons, and H^x is the methine proton. According to the coupling constants, H^a and H^b must be in *anti* and *gauche* positions to H^x, respectively, representing probably the staggered conformation lower in energy. This is also supported by the X-ray structure of $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$, the ^1H NMR data of which are essentially the same as those of 1.[8]

As expected, there are only two resonances in the same region of the ^1H NMR spectrum of 2. The doublets at 3.33 ($J = 12.1$ Hz) and 3.09 ($J = 12.1$ Hz) ppm can be assigned to H^x and H^a, respectively.

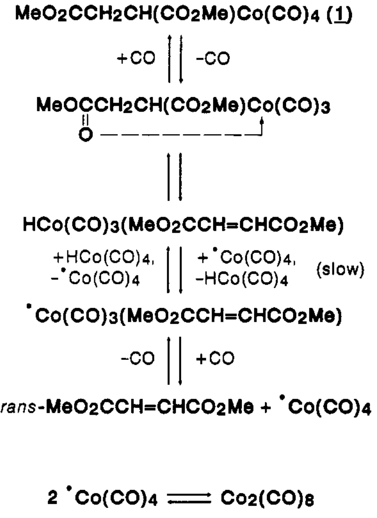
Comparison of these data for 1 and 2 reveals that the deuterium atom occupies the *gauche* position to H^x; that is, H^b in the same position in 1 must derive from $HCo(CO)_4$ used for the preparation of 1. Such a conformation, however, could be obtained only if the addition of $H(D)Co(CO)_4$ to dimethyl fumarate was *cis* (eq 10). Since dimethyl fumarate formed by the decomposition of 2 did not contain deuterium, it can be concluded unambiguously that the β-elimination of $HCo(CO)_4$ from 1 must be *syn.*



(10)

Mechanistic Considerations. The kinetic behavior of reaction 4 is in accordance with the reaction sequence outlined in Scheme 1. The proposed mechanism consists of a preequilibrium CO dissociation from 1 to generate a tricarbonyl species, followed by a fast intramolecular rearrangement to a tricarbonylhydridoolefincobalt intermediate, which then undergoes a rate-limiting hydrogen atom abstraction by $Co(CO)_4$ radicals. The origin of the $Co(CO)_4$ radicals is the equilibrium homolytic dissociation of $Co_2(CO)_8$ always present in solutions of 1. The reverse of this pathway has been suggested for the formation of

Scheme 1



1 from $HCo(CO)_4$ and dimethyl fumarate,[5f] as well as for similar reactions of some other olefins.[5b–e,g] Consequently, all of the reaction steps, including the slow hydrogen atom transfer and subsequent liberation of the olefin, must be reversible. In comparison with the "classic" mechanism of β-elimination established for alkyl–$Fe(CO)(PPh_3)Cp$ complexes,[6] we thus suggest three crucially different elements in this scheme: (1) the formation of a chelate complex using a carbonyl oxygen of the ester groups in promoting the loss of a CO ligand (this step will be discussed in detail later), (2) the catalytic role of $Co(CO)_4$ radicals, and (3) the complete reversibility of the process.

When 1 was prepared, the equilibrium was shifted to the side of 1 by using a large excess of dimethyl fumarate and by keeping the temperature somewhat low (≈10 °C). A similar shift in the reverse direction would not be effective for accumulating $HCo(CO)_4$ during the β-elimination reaction, since the same coordinatively unsaturated alkyl complex is requested for both its formation and consumption and the oxidative addition of $HCo(CO)_4$ to this intermediate[12b,c] and the subsequent reductive elimination of the products of reaction 5 take place faster than the transfer of the hydrogen atom. In the meantime, however, the oxidative addition of $HCo(CO)_4$ is the "driving force" for reaction 4 to become unidirectional, and thus its rate is conveniently measurable by the initial rate method.

Another CO-deficient intermediate also could form by insertion of a CO ligand into the carbon–cobalt bond of 1 either before or instead of CO dissociation. Its reaction with $HCo(CO)_4$ would lead to dimethyl formylsuccinate, but this compound was not detected among the reaction products. However, the reverse reaction of $HCo(CO)_4$ with dimethyl fumarate did afford some of the formylated product.[5f] The only significant difference between the two systems is that a large excess of dimethyl fumarate over 1 and $HCo(CO)_4$ was applied in the latter one. It is assumed that under such conditions the olefin might act as a weakly coordinating ligand to assist CO insertion into 1 and the coordinatively unsaturated acylcobalt species generated by subsequent liberation of dimethyl fumarate could be reduced by $HCo(CO)_4$. The catalytic effect of olefins on transformations of alkyl- and acylcobalt complexes, such as the equilibrium isomerization of *n*-butyryl- and isobutyrylcobalt tetracarbonyls, has been discovered recently[19] and will be explored in the case of the above reaction, as well.

Table 3. Activation Parameters of CO Exchange Reactions of $RCo(CO)_4$ Complexes

R	ligand	ΔH^{*} (kcal mol^{-1})	ΔS^{*} (eu)	lit
$MeO_2CCH_2CH(CO_2Me)$–	^{13}CO	7.7 ± 0.6	–44.2 ± 0.1	this work
EtO_2CCH_2–	^{13}CO	22.4 ± 1.2	4.7 ± 4.0	12b
MeC(=O)–	^{13}CO	22.0 ± 0.2	8.0 ± 0.5	24
$(CO)_4CoHg$–	^{14}CO	13 ± 1	–24 ± 2	23a
	$C^{18}O$	12.1 ± 2	–25 ± 6	23b
$(CO)_4CoCd$–	^{14}CO	11	–28	23a

There is one more possible reasoning, which should be taken into consideration for explaining the absence of $HCo(CO)_4$ in the reaction mixture. Once the $HCo(CO)_4 + {}^{\bullet}Co(CO)_4$ system is present in the process, it could lead to the decomposition of the hydride to $Co_2(CO)_8$ and dihydrogen.[20] To maintain the 1:1 fumarate:succinate ratio, however, H_2 should have to reduce 1 to $HCo(CO)_4$ and dimethyl succinate. This pathway seems to be unlikely because of two reasons: (1) the decomposition of $HCo(CO)_4$ would mean the incorporation of an extra and relatively slow reaction (slower than that with 1) into the secondary process, which must be at least as fast as reaction 4, and (2) the reactivity of H_2 toward 1 is expected to be slow compared to that of $HCo(CO)_4$ under ambient conditions.[21]

The considerable accelerating effect of Proton Sponge on the rate of β-elimination also merits comment. It cannot be explained simply by the reaction of $HCo(CO)_4$ with the added base, since the formation of the hydride seems to be rate-limiting. It is more reasonable to assume a reaction of the base with a species preceding the hydrogen atom transfer. One possibility could be a nucleophilic attack on the β-carbon atom of 1. This attack, however, is not expected to be stereospecific or deuterium atom specific. In addition, $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$ is inert toward Proton Sponge even at elevated temperatures, although its electronic characteristics are quite similar to those of 1 on the basis of their ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts. Rather we prefer a reaction of Proton Sponge with the tricarbonylhydridoolefincobalt intermediate, similar to that with $HCo(CO)_4$, followed by a fast CO-for-olefin exchange typical for $M^+[Co(CO)_4]^-$ salts showing no ion-pairing phenomenon.[22]

Finally, the ^{13}CO exchange reaction of 1 (eq 9) was studied in detail in order to gain more insight into the mechanism of its CO dissociation as the starting reaction of Scheme 1. In comparison with reported data for the CO exchange reactions of cobalt tetracarbonyl complexes (Table 3), the activation enthalpy is unusually small (7.7 ± 0.6 kcal mol^{-1}) and the entropy is a very large negative value (–44.2 ± 0.1 eu). The differences are even more pronounced if one considers the more closely related C–$Co(CO)_4$ bonded compounds, though only a single alkyl complex was studied so far. However, the activation parameters of cadmium– and mercury–cobalt tetracarbonyls are more similar to our data. For those peculiar reactions which have a ΔH^{*} smaller than expected for the Co–CO bond energy as well as a ΔS^{*} characteristic for an associatively activated process, but still obey the first-

---

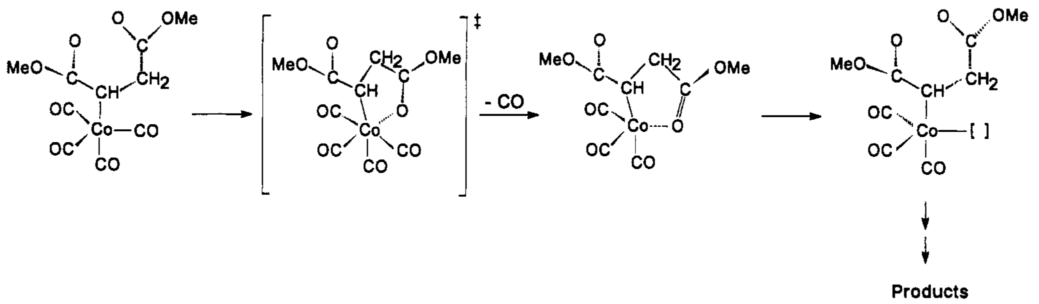
(19) Borovikov, M. S.; Kovács, I.; Ungváry, F.; Sisak, A.; Markó, L. *Organometallics* **1992**, *11*, 1576.

(20) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1980**, *193*, 383.

(21) Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 209.

(22) Ungváry, F.; Wojcicki, A. *J. Am. Chem. Soc.* **1987**, *109*, 6848.

Scheme 2



order rate law typical for a dissociation mechanism, CO insertion into the metal–cobalt bond was suggested by Basolo et al. as a low energy path to create a vacant coordination site for the entering ligand.[23a]

Such an explanation would be obvious for us, too, since CO insertion is a well-established transformation of alkylcobalt carbonyls and we did observe the corresponding acyl complex[11] at −20 °C, only about 10 deg lower than the minimum temperature of the kinetic measurements of the ^{13}CO exchange of 1. Addition of PPh$_3$ to 1 at 0 °C also results in the formation of an acyl complex, MeO$_2$CCH$_2$CH(CO$_2$Me)C(=O)Co(CO)$_3$PPh$_3$.[8] However, the phosphine substitution of alkylcobalt tetracarbonyls, unlike that of acylcobalt tetracarbonyls, seems to take place *via* a different pathway than the ^{13}CO exchange reaction. The mechanism of the ^{13}CO exchange of EtO$_2$CCH$_2$Co(CO)$_4$ was suggested to be dissociative[12b] on the basis of its first-order kinetics and the activation parameters $\Delta H^{\ddagger} = 22.4$ ($\pm$1.2) kcal mol^{-1} and $\Delta S^{\ddagger} = 4.7$ ($\pm$4.0) eu; nevertheless this complex also affords an acyl derivative, EtO$_2$CCH$_2$C(=O)Co(CO)$_3$PPh$_3$,[25] upon addition of PPh$_3$ at room temperature, which should be the result of alkyl migration. Thus, the outcome of phosphine substitution is not supportive of a mechanism of ^{13}CO exchange of 1. In addition, an alkyl migration–CO insertion mechanism is unlikely, because the formation of an acyl complex would prevent the β-hydride elimination itself.

Therefore we think that the origin of the unusual kinetic and thermodynamic behavior of this ^{13}CO exchange reaction lies in the particular structure of 1. It is evident that there is a possibility to form a five-membered metallacycle by the coordination of one of the carboxylic oxygens to cobalt (Scheme 2). Such a coordination could occur intramolecularly and associatively and would result in some gain in energy and in a considerably more structured transition state. Both features may contribute to the facile loss of a CO ligand from 1. In the resulting intermediate the coordinated oxygen is probably a very good leaving group and may generate a coordinatively unsaturated tricarbonyl species, which is available for CO coordination, β-elimination, or oxidative addition of HCo(CO)$_4$. This mechanistic suggestion explains both the first-order kinetics and the activation parameters characteristic for an associative pathway. In fact, no oxygen-to-cobalt coordination was observed to date in low oxidation state cobalt complexes which would be in agreement with the above scenario, but analogous five-membered metallacycles have been isolated with ruthenium[26] and manganese[27] carbonyl derivatives. However, an outer-sphere type chelating interaction of the ester group with the cobalt carbonyl moiety has already been suggested as an explanation of the irregular spectroscopic behavior of EtO$_2$CCH$_2$Co(CO)$_2$(PPh$_3$)$_2$,[25] PhCH$_2$O$_2$CCH$_2$Co(CO)$_3$L (L = CO, PPh$_3$),[12a] and (menthyl)O$_2$CCH$_2$Co(CO)$_3$L (L = CO, PPh$_3$, PPh$_2$(menthyl)).[28]

In order to further support the suggested mechanism, the rate constants of ^{13}CO exchange were extrapolated by calculation for 25 °C (Table 2). On the basis of this value the rate of CO dissociation from 1 proves to be 1–2 orders of magnitude faster even at relatively high concentrations of Co$_2$(CO)$_8$ than that of the β-elimination, that is, sufficiently rapid to be treated as a pre-equilibrium in Scheme 1 ($r_9 = 3.51 \times 10^{-5}$ M s^{-1}, $r_4 = 4.48 \times 10^{-7}$ and 1.60×10^{-6} M s^{-1} at [Co$_2$(CO)$_8$] = 0.003 and 0.038 M, respectively, if [1] = 0.01 M and [CO] = 0.011 M).

For comparison, a rate constant of the ^{13}CO exchange reaction of MeO$_2$CCH$_2$CH(CO$_2$Me)Co(CO)$_3$PPh$_3$ also has been determined (Table 2). The CO dissociation from this complex is about 2 orders of magnitude slower than that of 1, indicating that the high stability against β-elimination basically depends on its resistance to lose CO.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were carried out by standard Schlenk techniques[29] using deoxygenated, dry solvents and gases. Infrared spectra were recorded on a Specord IR 75 (Carl Zeiss, Germany) spectrometer in 0.061- and 0.21-mm solution cells with CaF$_2$ windows and were calibrated with benzene (1959.6 cm^{-1}) and polystyrene (1601.4 cm^{-1}). ^{1}H, ^{2}H, ^{13}C{^{1}H}, and ^{59}Co NMR spectra were obtained on a Varian Unity 300 spectrometer, working in 300-, 46.0-, 75.4-, and 70.9-MHz modes, respectively. The spectra were referenced to TMS except for ^{59}Co, where K$_3$[Co(CN)$_6$] was used as the standard. Gas chromatographic analyses were carried out on a HP 5830A chromatograph equipped with FID and an SP-2330 type 25-m capillary column.

Materials. 1,8-Bis(dimethylamino)naphthalene (Fluka) and 1-heptene (Fluka) were commercially available, and 1-heptene was distilled and stored under argon before use. Deuterated solvents and gases were obtained as follows: ^{13}CO of 99% isotope purity (MSD Isotopes), D$_2$O of 99.8% isotope purity (Aldrich), and CDCl$_3$ of 99.7% isotope purity (VEB Berlin-Chemie). Dimethyl fumarate was prepared from fumaric acid (Reanal, Hungary) and methanol in the presence of a catalytic amount of sulfuric acid and was recrystallized twice, first from methanol

---

[23] (a) Breitschaft, S.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2702. (b) Day, J. P.; Diemente, D.; Basolo, F. *Inorg. Chim. Acta* **1969**, *3*, 363.

[24] Roe, D. C. *Organometallics* **1987**, *6*, 942.

[25] Somlyai-Haász, J.; Haász, F.; Galamb, V.; Benedetti, A.; Zucchi, C.; Pályi, G.; Krümmling, T.; Happ, B.; Bartik, T. *J. Organomet. Chem.* **1991**, *419*, 205.

[26] Hiraki, K.; Ochi, N.; Takaya, H.; Fuchita, Y.; Shimokawa, Y.; Hayashida, H. *J. Chem. Soc., Dalton Trans.* **1990**, 1679.

[27] DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575.

[28] Galamb, V.; Pályi, G.; Kajtár, M. *Inorg. Chim. Acta* **1981**, *55*, L113.

and then from heptane. The cobalt complexes, $HCo(CO)_4$,[30] $MeO_2CCH_2CH(CO_2Me)Co(CO)_4$,[5f,8] and $MeO_2CCH_2CH(CO_2Me)Co(CO)_3PPh_3$,[8] were prepared according to literature methods.

Preparation of (1,2-Bis(methoxycarbonyl)ethyl-2-*d*$_1$)cobalt Tetracarbonyl (2). To a stirred solution of dimethyl fumarate (13.3 g, 90.3 mmol) in a mixture of CH_2Cl_2 (120 mL) and pentane (272 mL) under an atmosphere of CO at 9 °C was added D_2O (3 mL) by syringe followed by the addition of a cold (ca. -60 °C) 0.54 M solution of $DCo(CO)_4$ in pentane (25 mL) by canula. (The solution of $DCo(CO)_4$ was prepared from a 0.59 M solution of $HCo(CO)_4$ in pentane by the consecutive admixing and separation of D_2O (1.0, 1.5, and 2.5 mL) at 0 °C.) The pressure over the reaction mixture was then raised to 140 mmHg above the atmospheric pressure. After 2.5 h of continuous stirring, the resulting brown solution was concentrated under vacuum at -20 °C to about 100 mL and placed on dry ice overnight. Cold filtration at dry ice temperature on a P2 glass frit gave 10.4 g of yellow crystals of dimethyl fumarate and a light reddish yellow filtrate. Concentration under vacuum at -20 °C to about 10 mL and crystallization on dry ice overnight resulted in 0.50 g of a light orange solid, which was a mixture of $Co_2(CO)_8$ and dimethyl fumarate according to its IR spectrum. Repeating the above procedure, the final concentrate (ca. 7 mL) was diluted with 14 mL of pentane and crystallized at -79 °C overnight. Cold filtration, washing with 3 × 4 mL of pentane, and drying under vacuum at -20 °C resulted in 2.90 g (61% yield) of $CH_3O_2CCH^aDCH^x(CO_2CH_3)Co(CO)_4$ as heat- and air-sensitive, pale yellow crystals. IR (CH_2Cl_2, 0 °C): ν_{CO} 2112 (s), 2048 (s), 2032 (vs), 2023 (vs), 1734 (m), 1707 (m) cm^{-1}. ^1H NMR ($CDCl_3$, -20 °C): δ 3.71 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 3.33 (d, J_{ax} = 12.1 Hz, 1H, CH^x), 3.09 (d, J_{ax} = 12.1 Hz, 1H, CH^a) ppm. ^2H NMR (CH_2Cl_2, -20 °C): δ 2.54 (s) ppm. The $^{13}C\{^1H\}$ NMR data are identical to those of the perprotio congener.[5f,8]

Kinetic Measurements. In general, the kinetics was determined by using a thermostated (±0.05 °C) reaction vessel connected to an open mercury manometer for pressure indication. The vessel was also connected to a thermostated IR cuvette by two canulas to form a closed system, where samples were circulated by a 1-mL TLL Hamilton syringe and a T-stopcock operating together as a pump. The total volume of this system came to about 20 mL.

For kinetics of the thermal decomposition of **1**, a stock solution of **1** (0.058 M) in a 1:10 (v/v) CH_2Cl_2–octane mixture was injected into *n*-octane or into $Co_2(CO)_8$ dissolved in octane (typically 3–4 mL) previously equilibrated under constant conditions in pure CO or CO/Ar atmospheres to start an experiment. The initial concentrations of **1**, $Co_2(CO)_8$, and CO, as well as the temperature, were varied in the ranges shown in Table 1. The reactions were followed by the decrease of the highest ν_{CO} IR band of **1** at 2111 cm^{-1} (ϵ_M = 1700 M^{-1} cm^{-1}) completely separated from all other absorbances of the reaction mixtures. The concentration vs time plots were straight lines usually until ca. 30% conversion was achieved and were used to calculate the initial rates of reaction 3 (r_3). The rate of β-elimination (r_4) was obtained as half of r_3.

For kinetics of the cleavage of **1** by $HCo(CO)_4$, the above stock solution of **1** was injected into 2–4 mL of *n*-octane previously equilibrated at 20 °C under 742 mmHg of CO pressure. To this mixture was added without delay 0.1 mL of a $HCo(CO)_4$ stock solution (0.572 M) in hexane to start an experiment. The reaction was followed by the increase of the bridging ν_{CO} IR band of $Co_2(CO)_8$ at 1857 cm^{-1} (ϵ_M = 1735 M^{-1} cm^{-1}), since the highest ν_{CO} band of **1** was partly overlapped with that of $HCo(CO)_4$ at 2114 cm^{-1}. The concentration vs time plots were straight lines usually until ca. 20% of **1** was consumed and were used to calculate the initial rates of reaction 5 (r_5). The stoichiometry of the reaction was established by ^1H NMR spectroscopy.

For kinetics of the ^{13}CO exchange reaction of **1**, the above stock solution of **1** was injected into 4 mL of *n*-octane previously equilibrated under 742 mmHg of ^{13}CO pressure. The reaction was followed as described for the thermal decomposition. The highest ν_{CO} bands of the exchange products containing one, two, three, and four ^{13}CO ligands clearly appeared in the IR spectra as shifted ca. 9 cm^{-1} to lower wavenumbers from **1** as well as mutually from each other. The ln[**1**] vs time plots were straight lines for at least 3 half-lives of **1** (Figure 4) and were used to calculate $\tau_{1/2}$ and the first-order rate constants *k* (Table 2). The half-life of **1** was independent of its initial concentration. While the ^{13}CO exchange was followed the decomposition of **1** to $Co_2(CO)_8$ was negligible.

Acknowledgment. We thank the Hungarian Science Foundation for financial support under Grant No. OTKA 2325. We also thank BASF (Ludwigshafen) for a generous gift of BTS-Catalyst R 3-11. The assistance of Dr. G. Szalontai (Veszprém) in recording the NMR spectra is greatly appreciated.

OM930689Z

---

(29) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986.

(30) Kirch, L.; Orchin, M. *J. Am. Chem. Soc.* **1958**, *80*, 4428.