

# Kinetics and Equilibrium of the Olefin-Promoted Interconversion of *n*-Butyryl- and Isobutyrylcobalt Tetracarbonyl. The Aldehyde Isomer Ratio in the Cobalt-Catalyzed Olefin Hydroformylation

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The interconversion of *n*-butyrylcobalt tetracarbonyl (1) and isobutyrylcobalt tetracarbonyl (2) is catalyzed by ethene, propene, or 1-heptene. The equilibrium constant,  $K = [1]/[2]$ , is  $1.32 \pm 0.03$  (25 °C),  $1.38 \pm 0.02$  (45 °C),  $1.44 \pm 0.03$  (65 °C), and  $1.50 \pm 0.02$  (85 °C), which gives  $\Delta H = 0.47 \pm 0.2$  kcal/mol and  $\Delta S = 2.13 \pm 0.60$  cal/(mol K). The rate of the interconversion is first order with respect to both 1 (or 2) and olefin and is negative second order with respect to carbon monoxide. The rate constants for the conversion of 2 to 1 in the presence of 1-heptene are  $(8.06 \pm 0.15) \times 10^{-10}$  M s<sup>-1</sup> (25 °C),  $(7.85 \pm 0.17) \times 10^{-9}$  M s<sup>-1</sup> (35 °C), and  $(6.49 \pm 0.20) \times 10^{-8}$  M s<sup>-1</sup> (45 °C), which give  $E_a = 41.2 \pm 0.4$  kcal/mol. These data suggest that the aldehyde isomer ratio in the commercially important cobalt-catalyzed propene hydroformylation is mainly determined by the rate of isomerization of 1 to 2, which depends dramatically on the partial pressure of carbon monoxide and on the temperature. Thus, at low  $P_{CO}$ , where the rate of acyl isomerization is fast and comparable with the rate of acyl reduction, the 1.6 n/iso ratio of the butyraldehydes (110 °C,  $P_{CO} = 2.5$  bar) reflects closely the equilibrium isomer ratio of the precursor butyrylcobalt tetracarbonyls. On the other hand, at high  $P_{CO}$ , where the acyl isomerization is almost completely suppressed, the 4.4 n/iso butyraldehyde isomer ratio (110 °C,  $P_{CO} = 90$  bar) is the result of the reduction of an acylcobalt isomer mixture that consists mainly of *n*-butyrylcobalt tetracarbonyl, the kinetically favored acylcobalt product.

## Introduction

In the commercially important cobalt-catalyzed propene hydroformylation, *n*-butyraldehyde and isobutyraldehyde are produced under the optimized conditions of the industrial process in about a 4:1 molar ratio.<sup>1</sup> This isomer ratio decreases to about 1.6 if the hydroformylation is performed at low partial pressure of CO.<sup>2</sup> Speculations about the origin of the different isomer ratios are abundant, but it is still not clear which steps in the mechanism of hydroformylation govern the aldehyde isomer composition.

High-pressure and high-temperature infrared<sup>3</sup> and <sup>58</sup>Co NMR<sup>4</sup> spectroscopic studies have shown that under the actual catalytic conditions cobalt is present in the form of Co<sub>2</sub>(CO)<sub>8</sub>, HCo(CO)<sub>4</sub>, and the aldehyde precursor, an acylcobalt tetracarbonyl. There are conflicting reports about the isomerization of acylcobalt tetracarbonyls. Takegami et al. obtained a mixture of ester isomers from *n*-butyrylcobalt tetracarbonyl (1) or isobutyrylcobalt tetracarbonyl (2), prepared in situ, by allowing them to react with I<sub>2</sub> and alcohol in ether or ethyl acetate. In benzene or hexane, instead of a mixture of isomers, only the corresponding ester was formed.<sup>5</sup> Rupilius and Orchin found that isomerization and disproportionation of 1 or 2 at 25 °C under N<sub>2</sub> atmosphere give a mixture of butyraldehydes

in either ether or pentane.<sup>6</sup> On the other hand, at 80 °C and 80 bar of CO, isomerization of 1 and 2 did not take place in heptane<sup>7</sup> and butyrylcobalt and propylcobalt tetracarbonyls in ether at 80 °C and 160 bar of CO/H<sub>2</sub> = 1 gave only the corresponding aldehyde isomer product.<sup>8</sup>

We discovered that 1 and 2 in *n*-octane solution under a CO atmosphere rapidly isomerize in the presence of olefins. We report here the kinetics and thermodynamics of this isomerization and the implications with respect to the isomer composition of the hydroformylation products.

## Experimental Section

**General Techniques.** Reactions and associated manipulations were carried out under carbon monoxide (deoxygenated by passing through 1.5-m BTS contact (BASF), dried by passing through 25-cm KOH and P<sub>4</sub>O<sub>10</sub> columns) with oven-dried glassware or stainless-steel autoclave. Liquids were transferred using a carbon monoxide purged stainless-steel cannula or a gastight Hamilton syringe. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer using 0.519-mm KBr cuvettes. <sup>1</sup>H NMR spectra were recorded with a Tesla BS 487/C 80-MHz spectrometer using hexamethyldisiloxane as internal standard.

**Materials.** *n*-Octane (Carlo Erba) and 1-heptene (Fluka) were distilled under a carbon monoxide atmosphere. *n*-Butyryl-, isobutyryl-, and propionylcobalt tetracarbonyls were prepared by the published method<sup>9</sup> from HCo(CO)<sub>4</sub> and the corresponding ketenes and were used in the form of 0.5–0.7 M stock solutions in *n*-octane. The concentrations of the acylcobalt complexes in the stock solutions were determined by IR spectroscopy and quantitative cobalt analysis. Propane and ethene (99.9%, Tisza

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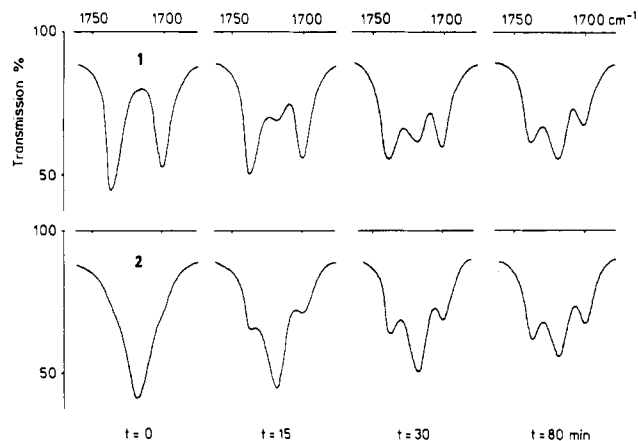
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**Figure 1.** Change of IR spectra in the acyl carbonyl stretching range of 1 and 2 (0.015 M) in *n*-octane containing 1-heptene (1.15 M) under CO (1 bar) at 45 °C.

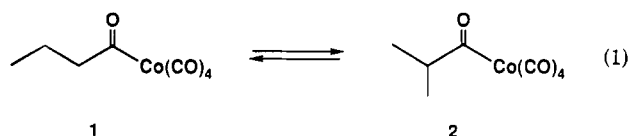
Chemical Co.) were used as delivered.

**Equilibrium Measurements.** Solutions of 1 or 2 were loaded at room temperature under a carbon monoxide atmosphere into a thermostated stainless-steel autoclave equipped with magnetic stirring. The solution was set under 10 bar of propene pressure at room temperature and was shaken at the desired temperature for the desired time. At the end of the reaction the autoclave was pressurized to 50 bar total pressure with carbon monoxide and rapidly cooled to +10 °C. After the pressure was released and the solution was purged with carbon monoxide, the infrared spectrum of the reaction mixture was recorded at +5 °C. To the remaining reaction mixture was added in 10% molar excess triphenylphosphine dissolved in *n*-octane. After 30 min at +10 °C the solvent was removed under vacuum, and the <sup>1</sup>H NMR spectrum of the residue was recorded in CDCl<sub>3</sub> solution.

**Kinetic measurements** were performed in a thermostated (±0.05 °C) glass reactor connected to a carbon monoxide filled 2-L buffer flask in order to maintain a constant pressure of carbon monoxide in the range of 0.2–1.2 bar. The actual total pressure was monitored on a mercury manometer measuring the pressure difference between the atmosphere and the reactor. The reaction was started by injection of an aliquot of the stock solution of 1 or 2 into the vigorously stirred *n*-octane–1-heptene mixture. Samples of the reaction mixture were withdrawn by a gastight syringe, and the infrared spectrum was recorded immediately at +5 °C under atmospheric pressure of carbon monoxide.

## Results

The infrared spectra of 0.01–0.1 M solutions of 1 and 2 in *n*-octane under atmospheric pressure of CO did not indicate any change of the composition below 50 °C for several hours. The addition of 1-heptene, propene, or ethene, however, caused a remarkably rapid change in the carbonyl stretching range of the spectrum (Figure 1). Regardless whether 1 or 2 was present originally, the infrared spectra were indistinguishable at the end of the reaction, indicating that 1 and 2 completely equilibrated (eq 1). Gas chromatographic analysis of the reaction

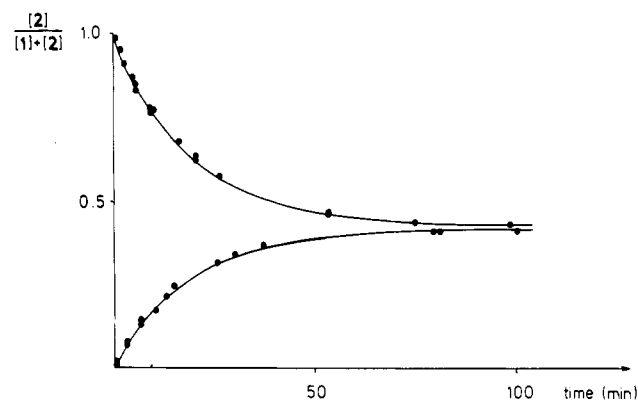


mixture showed that 1-heptene remained unchanged during reaction 1. After the addition of PPh<sub>3</sub> to such solutions, the <sup>1</sup>H NMR spectra showed clearly that mixtures of *n*-PrC(O)Co(CO)<sub>3</sub>PPh<sub>3</sub> and *i*-PrC(O)Co(CO)<sub>3</sub>PPh<sub>3</sub> were formed. The <sup>1</sup>H NMR and infrared spectra gave no indications of any acylcobalt carbonyl formation from the added olefin. This was carefully checked in the case of butyrylcobalt tetracarbonyls with 1-heptene and ethene

**Table I.** Values of the Equilibrium Constant (*K*) of the Isomerization Reaction between *n*-PrC(O)Co(CO)<sub>4</sub> (1) and *i*-PrC(O)Co(CO)<sub>4</sub> (2) in *n*-Octane Solution in the Presence of Propene<sup>a</sup> at Different Temperatures

temp, °C	acyl <sup>b</sup>	P <sub>CO</sub> , <sup>c</sup> bar	time, min	K = [1]/[2]
25	1		30	1.36
25	1		40	1.36
25	2		30	1.27
25	2		40	1.29
45	1		2	1.36
45	1	1	130 <sup>d</sup>	1.39
45	2		2	1.40
45	2	1	150 <sup>d</sup>	1.38
65	1	1	5	1.41
65	1	1	6	1.44
65	2	1	5	1.47
85	1	4	2	1.52
85	1	4	6	1.48
85	2	4	4	1.50

<sup>a</sup> P<sub>propene</sub> = 10 bar at room temperature. <sup>b</sup> At the beginning. <sup>c</sup> At room temperature. <sup>d</sup> With [1-heptene] = 1.15 M as the promoter.



**Figure 2.** Course of isomerization of 1 and 2 in the presence of 1-heptene (1.15 M) in *n*-octane solution under 1 bar of CO at 45 °C. Experimental points (●) and curves for the calculated reversible first-order kinetics are shown.

and in the case of EtC(O)Co(CO)<sub>4</sub> with propene.

The equilibrium in reaction 1 was approached experimentally from both sides using mostly propene as promoter. The concentrations 1 and 2 in the reaction mixtures were calculated from the infrared spectra<sup>10</sup> and were used to calculate the equilibrium constant  $K = [1]/[2]$  in Table I. Using 1-heptene as promoter led to the same equilibrium constant as propene.

The *n*/*i* ratios obtained from the <sup>1</sup>H NMR spectra of the PPh<sub>3</sub>-substituted derivatives<sup>11</sup> of the equilibrium mixtures were in excellent agreement with the *K* values in Table I.

The *K* values in Table I show that the *n*/*i* ratio favors the *n*-butyrylcobalt tetracarbonyl and from the equilibrium constants between 25 and 85 °C  $\Delta H = 0.47 \pm 0.2$  kcal/mol and  $\Delta S = 2.13 \pm 0.60$  cal/(mol K) can be calculated for reaction 1.

Kinetic measurements of the interconversion of 1 and 2 between 25 and 45 °C were performed using 1-heptene as a promoter in *n*-octane solution and were monitored by infrared spectroscopy. The change of concentrations with time fit a reversible first-order kinetics with respect to 1 and 2 (Figure 2). The data in Table II show that the reaction is first order in 1-heptene, negative second order in CO, and zero order in Co<sub>2</sub>(CO)<sub>8</sub>. The observed rate

(10) Using  $\epsilon_M^{1717}(1) = 615 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_M^{1737}(2) = 548 \text{ M}^{-1} \text{ cm}^{-1}$ .

(11) <sup>1</sup>H NMR: *n*-PrCOC(O)Co(CO)<sub>3</sub>PPh<sub>3</sub>  $\delta$  0.88 (3 H, t, *J* = 7.0 Hz), 1.59 (2 H, sextet, *J* = 8.0 Hz), 3.16 (2 H, t, *J* = 7.0 Hz); *i*-PrCOC(O)Co(CO)<sub>3</sub>PPh<sub>3</sub>  $\delta$  1.11 (6 H, d, *J* = 7.0 Hz), 3.50 (1 H, septet, *J* = 7.0 Hz) ppm.

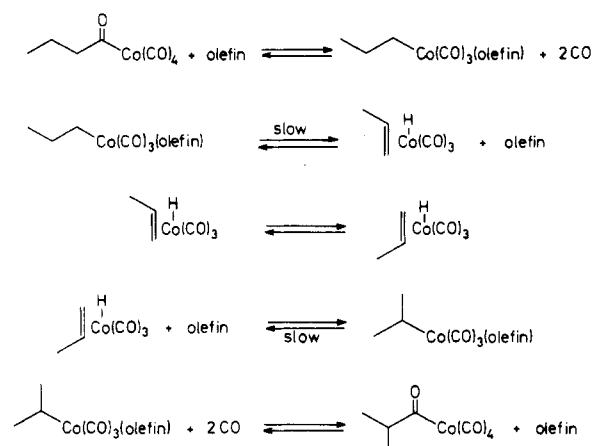
**Table II. Representative Kinetic Data for the Interconversion of *n*-PrC(O)Co(CO)<sub>4</sub> (1) and *i*-PrC(O)Co(CO)<sub>4</sub> (2) Promoted by 1-Heptene in *n*-Octane Solution under CO**

temp, °C	acyl	10 <sup>2</sup> [acyl] <sub>0</sub> , M	[1-heptene], M	10 <sup>2</sup> [CO], <sup>a</sup> M	10 <sup>5</sup> <i>k</i> <sub>21</sub> , <sup>b</sup> s <sup>-1</sup>	10 <sup>9</sup> <i>k</i> <sub>21</sub> , <sup>c</sup> M s <sup>-1</sup>
25	1	1.67	1.15	1.16	0.739	0.868
25	1	1.49	1.15	1.16	0.625	0.739
25	1	1.67	1.15	1.15	0.668	0.768
25	2	1.50	1.15	1.16	0.653	0.771
25	2	1.43	1.15	1.15	0.710	0.831
25	2	1.43	1.15	1.15	0.691	0.795
25	2	0.85	1.16	1.16	0.777	0.900
25	2	0.85	1.16	0.885	1.29	0.873
25	2	0.85	1.16	0.885	1.25	0.842
25	2	0.80	1.16	0.735	1.59	0.741
25	2	0.85	1.16	0.598	2.73	0.841
25	2	0.80	1.16	0.463	4.40	0.814
25	2	0.85	0.29	0.466	1.02	0.766
25	2	0.85	0.29	0.334	1.92	0.738
35	1	1.49	1.15	1.20	6.55	8.20
35	2	1.50	1.15	1.20	6.21	7.78
35	2	1.42	1.15	1.20	6.09	7.63
35	2	1.66 <sup>d</sup>	1.15	1.21	6.09	7.75
35	2	1.15	0.28	1.21	1.63	8.53
35	2	1.01	0.14	1.20	0.76	8.06
35	2	0.85	1.16	0.515	31.0	7.09
45	1	1.54	1.15	1.23	55.2	72.6
45	1	1.49	1.15	1.23	50.0	65.8
45	1	1.73	1.15	1.23	48.3	63.5
45	2	1.50	1.15	1.23	44.2	58.1
45	2	1.26	1.15	1.23	47.1	62.0
45	2	1.50	1.15	1.23	51.2	67.4

<sup>a</sup> Calculated from *P*<sub>CO</sub> and the solubility of CO in *n*-octane.

<sup>b</sup> Pseudo-first-order rate constant according to  $d \ln[x - (K + 1)^{-1}] / dt = -k'_{21}(K^{-1} + 1)$  in experiments starting from 2 or  $d \ln[(K + 1)^{-1} - x] / dt = k'_{21}(K^{-1} + 1)$  in experiments starting from 1 using the equilibrium constants from Table I:  $x = [2]/([1] + [2])$ . <sup>c</sup> Specific rate constant  $k_{21} = k'_{21}[1\text{-heptene}]^{-1}[\text{CO}]^2$ . <sup>d</sup> In the presence of  $[\text{Co}_2(\text{CO})_8] = 0.033 \text{ M}$ .

### Scheme I



steeply increases as the temperature increases. From the *k*<sub>21</sub> values in Table II, *E*<sub>a</sub> = 41.2 ± 0.4 kcal/mol was calculated.

### Discussion

The orders in 1-heptene and CO can be explained by assuming a preequilibrium between the starting acyl complex and the corresponding olefin-substituted alkylcobalt tricarbonyl (see the first and the last equilibria in Scheme I).<sup>12</sup> A possible explanation for the role of the olefin

(12) In these equilibria alkylcobalt tetracarbonyls,  $\text{RCO}(\text{CO})_4$ ,<sup>13</sup> are probably intermediates, and in addition several olefin-substituted intermediates such as  $\text{RC}(\text{O})\text{Co}(\text{CO})_3(\text{olefin})$  and  $\text{RC}(\text{O})\text{Co}(\text{CO})_2(\text{olefin})_2$  may be involved. We obtained spectroscopic evidence for the reversible and irreversible formation of new alkyl- and acylcobalt complexes in experiments with different substituted olefins. Their isolation and identification are in progress.

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**Table III. Comparison of the Rates of Propene Hydroformylation (*r*<sub>ald</sub>) with the Rates of *n*-Butyrylcobalt Tetracarbonyl Isomerization (*r*<sub>12</sub>) at 110 °C**

<i>P</i> <sub>CO</sub> , bar	10 <sup>4</sup> <i>r</i> <sub>ald</sub> , <sup>a</sup> M s <sup>-1</sup>	10 <sup>4</sup> <i>r</i> <sub>12</sub> , <sup>b</sup> M s <sup>-1</sup>
2.5	61	77
90	1.7	0.059

<sup>a</sup> Using the specific rate constant  $k_{\text{ald}}^{110^\circ\text{C}} = 0.00114 \text{ s}^{-1}$  for 1-pentene (obtained with  $[\text{Co}]^{110^\circ\text{C}} = 0.1171 \text{ M}$  and  $P_{\text{CO}} = P_{\text{H}_2} = 150 \text{ bar}$ ) from ref 19 applied to the experimental conditions ( $[\text{propene}]^{110^\circ\text{C}} = 2.833 \text{ M}$ ,  $[\text{Co}]^{110^\circ\text{C}} = 0.006962 \text{ M}$ ,  $P_{\text{H}_2} = 80 \text{ bar}$  at 110 °C and  $P_{\text{CO}} = 2.5$  or 90 bar at 110 °C) in ref 2, based on the established kinetics:  $r_{\text{ald}} = k[\text{olefin}][\text{Co}]P_{\text{H}_2}/P_{\text{CO}}$  from ref 20. <sup>b</sup> Using the extrapolated value of  $k_{12}^{110^\circ\text{C}} = 0.0075 \text{ M s}^{-1}$  ( $k_{12} = k_{21}/K$ ) from data in Tables I and II,  $[\text{propene}]^{110^\circ\text{C}} = 2.833 \text{ M}$ ,  $[\text{Co}]^{110^\circ\text{C}} = 0.02777 \text{ M}$ ,  $[\text{Co}]^{110^\circ\text{C}}_{P_{\text{CO}}=2.5\text{bar}} = 0.02777 \text{ M}$ ,  $[\text{Co}]^{110^\circ\text{C}}_{P_{\text{CO}}=90\text{bar}} = 1.0 \text{ M}$ , and  $[\textit{n}\text{-PrC}(\text{O})\text{Co}(\text{CO})_4]^{110^\circ\text{C}} = 4\%$  of  $0.006962 \text{ M}$ .<sup>21</sup>

promoter is that it shifts the acyl-alkyl equilibrium<sup>14</sup> toward the alkyl side by coordination to the alkyl complexes. The olefin in these complexes might be only weakly bonded and would easily be dissociated<sup>15</sup> during the rate-determining β-hydride transfer (second and fourth reaction in Scheme I). The internal rotation of the coordinated propene in the resulting hydridocobalt intermediate is probably very fast, and the reinsertion of propene into the Co-H bond has to be much faster than its exchange reaction with the promoter olefin. This could be the reason for the lack of acylcobalt carbonyl formation from the added olefin.

From the kinetic and thermodynamic data of butyrylcobalt tetracarbonyl isomerization a conclusion can be drawn with regard to the aldehyde isomer composition in the cobalt-catalyzed propene hydroformylation.

Extrapolation of our *K* values to 110 °C gives 1.56 for the ratio of the *n*-butyryl- to isobutyrylcobalt tetracarbonyls in equilibrium, which practically coincides with the value of 1.6 for the butyraldehyde isomer ratio obtained at the same temperature using *P*<sub>CO</sub> = 2.5 bar in propene hydroformylation but deviates significantly from the corresponding value of 4.4 obtained using *P*<sub>CO</sub> = 90 bar.<sup>2</sup> This suggests that at low *P*<sub>CO</sub> the aldehyde product results from an almost equilibrated *n*-butyryl- and isobutyrylcobalt tetracarbonyl precursor<sup>17</sup> but at high *P*<sub>CO</sub> the butyrylcobalt tetracarbonyl precursor is mainly the *n*-isomer. Apparently this latter isomer is the kinetically favored product of the "addition" of  $\text{CoH}(\text{CO})_4$  to the olefinic double bond; such a conclusion is in accord with the  $\text{Co}^{\delta+}\text{-H}^{\delta-}$  polarity of the cobalt-hydrogen bond.<sup>18</sup>

(14) The butyrylcobalt tetracarbonyl-propylcobalt tetracarbonyl equilibrium under atmospheric pressure of CO is far to the acyl side for the neat substance or in dilute solutions. When the partial pressure of CO is decreased, the highest energy band of the propylcobalt tetracarbonyl appears in the infrared spectrum as a recognizable shoulder at 2099 cm<sup>-1</sup> of the 2104-cm<sup>-1</sup> butyrylcobalt tetracarbonyl band. From the intensity ratio of these bands and from the concentration of CO in the solution we obtained a rough estimate,  $(3 \pm 1) \times 10^{-6} \text{ M}$ , of the equilibrium constant of the reaction  $\text{PrC}(\text{O})\text{Co}(\text{CO})_4 \rightleftharpoons \text{PrCo}(\text{CO})_4 + \text{CO}$ .

(15) An alternative explanation may be that the olefin first leaves the alkyl complex and an alkylcobalt tricarbonyl is formed, which then undergoes β-hydride transfer. This would mean that the olefin catalyzes the formation of a vacant coordination site; an analogous effect of  $\text{Ph}_3\text{PO}$  in the migratory insertion of CO has been described.<sup>16</sup>

(16) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* 1986, 108, 345.

(17) From a completely equilibrated butyrylcobalt tetracarbonyl mixture, an even lower ratio than 1.56 can be expected for the isomeric butyraldehydes because 2 has a somewhat higher reactivity than 1 in the aldehyde-forming reductive elimination.<sup>7</sup>

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To support this conclusion, we compared the rates of propene hydroformylation with the rates of *n*-butyrylcobalt tetracarbonyl isomerization at 2.5 bar and at 90 bar of  $P_{CO}$  (Table III). At 2.5 bar of  $P_{CO}$ , the rate of acyl isomerization is indeed higher than the rate of the overall aldehyde formation, and this makes an equilibration of the acyl isomers prior to the irreversible aldehyde formation conceivable under these conditions. At 90 bar of  $P_{CO}$ , however, the rate of acyl isomerization (because of its negative second order in CO) is 29 times slower than the rate of the

aldehyde formation, and this severely hampers the isobutyrylcobalt tetracarbonyl formation from the primarily formed *n*-acyl isomer.

Finally, it should be mentioned that we have already repeatedly observed and described the consecutive isomerization of the kinetically favored acylcobalt carbonyl isomers formed from olefins and  $CoH(CO)_4$  as primary products to the thermodynamically more stable isomers. In accord with our present findings, the olefins (styrene<sup>22</sup> or ethyl acrylate<sup>23</sup>) in those experiments were always present in excess with respect to the hydride.

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**Registry No.** 1, 38722-67-7; 2, 38784-32-6; CO, 630-08-0;  $EtCoCo(CO)_4$ , 16901-54-5;  $HCo(CO)_4$ , 16842-03-8;  $PrCo(CO)_4$ , 82687-61-4; ethene, 74-85-1; propene, 115-07-1; 1-heptene, 592-76-7.

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(21) The steady-state concentration of octanoylcobalt tetracarbonyl at 80 °C has been reported as ca. 20% of the total cobalt on the basis of IR spectroscopic measurements of the band intensity at 2003  $cm^{-1}$  using an  $\epsilon_M$  value of 2740  $M^{-1} cm^{-1}$ .<sup>3</sup> The  $\epsilon_M$  value of the *n*-butyryl- and isobutyrylcobalt tetracarbonyls at 2004 and 2003  $cm^{-1}$ , however, is 4950 and 4900  $M^{-1} cm^{-1}$ , respectively,<sup>9b</sup> and therefore, 10% of the total cobalt in the form of acyl complexes under those conditions seems to be more realistic. The most recent <sup>59</sup>Co NMR spectrum revealed 4% of the total cobalt to be in the form of butyrylcobalt tetracarbonyl as the steady-state intermediate in propene hydroformylation at 80 °C.<sup>4</sup> We used this lowest value to calculate the actual acyl concentration in Table III.

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## Oxidative Addition of a P–O–P Linkage and Metal–Metal Bond Formation across a Dimolybdenum Cage

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The dimolybdenum cage complex  $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$  was reacted with tertiary phosphines of the type  $PPh_2R$  ( $R = Ph, Me, H$ ) in refluxing toluene. In each case, incorporation of a single phosphine led to the loss of three carbonyls to form orange complexes of the type  $Mo(CO)_3[{}^iPr_2NPO]_4Mo(CO)_2PPh_2R$  (1a, 1b, 1c). One- and two-dimensional <sup>31</sup>P NMR spectroscopy suggested substantial alterations of the parent adamantanoid cage structure upon CO replacement. By contrast, substitutions using trimethyl phosphite under milder conditions yielded both mono- and disubstituted products:  $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$  (2) and  $Mo(CO)_3P(OMe)_3[{}^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$  (3) with the original core structure intact. The former can be shown by <sup>31</sup>P COSY NMR spectroscopy to be a mixture of *fac*- and *mer*-substituted diastereomers. The latter was found to be a mixture of all four disubstituted diastereomers. Upon further heating, both of these transformed to orange-red  $Mo(CO)_3[{}^iPr_2NPO]_4Mo(CO)_2P(OMe)_3$  (1d) an analogue of complexes 1a–1c. The X-ray molecular structure of 1d has been determined. Crystal data: monoclinic,  $P2_1/n$ ,  $a = 13.026$  (3) Å,  $b = 21.054$  (3) Å,  $c = 18.118$  (3) Å,  $\beta = 103.46$  (2)°,  $V = 4832$  (2) Å<sup>3</sup>,  $Z = 4$ , final  $R = 0.042$ , and  $R_w = 0.044$  for 6070 reflections and varying 497 parameters. This revealed that a cage P–O–P bond has been cleaved near the substitution site with the resulting phosphinito oxygen replacing a second CO. Additionally, the phosphido group generated displaced a third CO at the other Mo center to bridge the two metals which are now within bonding distance (3.173 (1) Å) of each other. Similar reactions using pyridine also produced a related orange-red product,  $Mo(CO)_3[{}^iPr_2NPO]_4Mo(CO)_2NC_5H_5$  (1e). This pyridine ligand is readily displaced by CO gas to generate  $Mo(CO)_3[{}^iPr_2NPO]_4Mo(CO)_3$  (1f). The X-ray structure of 1f has also been determined. Crystal data: monoclinic,  $C2/c$ ,  $a = 36.523$  (7) Å,  $b = 13.287$  (5) Å,  $c = 20.348$  (3) Å,  $\beta = 109.48$  (1)°,  $V = 9310$  (4) Å<sup>3</sup>,  $Z = 8$ , final  $R = 0.055$ , and  $R_w = 0.074$  for 4723 reflections and 452 variables. A similar polycyclic core structure to 1d was found. Intermediates similar to 2 and 3 can be isolated in low yields from the  $PPh_2H$  reaction at below 100 °C.

### Introduction

Nucleophilic substitution reactions at group VI metal carbonyls have been extensively studied.<sup>1</sup> For tetracarbonylmetal diphosphine chelate complexes, CO substitutions usually result in formation of either axial-substituted *mer*- or equatorial-substituted *fac*- $M(CO)_3P_3$  products.<sup>2</sup> The adamantanoid bimetallic cage complex

$Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$  (Figure 1) contains two mutually orthogonal  $Mo(CO)_4P_2$  centers which are sub-

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