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# Intermediate Complexes in the Octacarbonyl Dicobalt-Initiated Living Polymerization of 3-Methyl-1,2-butadiene

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**Abstract:** In the reaction of octacarbonyl dicobalt with 3-methyl-1,2-butadiene at room temperature dinuclear $\eta^3$-allyl-type complexes are formed which contain $2 + n$ ($n = 0, 1, 2, 3, \cdots$) five-carbon units depending on the applied molar ratio. These complexes are the individual compounds in the octacarbonyl dicobalt-initiated living polymerization of 3-methyl-1,2-butadiene. The first three members in this series of complexes containing two (**1**), three (**2**), and four (**3**) five-carbon units have been isolated and characterized by IR, Raman, $^1$H, and $^{13}$C NMR spectroscopies, molecular weight, and for **1** and **2** also by single-crystal X-ray diffraction. The first two molecules of 3-methyl-1,2-butadiene establish the formation of two ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl parts which are linked together at the central allylic carbon by a carbonyl group. By the addition of 3-methyl-1,2-butadiene in excess, the monomer inserts into the unsubstituted allylic carbon−cobalt bond in a 1,2-fashion, pushing the cobalt atoms further apart. The X-ray structures of **1** and **2** disclose that the 1,2-polymer chain grows in a helical manner. The rate of the insertion of the monomer is first order with respect of both the 3-methyl-1,2-butadiene and the dicobalt complex and is negative first order with respect of carbon monoxide. The observed rate constants of the formation of **1**−**3** at 30 °C are $14.3 \times 10^{-4}$, $1.75 \times 10^{-4}$, and $0.79 \times 10^{-4}$ s$^{-1}$, reproducible to within 5, 10, and 7%, respectively.

## Introduction

An unidentified organocobalt complex formed in the reaction of $Co_2(CO)_8$ and allenes having a hydrogen atom bonded to an allenic carbon atom was found to initiate the polymerization of allenes.[1] Nakamura claimed that in the presence of an excess of $Co_2(CO)_8$, allene yields $[C_3H_4Co(CO)_3]_2$ and suggested a structure for this complex[2] (see Figure 1), which has been since extensively reviewed in the literature.[3] However, neither the composition nor the structure of this compound has been confirmed by others.

We studied the complex formation in the reaction of $Co_2(CO)_8$ and 3-methyl-1,2-butadiene as a model and observed the formation of a series of complexes which represent individual compounds in a living polymerization. Complexes containing two, three, and four dimethylallene units were isolated, and their structures were determined by single-crystal X-ray diffraction (complexes **1** and **2**) and NMR spectroscopy (complexes **1**−**3**).

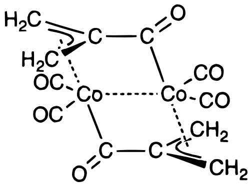

**Figure 1.** Suggested structure of the product from the reaction of 1,2-propadiene and $Co_2(CO)_8$.[2]

## Results and Discussion

Addition of excess 3-methyl-1,2-butadiene to solutions of octacarbonyl dicobalt in *n*-octane at room temperature results in evolution of carbon monoxide and the formation of a polymer as a light yellow air-sensitive precipitate. The infrared spectrum of the reaction mixture showed characteristic changes in the carbonyl stretching range during the reaction (Figure 2). Experiments with gradual addition of the 1,2-diene revealed that distinct complexes were formed according to the stoichiometries of eqs 1−3.

$$Co_2(CO)_8 + 2Me_2C{=}C{=}CH_2 \rightarrow Co_2(CO)_7(Me_2C{=}C{=}CH_2)_2 + CO \quad (1)$$

$$Co_2(CO)_7(Me_2C{=}C{=}CH_2)_2 + Me_2C{=}C{=}CH_2 \rightarrow Co_2(CO)_7(Me_2C{=}C{=}CH_2)_3 \quad (2)$$

$$Co_2(CO)_7(Me_2C{=}C{=}CH_2)_3 + Me_2C{=}C{=}CH_2 \rightarrow Co_2(CO)_7(Me_2C{=}C{=}CH_2)_4 \quad (3)$$

Thus, by mixing a solution of 1 mol of $Co_2(CO)_8$ with 1 mol of 3-methyl-1,2-butadiene at 25 °C led to the evolution of 0.5 mol of CO. The infrared spectrum of the reaction mixture showed in addition to the unreacted $Co_2(CO)_8$ the formation of a new complex **1** at 2071 (m), 2064 (s), 2012 (s), 2007 (vs), 1998 (s), and 1672 (vw) cm$^{-1}$. Addition of a second mole of the 1,2-diene led to the release of an additional 0.5 mol of CO

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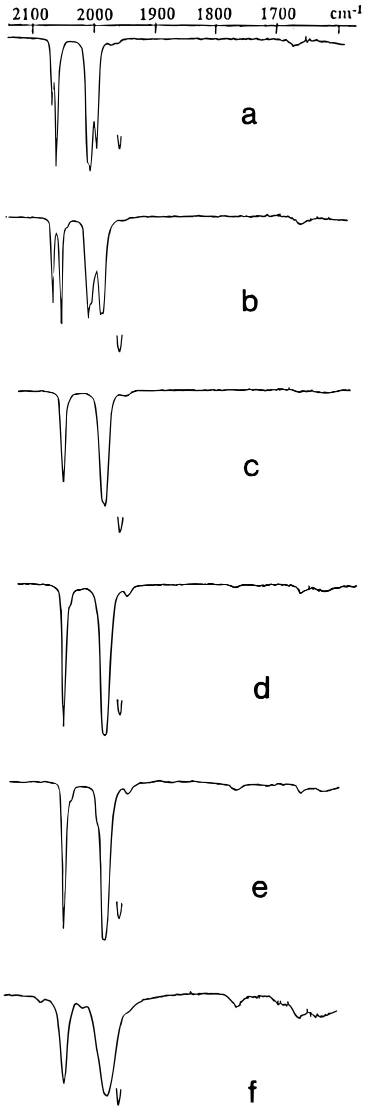

**Figure 2.** Infrared spectra in the $\nu$(CO) range of the complexes formed in the reaction of $Co_2(CO)_8$ with 3-methyl-1,2-butadiene at different molar ratios at 25 °C; $Me_2C{=}C{=}CH_2/Co_2(CO)_8 = 2$ (a), 3 (b), 4 (c), 10 (d), 40 (e and f). Spectra a−e are solution spectra in *n*-octane, and f was recorded in a KBr pellet.

and the practically complete conversion of all $Co_2(CO)_8$ into **1** (Figure 2a). Addition of a third mole of the 1,2-diene did not give additional CO evolution, but gave an almost complete conversion of **1** into another new carbonyl cobalt complex (**2**) with $\nu$(CO) bands at 2067 (s), 2054 (s), 2010 (s), 2006 (s), 1991 (s), 1987 (s), and 1663 (vw) $cm^{-1}$ (Figure 2b). The formation of the third new product **3** could be observed in the infrared spectrum having $\nu$(CO) bands at 2052 (s), 1984 (vs), and 1630 (vw) $cm^{-1}$, upon addition of a fourth mole of the 1,2-diene (Figure 2c). No further change of the infrared spectra could be observed upon addition of more 1,2-diene. The yellow solutions and precipitate formed in the reaction of $Co_2(CO)_8$ with either 10 or 40 mols of the 1,2-diene showed $\nu$(CO) bands almost identical with that of product **3** (Figure 2d−f).

Complexes **1**−**3** could be isolated from the reaction mixtures by chromatography on alumina with pentane or pentane−$CH_2Cl_2$ at 0 °C and subsequent crystallization at −20 °C as air-sensitive yellow crystals.

The composition of **1**−**3** deduced from the stoichiometry of their formation according to eqs 1−3 could be verified by osmometric molecular weight determination of the isolated complexes. The $^{13}C$ NMR spectra of the complexes show

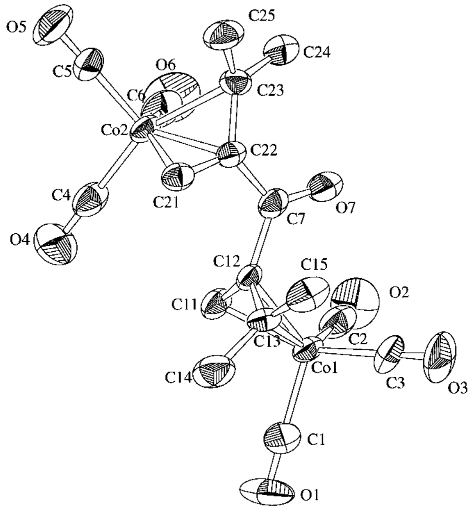

**Figure 3.** An ORTEP (50% probability ellipsoids) view of $Co_2(CO)_7(Me_2C{=}C{=}CH_2)_2$ (**1**) as determined by X-ray diffraction. Hydrogen atoms are omitted for clarity.

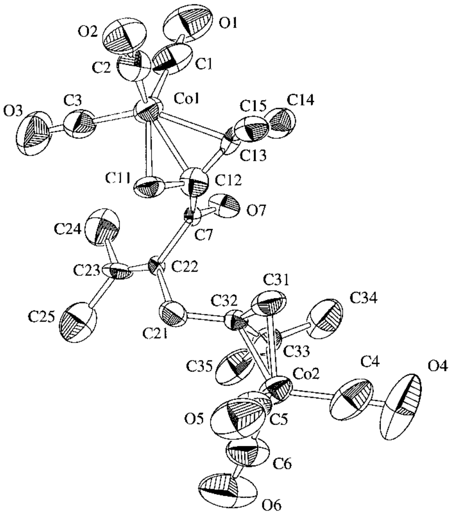

**Figure 4.** An ORTEP (50% probability ellipsoids) view of $Co_2(CO)_7(Me_2C{=}C{=}CH_2)_3$ (**2**) as determined by X-ray diffraction. Hydrogen atoms are omitted for clarity.

carbon resonances which are in the chemical shift range of known $\eta^3$-allyl-type complexes.[4]

The X-ray crystal structures of **1** (See Figure 3) and **2** (See Figure 4) revealed that these compounds are ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl-type complexes in which two such parts are linked together at the central carbon of the allyl group by a ketonic carbon and by a three-carbon chain, respectively (cf., Scheme 1). In complex **1**, one allylic system, C(21), C(22), C(23), C(24), C(25) (see Figure 3), and the ketone carbonyl group are nearly coplanar and this plane approaches orthogonality (81°) with the other $\eta^3$-3,3-dimethylallyl group. In complex **2,** the chain of five carbon atoms between the cobalt atoms adopts an approximate helical pattern. The progression of dihedral angles (see Figure 4) C(11)−C(12)−C(7)−C(22), 20(1)°; C(12)−C(7)−C(22)−C(21), 65(1)°; C(7)−C(22)−C(21)−

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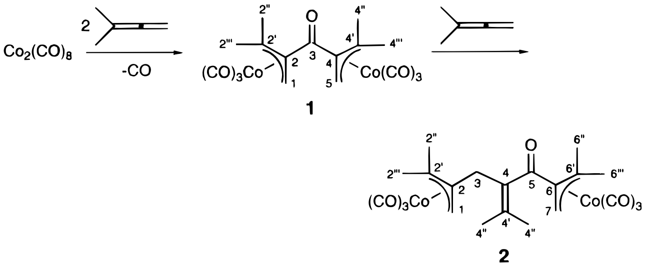
**Scheme 1**



C(32), 42(1)°; and C(22)−C(21)−C(32)−C(33), 70(2)° indicates a steady rotation of the carbon chain in the same direction, generating a helical twist in the molecule. The infrared spectra of **1** and **2** in the $\nu$(CO) range reflect the low symmetry of these molecules: the six terminal carbonyl groups result in five and six different $\nu$(CO) bands, respectively. The ketonic carbonyl of these complexes give a very weak $\nu$(CO) band in the infrared spectrum of their solutions or in KBr pellets, but a stronger absorption at the same wavenumber in the Raman spectrum in the solid state.

It is interesting to note that although the bond structure of **1** is symmetric (Scheme 1), the actual unsymmetrical structure of the crystalline state (Figure 3) appears to be maintained in solution as well since two different sets of $^{13}$C resonances were found for the two coordinated allyl groups. Due to the inherent asymmetric bond structure of **2**, all carbon resonances, except the ketone carbonyl carbon are doubled indicating the different chemical environments of these carbons. In addition, these resonances—with the exception of the central allylic carbon resonances—are further doubled indicating that **2** is present in solution in the form of two diastereomers in nearly equal proportions. The ratio of isomers does not change between room temperature and −43 °C, according to the $^{13}$C NMR spectra. This suggests that the isomers are diastereomers rather than restricted conformations.

To examine the above complex formations in more detail, we measured the kinetics of these and related reactions. The reaction of $Co_2(CO)_8$ and 3-methyl-1,2-butadiene (**A**) under carbon monoxide was followed by measuring the rates of CO evolution which accompany the formation of **1**. Table 1 compiles the results of these measurements. The initial rates of CO evolution were found to be first order in 1,2-diene and in $Co_2(CO)_8$ and negative first order in CO. The observed rate constant for this reaction was found to be $k_1$ (30 °C) = 14.3 × $10^{-4}$ s$^{-1}$. The kinetics of the reactions in eqs 2 and 3 were followed by infrared spectroscopy measuring the decrease of intensity of the highest $\nu$(CO) band of **1** at 2071 cm$^{-1}$ and **2** at 2067 cm$^{-1}$, respectively. Table 2 compiles the results of these measurements. These reactions (eqs 2 and 3) were found to be first order with respect to both the starting complexes and the 1,2-diene and negative first order with respect to CO. The rate constants were found to be $k_2$ (30 °C) = 1.75 × $10^{-4}$ s$^{-1}$ and $k_3$ (30 °C) = 0.79 × $10^{-4}$ s$^{-1}$, respectively.

The inverse dependence of the rates on the carbon monoxide concentration suggests that either coordinatively unsaturated cobalt complexes or fast CO substitution equilibria prior to the rate-determining process are involved in all the reactions investigated.

In the reaction of 3-methyl-1,2-butadiene with octacarbonyl dicobalt both tetracarbonyl cobalt radical and the coordinatively unsaturated heptacarbonyl dicobalt have to be considered as the possible reactive intermediates. Sources of these species might be the well-established equilibrium reactions (eqs 4 and 5).[6]

**Table 1.** Initial Rates of CO Evolution ($r_1$) and the Observed Rate Constant ($k_1$ = [CO)]$r_1$/[$Co_2(CO)_8$][**A**] in the Reaction of $Co_2(CO)_8$ with 3-Methyl-1,2-butadiene (**A**) in *n*-Octane Solution (eq 1) under Various Condition

| $T$, °C | $10^2[Co_2(CO)_8]$ (M) | $10^2$[**A**] (M) | $10^2$[CO]$^a$ (M) | $10^6 r_1$ M (s$^{-1}$) | $10^4 k_1$ (s$^{-1}$) |
|---|---|---|---|---|---|
| 15 | 6.67 | 1.33 | 1.04 | 18.9 | 2.09 |
| 15 | 3.33 | 1.33 | 1.04 | 10.1 | 2.23 |
| 15 | 3.33 | 1.33 | 1.04 | 10.2 | 2.25 |
| 15 | 1.48 | 2.80 | 1.06 | 8.60 | 2.20 |
| 15 | 1.48 | 0.00$^b$ | 1.06 | 0.62 | |
| 15 | 1.48 | 2.80$^b$ | 1.06 | 9.48 | |
| 15 | 1.48 | 0.00$^c$ | 1.06 | 15.1 | |
| 15 | 1.48 | 2.80$^c$ | 1.06 | 23.4 | |
| 15 | 1.60 | 1.33 | 1.04 | 5.20 | 2.37 |
| 15 | 0.67 | 1.33 | 1.04 | 2.12 | 2.33 |
| 15 | 3.33 | 0.67 | 1.04 | 5.20 | 2.23 |
| 15 | 3.33 | 3.33 | 1.04 | 23.5 | 2.08 |
| 15 | 3.33 | 3.33 | 1.04 | 24.6 | 2.17 |
| 15 | 3.33 | 6.67 | 1.04 | 45.6 | 2.01 |
| 15 | 3.33 | 3.33 | 1.79 | 13.4 | 2.12 |
| 15 | 3.33 | 1.33 | 0.52 | 18.4 | 2.06 |
| 20 | 4.00 | 4.00 | 1.03 | 66.7 | 4.30 |
| 25 | 2.00 | 8.00 | 1.03 | 107 | 6.9 |
| 25 | 2.00 | 4.00 | 1.03 | 61.9 | 7.6 |
| 25 | 4.00 | 4.00 | 1.03 | 104 | 6.4 |
| 25 | 4.00 | 2.00 | 1.03 | 60.4 | 7.4 |
| 30 | 4.00 | 4.00 | 1.04 | 230 | 14.3 |

$^a$ Calculated from $P_{CO}$ and the solubility of CO in *n*-octane.$^5$ $^b$ In the presence of 0.010 M 2,2,6,6-tetramethylpiperidin-1-oxyl, free radical (TEMPO). $^c$ In the presence of 0.002 M 2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy, free radical (Galvinoxyl).

$$Co_2(CO)_8 \rightleftharpoons 2{\bullet}Co(CO)_4 \tag{4}$$

$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO \tag{5}$$

The free radical TEMPO[9] reacts with octacarbonyl dicobalt and gives a well characterized complex, Co(TEMPO)$(CO)_2$, and carbon monoxide.[10] The complex formation is believed to occur through scavenging of the tetracarbonyl cobalt radicals by the free radical TEMPO. We found that the free radical galvinoxyl[11] reacts with octacarbonyl dicobalt in a similar way leading to a complex and carbon monoxide. We measured the rates of carbon monoxide evolution of both reactions in the presence and in the absence of 3-methyl-1,2-butadiene. The data in Table

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(6) The reversible formation of •Co(CO)$_4$ from $Co_2(CO)_8$ has been demonstrated (ref 7a), and the equilibrium constant was determined from high-pressure high-temperature IR measurements (ref 7b), and recently from magnetic susceptibility measurements (ref 7c). In the latter reference, an Arrhenius plot for Co−Co bond homolysis in $Co_2(CO)_8$ based on the $^{59}$Co NMR line widths has been given as $E_a$ = 17 ± 2 kcal mol$^{-1}$ and $A = 2 \times 10^{12}$ s$^{-1}$ between 220 and 160 °C. Although the reliability of the rate constant derived by the extrapolation far beyond this range is not warranted, it gives a mean value of 1.07 s$^{-1}$ for 30 °C, which is on the same order of magnitude as the rate constant of the formation of $Co_2(CO)_7$ from $Co_2(CO)_8$ at the same temperature. $Co_2(CO)_8$ is known to exchange carbon monoxide at a rate of 0.232 s$^{-1}$ at 30 °C (interpolated from experimentally observed rate constants at −20, −5, 0, 5 (refs 8a,b), and 40−80 °C (ref 8c)) by a dissociative mechanism through $Co_2(CO)_7$. A rate constant approximately six-times smaller than above has been inferred by others from the reaction with AsPh$_3$ (ref 8d) or $^{13}$CO (refs 8d,e).

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(9) TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical.

(10) Jaitner, P.; Huber, W.; Gieren, A.; Betz, H. *J. Organomet. Chem.* **1986**, *311*, 379−385.

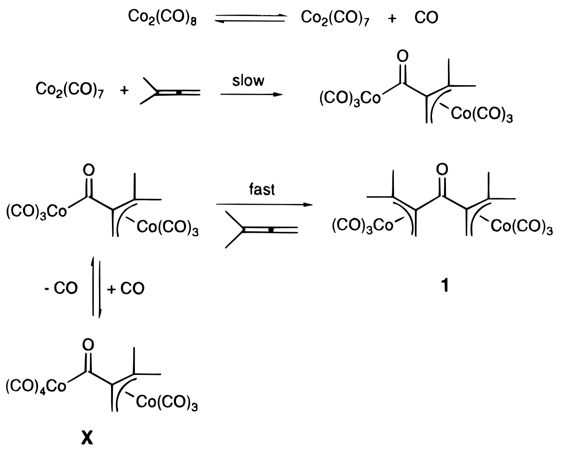
(11) Galvinoxyl = 2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy, free radical.

**Table 2.** Initial Rates $r_2$ and $r_3$ and the Observed Rate Constants ($k_2$ = [CO)]$r_2$/[**1**][**A**] and $k_3$ = [CO)]$r_3$/[**2**][**A**]) in the Reaction of **1** and **2** in eqs 2 and 3, respectively, with 3-Methyl-1,2-butadiene (**A**) in n-Octane Solution at 30 °C

| $10^2$[**1**] (M) | $10^2$[**A**] (M) | $10^2$[CO]$^a$ (M) | $10^7r_2$ (M $s^{-1}$) | $10^4k_2$ ($s^{-1}$) | $10^2$[**2**] (M) | $10^2$[**A**] (M) | $10^2$[CO]$^a$ (M) | $10^7r_3$ (M $s^{-1}$) | $10^4k_3$ ($s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1.13 | 0.32 | 1.00 | 6.75 | 1.86 | 0.31 | 0.48 | 0.98 | 1.27 | 0.84 |
| 0.59 | 0.32 | 0.99 | 3.90 | 2.04 | 0.31 | 0.48 | 0.73 | 1.59 | 0.81 |
| 0.44 | 0.31 | 0.99 | 2.61 | 1.89 | 0.31 | 0.48 | 1.48 | 0.89 | 0.88 |
| 0.30 | 0.32 | 1.00 | 1.69 | 1.76 | 0.31 | 1.48 | 1.10 | 3.17 | 0.76 |
| 0.30 | 0.30 | 0.96 | 1.46 | 1.56 | 0.10 | 0.48 | 1.09 | 0.33 | 0.75 |
| 0.32 | 0.38 | 0.76 | 2.48 | 1.55 | 0.30 | 0.99 | 1.10 | 2.07 | 0.76 |
| 0.30 | 0.38 | 1.33 | 1.28 | 1.49 | 0.62 | 0.48 | 1.08 | 2.23 | 0.81 |
| 0.30 | 0.64 | 1.00 | 3.33 | 1.73 | 0.31 | 0.48 | 0.83 | 1.40 | 0.78 |
| 0.30 | 1.07 | 1.02 | 5.46 | 1.73 | 0.31 | 0.40 | 1.12 | 0.85 | 0.77 |
| 0.30 | 1.60 | 1.01 | 8.51 | 1.79 | 0.32 | 0.48 | 1.12 | 1.14 | 0.83 |
| | | | | | 0.30 | 1.46 | 0.29 | 10.5 | 0.70 |

[a] Calculated from $P_{CO}$ and the solubility of CO in *n*-octane.[5]

**Scheme 2**



1 show that the observed initial rates of carbon monoxide evolution in the presence of 3-methyl-1,2-butadiene and the free radicals correspond to the sum of the rates measured at the same concentrations but in separate experiments. This means that the rate of reaction in eq 1 is not influenced by the presence of those radical scavengers, suggesting that the tetracarbonyl cobalt radical does not play any role in the reaction of octacarbonyl dicobalt and 3-methyl-1,2-butadiene.

On the other hand, the observed negative effect of carbon monoxide on the rate of the reaction in eq 1 is indicative that heptacarbonyl dicobalt may be involved in the reaction of octacarbonyl dicobalt with the first mole of 3-methyl-1,2-butadiene (Scheme 2) similar to that of acetylenes[12] and conjugated dienes.[13] We were not able to find evidence for the formation of an intermediate complex containing only one 3-methyl-1,2-butadiene unit (**X**) probably because its formation is followed by a much faster insertion of the second mole of 1,2-diene.

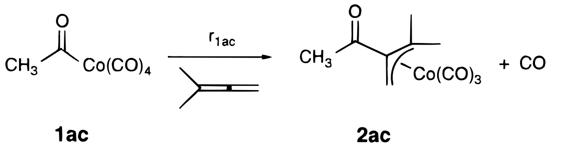
Acetylcobalt tetracarbonyl (**1ac**) reacts with allene leading to (2-acetyl-$\eta^3$-allyl)cobalt tricarbonyl and carbon monoxide.[14] The analogous reaction with 3-methyl-1,2-butadiene at 15 °C gave (2-acetyl-$\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl (**2ac**) and carbon monoxide (eq 6).

The rate of CO evolution in the reaction (eq 6) at 15 °C was found to be first order in acetylcobalt tetracarbonyl, less than first order in 3-methyl-1,2-butadiene and less than negative first order in carbon monoxide (Table 3). The latter two apparent orders decreased by increasing the concentrations of the corresponding reagents. This kinetic behavior is in accordance with a reversible dissociation of CO from acetylcobalt tetracarbonyl, followed by a reaction with 3-methyl-1,2-butadiene (Scheme 3). Assuming steady-state concentration for the acetylcobalt tricarbonyl intermediate, the rate can be described by eq 7 or after rearrangement by eq 8. A plot of [**1ac**]/$r_{1ac}$ against [CO]/[**A**] (Figure 5) allows $k_a$ (15 °C) = 6.5 × $10^{-3}$ $s^{-1}$ and the ratio of $k_{-a}/k_b$ (15 °C) = 1.03 to be calculated from the intercept and the slope, respectively.

**Table 3.** Initial Rates of CO Evolution ($r_{\mathbf{1ac}}$) in the Reaction of **1ac** with 3-Methyl-1,2-butadiene (**A**) in *n*-Octane Solution (eq 6) at 15 °C

| $10^2$[**1ac**] (M) | $10^2$[**A**] (M) | $10^2$[CO]$^a$ (M) | $10^5r_{\mathbf{1ac}}$ (M $s^{-1}$) |
|---|---|---|---|
| 0.50 | 0.50 | 0.971 | 1.10 |
| 0.50 | 1.00 | 0.975 | 1.68 |
| 1.00 | 0.70 | 0.977 | 2.71 |
| 1.00 | 1.00 | 0.967 | 3.23 |
| 1.00 | 1.40 | 0.974 | 3.79 |
| 1.00 | 2.50 | 0.973 | 4.38 |
| 1.00 | 4.00 | 0.971 | 5.02 |
| 2.00 | 1.00 | 0.971 | 6.53 |
| 4.00 | 1.00 | 0.969 | 12.93 |
| 1.00 | 1.00 | 0.328 | 4.62 |
| 1.00 | 1.00 | 0.463 | 4.41 |
| 1.00 | 1.00 | 0.692 | 3.65 |
| 1.00 | 1.00 | 1.495 | 2.49 |

[a] Calculated from $P_{CO}$ and the solubility of CO in *n*-octane.[5]



(6)

$$r_{\mathbf{1ac}} = k_a k_b[\mathbf{1ac}][\mathbf{A}]/(k_b[\mathbf{A}] + k_{-a}[\mathrm{CO}]) \qquad (7)$$

$$[\mathbf{1ac}]/r_{\mathbf{1ac}} = k_{-a}[\mathrm{CO}]/k_a k_b[\mathbf{A}] + 1/k_a \qquad (8)$$

The value of the observed rate constant $k_a$ shows an excellent agreement with those obtained from CO-exchange[8b,c] and $Ph_3P$-substitution[15] reactions of acetylcobalt tetracarbonyl and is about 40 times higher than the observed rate constant of the reaction of octacarbonyl dicobalt with 3-methyl-1,2-butadiene at the same temperature suggesting that the intermediate **X** in Scheme 2 might indeed be formed slowly and reacts fast to give **1**.

In the reaction of 3-methyl-1,2-butadiene with the complexes **1**, **2**, **3**, ···, the insertion of the 1,2-diene occurs in the coordination sphere of cobalt of these (2-substituted-$\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl compounds. In the case when

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(12) (a) Ellgen, P. *Inorg. Chem.* **1972**, *11*, 691−695. (b) Ungváry, F.; Markó, L. *Chem. Ber.* **1972**, *105*, 2457−2461.

(13) Ungváry, F.; Shanshool, J; Markó, L. *J. Organomet. Chem.* **1985**, *296*, 155−159.

(14) Otsuka, S.; Nakamura, A. *Inorg. Chem.* **1972**, *11*, 644−645.

(15) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 651−654.

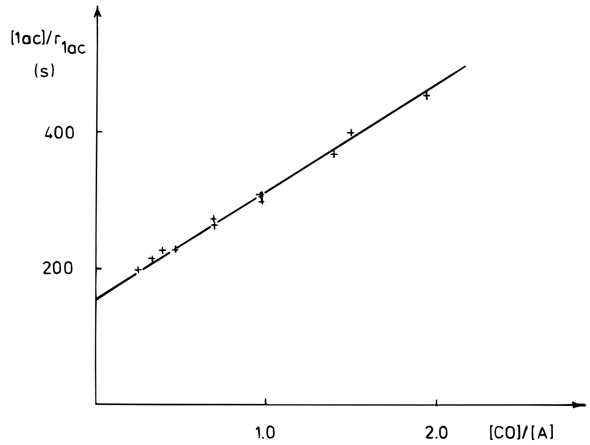
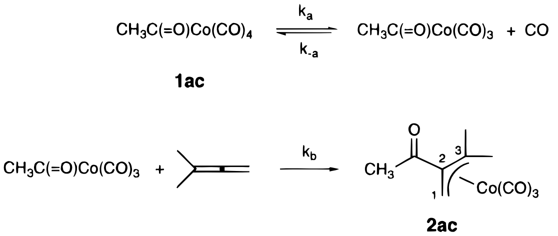
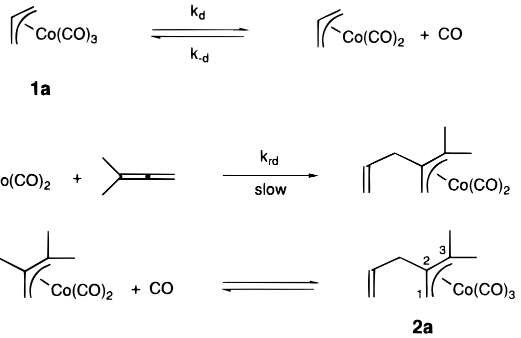


**Figure 5.** Plot of [**1ac**]/$r_{1ac}$ against [CO]/[**A**] for reaction 6.

**Scheme 3**



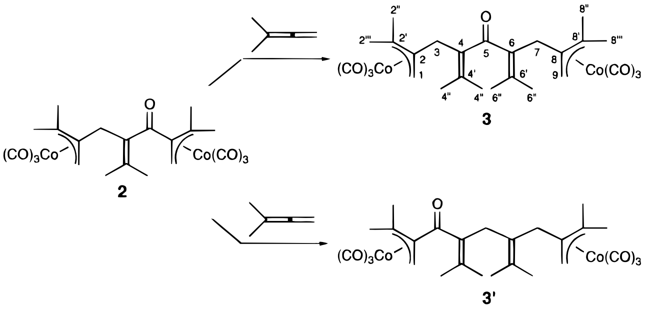
**Scheme 4**

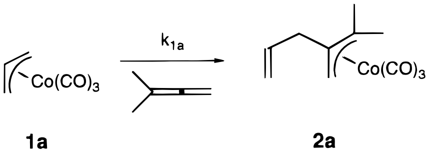


$\eta^3$-allylcobalt tricarbonyl (**1a**) reacts with 3-methyl-1,2-butadiene (eq 9), (2-allyl-$\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl (**2a**) is formed[16] in the analogous reaction. The kinetic pattern of this reaction (eq 9) was found to be the same as those observed for the reactions of $Co_2(CO)_8$, **1**, and **2** with 3-methyl-1,2-butadiene. That means first order with respect to both **1a** and **A** and negative first order with respect to carbon monoxide. This suggests a fast equilibrium dissociation of CO from **1a** followed by a rate-determining reaction with 3-methyl-1,2-butadiene (Scheme 4). The value of the observed rate constant of $k_{1a}$ (30 °C) $= r_{1a}[CO]/[\mathbf{1a}][\mathbf{A}] = 0.96 \times 10^{-4}\ s^{-1}$ is very close to that of the reaction of **2** with 3-methyl-1,2-butadiene ($0.79 \times 10^{-4}\ s^{-1}$) and is 2 orders of magnitude smaller than the rate of CO dissociation from **1a**, $k_d$ (30 °C) $= 0.0223\ s^{-1}$, obtained in the reaction of **1a** with $PPh_3$.[17]

In eq 9, as well as in reactions of the other $\eta^3$-allyl-type complexes, the 3-methyl-1,2-butadiene adds most probably to a vacant coordination site of cobalt and then bond formation occurs between the allyl part and the central carbon of the 1,2-diene with concomitant restoration of the $\eta^3$-allyl structure around the cobalt (Scheme 4). The vacant coordination site on the cobalt can be formed from the $\eta^3$-allyl compounds either by a $\eta^3$-$\eta^1$-allyl conversion or by CO dissociation. The latter case seems to be more likely since none of the $\eta^3$-allylcobalt tricarbonyl complexes in this work could be transformed into $\eta^1$-allylcobalt tetracarbonyls by 50 bar of carbon monoxide at 35 °C. Carbon monoxide dissociation from $\eta^3$-allylcobalt tricarbonyl complexes on the other hand is a well established step in their substitution reaction with triphenylphosphine.[17]

**Scheme 5**





(9)

The bond structure of **2** is unsymmetrical. Thus, its reaction with 3-methyl-1,2-butadiene (eq 3) may lead to the symmetric bond structure of **3** and/or to the unsymmetrical bond structure of **3′** (Scheme 5). Unfortunately, a useful single crystal from the product of this reaction (eq 3) could not be found, and therefore, the crystal structure could not be determined. However, both the infrared and the $^{13}C$ NMR spectra were suitable for elucidation of the actual bond structure of the product. The infrared spectrum of the product shows only two $\nu(C{\equiv}O)$ bands at 2052 (s) and 1984 (vs) $cm^{-1}$ in accordance with the expectation for **3**, containing two identically substituted ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl parts far enough from each other to be moving freely. For **3′**, two pairs of absorbances appear in the infrared spectrum according to the two differently substituted ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl parts in the molecule. The $\nu(C{\equiv}O)$ bands of **3** in *n*-octane solution at 2052 (s) and 1984 (vs) $cm^{-1}$ closely resemble the $\nu(C{\equiv}O)$ bands of ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl in hexane solution[18] at 2056.5 (s) and 1989.8 (vs) $cm^{-1}$. These two characteristic bands can be seen in the infrared spectrum of products containing more than four allene units as well, indicating that $\eta^3$-allyl-type cobalt complexes are present in all phases of the growing polymer. On the other hand, the $^{13}C$ NMR spectrum shows resonances of four primary carbons, two secondary carbons, and four quaternary carbons, as expectated for **3** having a symmetrical bond structure. For **3′**, at least twice as many resonances for each type of carbon would have been found owing to its asymmetric bond structure.

The complexes **2ac** and **2a** can be regarded as model compounds of **2** in a sense that **2ac** mimics the 2-acyl-side and **2a** mimics the 2-alkyl-side of **2** (Scheme 6). By comparison of the rates of the reaction of 3-methyl-1,2-butadiene with **2ac** and **2a**, we found that **2ac** reacts about 10 times as fast as **2a** (see experimental part), which independently supports that indeed the 2-acyl-side in **2** is the preferred site of reaction with the 1,2-diene.

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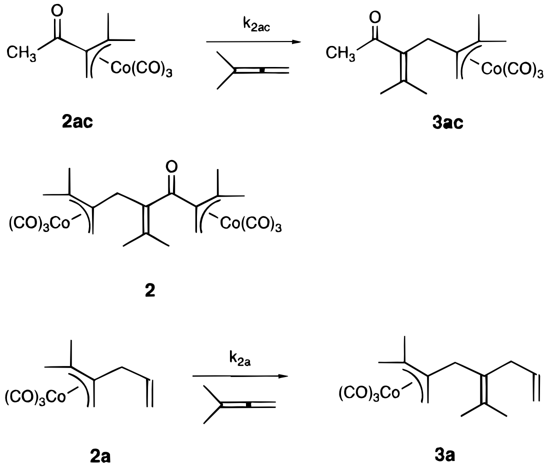
(16) The reaction was followed by measuring the decrease of the absorbance of the reaction mixture at 2064 $cm^{-1}$. Molar absorbance of **1a** in *n*-octane at 30 °C: $\epsilon_M^{2064}$ (**1a**) = 4383.2 $cm^2\ mmol^{-1}$.

(17) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85,* 655−657.

(18) Bor, G. *Collect. Pap. Symp. Coord. Chem. Tihany* **1964**, 397−417.

**Scheme 6**



## Conclusion

In the reaction of $Co_2(CO)_8$ with 3-methyl-1,2-butadiene dinuclear $\eta^3$-allyl-type complexes are formed which contain 2, 3, 4, and so on five-carbon units depending on the applied molar ratio. The first two moles of 3-methyl-1,2-butadiene form ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl groups linked together at the central carbon of the allyl group by a carbonyl group. On both cobalt terminals of this complex a 1,2-polymer chain of 3-methyl-1,2-butadiene units can grow between the ($\eta^3$-3,3-dimethylallyl)cobalt tricarbonyl parts and the ketonic carbonyl link. 3-Methyl-1,2-butadiene enters the chain by coupling with its $C_2$ position to the unsubstituted end of the original $\eta^3$-3,3-dimethylallyl part and replacing the latter on the cobalt. The rate of 3-methyl-1,2-butadiene incorporation declines with the number of allene units present in the complex. This allows the preparation of the first three complexes with 2, 3, and 4 allene units, respectively. The structure of these complexes reveal the helical nature of a living polymer containing a ketonic carbonyl group and carbon−carbon double bonds suitable for further chemical modifications.

## Experimental Section

**General.** The solvents were dried in the usual way and stored under carbon monoxide. 3-Methyl-1,2-butadiene (Aldrich) was distilled under a carbon monoxide atmosphere. All reactions were carried out under deoxygenated (BTS catalyst R 3-11) and dry ($P_4O_{10}$) carbon monoxide. Octacarbonyl dicobalt[19] was doubly recrystallized first from $CH_2Cl_2$ and then from n-heptane under carbon monoxide.

Infrared spectra were recorded on a Carl Zeiss Jena Specord IR 75 spectrophotometer in KBr pellets or in 0.030-, 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 $cm^{-1}$). Raman spectra of the solids were recorded on a FT-RAMAN (Bio-Rad) instrument using a Nd laser. All manipulations involving air-sensitive compounds were carried out by standard Schlenk techniques.[20]

$^1H$ and $^{13}C$ NMR spectra were obtained on a Varian Unity 300 spectrometer working in 300- and 75.43-MHz modes, respectively, and were referenced to TMS. Molecular weight measurements were made in benzene or *n*-pentane using a KNAUR (Germany) osmometer calibrated with solutions of squalane and triphenylphosphine.

Analyses (C, H) were performed by the Analytical Department of the University of Veszprém using a CHNSO Analysator (Carlo Erba). Cobalt analyses were performed using established microanalytical methods.

**Reaction of Octacarbonyl Dicobalt with 3-Methyl-1,2-butadiene (A).** (a) To a solution of $Co_2(CO)_8$ (68.4 mg, 0.2 mmol) in *n*-octane (5 mL) under carbon monoxide atmosphere, was added 3-methyl-1,2-butadiene (0.2 mL, 2.0 mmol) at room temperature all at once. Immediate gas evolution (0.2 mmol) occured which ceased in a few minutes while the color of the solution turned to dark yellow. In the course of 3 days an oligomer separated from this solution as a yellow precipitate (85 mg), which was filtered off, washed with *n*-pentane, and dried under CO. Anal. Calcd for $C_{57}H_{80}O_7Co_2$ C, 68.80; H, 8.10; Co, 11.84. Found: C, 67.37; H, 8.43; Co, 11.63. IR spectrum of the yellow filtrate $\nu(C\equiv O)$ (*n*-octane): 2054 (s) and 1985 (vs) $cm^{-1}$. IR of the yellow precipitate $\nu(C\equiv O)$ (in KBr pellet): 2055 (s) and 1984 (vs) $cm^{-1}$.

(b) Performing the above reaction with 0.2 mmol of $Co_2(CO)_8$ and with the gradual addition of the 3-methyl-1,2-butadiene in 0.2 mmol increments resulted in the evolution of 0.2 mmol of gas following the addition of 0.4 mmol of 3-methyl-1,2-butadiene. IR $\nu(C\equiv O)$ (*n*-octane): 2071 (m), 2064 (s), 2012 (s), 2007 (vs), 1998 (s), and 1672 (vw) ($\nu(C{=}O)$) $cm^{-1}$. Addition of another 0.2 mmol of 3-methyl-1,2-butadiene did not result in further gas evolution, but the IR $\nu(CO)$ (*n*-octane) of the reaction mixture changed in 2 h to 2067 (s), 2054 (s), 2010 (s), 2006 (s), 1991 (s), 1987 (s) and 1663 (vw) $cm^{-1}$. Addition of another 0.2 mmol of 3-methyl-1,2-butadiene to the reaction mixture gave no further gas evolution or color change but a new IR spectrum in the $\nu(C\equiv O)$ range at 2052 (s) and 1984 (vs) $cm^{-1}$. Addition of 1.2 mmol of 3-methyl-1,2-butadiene to the reaction mixture did not result in any change of the IR spectrum after 3 days. Addition of 0.6 mL (6 mmol) of 3-methyl-1,2-butadiene to the reaction mixture resulted in the slow formation of a polymer as a yellow precipitate (123 mg) over 10 days. Anal. Calcd for $C_{207}H_{320}O_7Co_2$: C, 81.83; H, 10.61; Co, 3.88. Found: C, 79.55; H, 11.01; Co, 4.01. IR (KBr) $\nu(C\equiv O)$: 2055 (s) and 1984 (vs) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$ 1.76 (6H, $CH_3$), 2.96 (2H, $CH_2$) and traces at 1.26, 1.28, 1.55, 1.67, 1.82, and 2.11. $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.04 ($CH_3$), 34.15 ($CH_2$), 127.33, 127.66, 127.99 ($CH_2C{=}C$), and 132.39 ($(CH_3)_2C{=}C$). Mol wt (osmometric in benzene) 2993.4, calcd for $C_{207}H_{320}O_7Co_2$ 3038.54.

**Preparation of Hexacarbonyl $\mu$-($\eta^{3:3}$-2,4-Diisopropylidene-3-oxopentane-1,5-diyl)dicobalt (1).** To a stirred solution of $Co_2(CO)_8$ (513 mg, 1.5 mmol) in *n*-octane (7.5 mL) under carbon monoxide atmosphere at room temperature a solution of 3-methyl-1,2-butadiene (0.3 mL, 3 mmol) in *n*-octane (2.7 mL) was added in 10 min and was stirred for 4 h. The orange yellow solution obtained was concentrated under vacuum to 4 mL (total volume), and was transferred to the top of an ice-water-cooled 25 × 400 mm column filled with alumina (Brockman II). Flash chromatography under carbon monoxide (1.2 bar) with pentane (200 mL) gave a well-separated yellow main fraction. Concentration at −10 °C to about 4 mL and crystallization at −20 °C gave **1** as yellow crystals (567 mg, 1.26 mmol) in 84% yield based on $Co_2(CO)_8$. Recrystallization from *n*-pentane at −20 °C gave suitable crystals for the X-ray diffraction measurements. Anal. Calcd for $C_{17}H_{16}O_7Co_2$: C, 45.36; H, 3.58; Co, 26.18. Found: C, 44.98; H, 4.20; Co, 25.69. IR (*n*-octane) $\nu(C\equiv O)$: 2071 (m), 2064 (s), 2012 (s), 2007 (vs), 1998 (s), and 1672 (vw) ($\nu(C{=}O)$) $cm^{-1}$. IR (KBr) $\nu(C\equiv O)$: 2075 (s), 2062 (s), 2016 (s), 2005 (s), 2000 (s), 1989 (s), and 1660 (w) ($\nu(C{=}O)$) $cm^{-1}$. Raman (solid) $\nu(C\equiv O)$: 2074.5 (m), 2056.9 (vw), 2019.7 (s), 2006.5 (s), 1997.3 (s), 1983.9 (s), and 1659.8 (w) ($\nu(C{=}O)$) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 1.46 (6H, anti $CH_3$), 1.90, 1.96 (6H, syn $CH_3$), 2.81, 2.82, 3.16, 3.46 (4H, syn and anti H in $CH_2$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 27.38, 27.71, 28.44, 29.13 (syn and anti $CH_3$ ($C_{2''}$, $C_{4''}$ and $C_{2'''}$, $C_{4'''}$)), 45.43, 46.22 ($C_1$ and $C_5$), 85.73, 86.97 ($C_{2'}$ and $C_{4'}$ ), 97.11 ($C_2$ and $C_4$), 197.91, 199.58, 201.69 ($CO$) (cf., Scheme 1 for numbering). Mol wt (in *n*-pentane) 450, calcd for $C_{17}H_{16}O_7Co_2$ 450.17.

**Preparation of Hexacarbonyl $\mu$-($\eta^{3:3}$-2,4,6-triisopropylidene-5-oxoheptane-1,7-diyl)dicobalt (2).** Using the same procedure for the preparation of **1** but to the reaction mixture of $Co_2(CO)_8$ (513 mg, 1.5 mmol) and 3-methyl-1,2-butadiene (0.3 mL, 3 mmol) in *n*-octane (10.5 mL), after 4 h of reaction time another portion of 3-methyl-1,2-butadiene (0.15 mL, 1.5 mmol) in *n*-octane (1.35 mL) was added, and the solution was stirred at room temperature for 10 h. Flash chromatography at 0 °C on alumina (Brockman II) under carbon monoxide (1.2 bar) with pentane (300 mL) gave a yellow second fraction (300 mL). Concentration of the solution to about 4 mL at −10 °C and crystallization at

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(19) Szabó, P.; Markó, L.; Bor, G. *Chem. Tech. (Leipzig)* **1961**, *13*, 549−550.

(20) Shriver, D. F.; Drezdzon, M. A. *The manipulation of Air-Sensitive compounds*; Wiley: Malabar, FL, 1986.

−20 °C gave **2** as yellow crystals (518 mg, 1.00 mmol) in 67% yield. Recrystallization from *n*-pentane at −20 °C gave suitable crystals for the X-ray structure determination. Anal. Calcd for $C_{22}H_{24}O_7Co_2$: C, 50.98; H, 4.66; Co, 22.74. Found: C, 51.00; H, 5.12; Co, 23.22. IR (*n*-octane) $\nu$(C≡O): 2067 (s), 2054 (s), 2010 (s), 2006 (s), 1991 (s), 1987 (s), and 1663 (vw) ($\nu$(C=O)) cm$^{-1}$. IR (KBr) $\nu$(C≡O): 2066 (s), 2052 (vs), 2008 (s), 2001 (s), 1992 (vs), 1964 (s), 1653 (w) ($\nu$(C=O)), and 1645 (vw) ($\nu$(C=C)) cm$^{-1}$. Raman $\nu$(C≡O) (solid): 2054.2 (w), 2051.1 (m), 2003.4 (s), 1990.0 (vs), 1977.1 (s), 1969.4 (m), 1653 (w) ($\nu$(C=O)), and 1645 (m) ($\nu$(C=C)) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.32, 1.34, 1.46, 1.49 (6H, anti $CH_3$), 1.77, 1.78, 1.82, 1.84, 1.96, 2.06, (6H, syn $CH_3$), 2.67, 2.73, 3.14, 3.35 (2H, anti H in $CH_2$), 2.67, 2.76, 3.10, 3.24 (2H, syn H in $CH_2$), 3.00, 3.03, 3.05, 3.09, 3.57, 3.59, 3.62, 3.64 (2H, $CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 20.18, 20.47, 22.82, 22.93 (anti $\mathit{C}H_3$ ($C_{2'''}$ and $C_{6'''}$)), 26.75, 26.98, 28.06, 28.16 ($C_{4''}$), 28.16, 28.35, 28.45, 29.17 (syn $\mathit{C}H_3$ ($C_{2''}$ and $C_{6''}$)), 38.25, 38.92 ($C_3$), 45.87, 46.47, 49.15, 49.59 ($C_1$ and $C_7$ ), 86.75, 87.85, 88.47, 89.58, 90.36, 91.48 ($C_{2'}$ and $C_{6'}$ ), 99.04, 99.75 ($C_2$ and $C_6$), 134.70, 134.79, 134.97, 135.54 ($C_4$, and $C_{4'}$)), 201.5, 201.69, 203.58 (*C*O) ppm (cf., Scheme 1 for numbering). Mol wt (in *n*-pentane) 518.9, calcd for $C_{22}H_{24}O_7Co_2$: 518.29.

**Preparation of Hexacarbonyl $\mu$-($\eta^{3:3}$-2,4,6,8-Tetraisopropylidene-5-oxononane-1,9-diyl)dicobalt (3).** Using the same procedure as in the preparation of **2** but to the rection mixture obtained from $Co_2(CO)_8$ (513 mg, 1.5 mmol) and 3-methyl-1,2-butadiene (0.45 mL, 4.5 mmol) in *n*-octane (11.8 mL) an other portion of 3-methyl-1,2-butadiene (0.15 mL, 1.5 mmol) in *n*-octane (1.35 mL) was added, and the solution was stirred at room temperature for 48 h. Flash chromatography on alumina (Brockman II) at 0 °C under carbon monoxide (1.2 bar) with pentane−methylene dichloride (97:3) mixture (300 mL) gave a well-separated third yellow fraction. Concentration of this solution to about 4 mL at −10 °C and crystallization at −20 °C gave **3** as yellow crystals (615 mg, 1.05 mmol) in 70% yield based on $Co_2(CO)_8$. Crystals obtained by repeated recrystallizations were not suitable for X-ray structure determination. Anal. Calcd for $C_{27}H_{32}O_7Co_2$: C, 55.30; H, 5.50; Co, 20.10. Found: C, 54.94; H, 5.36; Co, 20.31. IR $\nu$(C≡O) (*n*-octane): 2052 (s), 1984 (vs), and 1630 (vw) cm$^{-1}$. IR $\nu$(C≡O) (KBr): 2056 (vs), 2010 (sh), 1997 (sh), 1991 (s), 1971 (s), 1961 (vs), 1619 (sh) ($\nu$(C=O)), and 1608 (m) ($\nu$(C=C)) cm$^{-1}$. Raman $\nu$(C≡O) (solid): 2055.8 (m), 1995.7 (m), 1980.7 (s), 1961.0 (vs), 1619.5 (vw) ($\nu$(C=O)), and1608.5 (w) ($\nu$(C=C)) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.33, 1.82, (12H, syn and anti $CH_3$), 1.87, 1.90 (12H, C=C$(CH_3)_2$), 2.65, 3.10 (4H, syn and anti H in $CH_2$), 3.29 (d, 4H, $CH_2$, $J$ = 15 Hz), 3.44, 3.49 (2H, syn H in $CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.45 (anti $CH_3$ ($C_{2'''}$ and $C_{8'''}$)), 27.31, 28.23 ($C_{4''}$ and $C_{6''}$), 30.89 (syn $CH_3$ ($C_{2''}$ and $C_{8''}$)), 36.13 ($C_3$ and $C_7$), 49.00 ($C_1$ and $C_9$), 87.81 ($C_{2'}$ and $C_{8'}$ ), 100.78 ($C_2$ and $C_8$), 135.83 ($C_{4'}$ and $C_{6'}$), 141.26 ($C_4$ and $C_6$), 201.5, 203.7 (CO) (cf., Scheme 5 for numbering). Mol wt (in *n*-pentane): 576.6, calcd for $C_{27}H_{32}O_7Co_2$: 586.40.

**Preparation of Tricarbonyl (2-Acetyl-$\eta^3$-3,3-dimethylallyl)cobalt (2ac).** To acetylcobalt tetracarbonyl[21] (321 mg, 1.5 mmol) in *n*-octane (9.6 mL) was added 3-methyl-1,2-butadiene (0.15 mL, 1.5 mmol) in *n*-octane (1.35 mL) at room temperature, and the solution was stirred for 45 min. Concentration of the reaction mixture under vacuum at 0 °C to about 3 mL and flash chromatography on alumina (Brockman II) at 0 °C under carbon monoxide (1.2 bar) with pentane (300 mL) or pentane−methylene dichloride (97:3) mixture (30 mL) gave a yellow main fraction. Evaporation of the solvent below 0 °C and crystallization of the residue from pentane (4 mL) at −79 °C gave **2ac** as yellow crystals (312 mg, 1.23 mmol) in 82% yield (mp −30 °C). Anal. Calcd for $C_{10}H_{11}O_4Co$: C, 47.26; H, 4.36; Co, 23.19. Found: C, 48.30; H, 4.45; Co, 22.84. IR (*n*-octane) $\nu$(C≡O): 2068 (s), 2010 (s) 2006 (s), and 1688 (m) ($\nu$(C=O)) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.40 (s, 3H, anti $CH_3$), 1.98 (s, 3H, syn $CH_3$), 2.27 (s, 3H, $COCH_3$), 2.69 (d, 1H, anti H, $J_{gem}$ = 1.76 Hz), 3.32 (d, 1H, syn H, $J_{gem}$ = 1.76 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 25.75 (anti $\mathit{C}H_3$), 28.03 (syn $CH_3$), 29.72 (CO$\mathit{C}H_3$), 45.57 ($C_1$), 88.55 ($C_3$), 90.88 ($C_2$), 200.78 (*C*O$CH_3$), 202 (CO) (cf., Scheme 3 for numbering).

**Preparation of Tricarbonyl (2-Allyl-$\eta^3$-3,3-dimethylallyl)cobalt (2a).** To $\eta^3$-allylcobalt tricarbonyl[23] (276 mg, 1.5 mmol) in *n*-octane (9.0 mL) at room temperature was added 3-methyl-1,2-butadiene (0.2 mL, 2.0 mmol) and the solution was stirred for 5 h. Concentration of the reaction mixture under vacuum at 0 °C to about 3 mL volume and flash chromatography at 0 °C on alumina (Brockman II) under CO (1.2 bar) with pentane (60 mL) gave a yellow main fraction from which **2a** was isolated as a yellow oil (302 mg, 1.2 mmol) in 80% yield by evaporation of the solvent below 0 °C. IR $\nu$(C≡O) (*n*-octane): 2055 (s) ($\epsilon_M^{2055}$ (30 °C) = 3743.6 cm$^2$ mmol$^{-1}$, 1991 (vs), 1987 (vs), and 1639 (vw) ($\nu$(C=C)) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.38 (s, 3H, anti $CH_3$), 1.72 (d, 2H, $J$ = 17 Hz, allylic $CH_2$), 1.81 (s, 3H, syn $CH_3$), 2.71 (s, 1H, anti H), 3.15 (s, 1H, syn H), 5.06 (m, 2H, allylic =$CH_2$), 5.81 (m, 1H, allylic =CH). $^{13}$C NMR ($CDCl_3$): $\delta$ 26.17 (anti $CH_3$), 28.17 (syn $\mathit{C}H_3$), 40.85 ($\mathit{C}H_2CH{=}CH_2$), 48.61 ($C_1$), 88.01 ($C_3$), 99.95 ($C_2$), 116.03 ($CH_2\mathit{C}H{=}CH_2$), 136.15 ($CH_2CH{=}\mathit{C}H_2$), 204 (CO) (cf., Scheme 4 for numbering).

**Kinetic Experiments of the Reaction of Octacarbonyl Dicobalt with 3-Methyl-1,2-butadiene (A).** The reaction under carbon monoxide atmosphere was followed by measuring the initial rates of CO evolution using a gasometric apparatus. In a typical experiment, a Teflon-coated magnetic stirring bar and a solution of $Co_2(CO)_8$ (68.4 mg, 0.2 mmol) in *n*-octane (9.6 mL) were placed in a two-necked, water-jacketed (25 °C) reaction vessel fitted with a reflux condenser (12 °C) connected to a thermostatted gas buret (12 °C), a U-shaped manometer filled with *n*-octane, and a silicon-disk-capped stopcock. The reaction was started by injecting 3-methyl-1,2-butadiene in a 1 M solution in *n*-octane (0.4 mL). The initial rate was calculated from the gas buret readings collected in the first 1−3 min (3−9 points). The effect of carbon monoxide concentration on the rate of gas evolution was studied by using different total pressures (0.5−3.4 bar) in the gasometric apparatus. The rates are reproducible to within 5%.

**Kinetic Experiments of the Reaction of Hexacarbonyl $\mu$-($\eta^{3:3}$-2,4-Diisopropylidene-3-oxopentane-1,5-diyl)dicobalt (1) with 3-Methyl-1,2-butadiene (A).** The reaction was followed by measuring the decrease of the absorbance of the reaction mixture at 2071 cm$^{-1}$ using the above apparatus, but circulating the reaction mixture through an IR cuvette (0.021 cm $CaF_2$) by the means of a syringe pump (Hamilton) and Teflon spaghetti (gauge 18). The molar absorbance of **1** in *n*-octane at 30 °C is $\epsilon_M^{2071}(\mathbf{1}) = 2701.5$ cm$^2$ mmol$^{-1}$. Initial rates were calculated from the measured absorbances in the first few minutes. The rates are reproducible to within to 10%.

**Kinetic Experiments of the Reaction of Hexacarbonyl $\mu$-($\eta^{3:3}$-2,4,6-Triisopropylidene-5-oxoheptane-1,7-diyl)dicobalt (2) with 3-Methyl-1,2-butadiene (A).** The reaction was followed by measuring the decrease of the absorbance of the reaction mixture at 2067 cm$^{-1}$ using the above apparatus. The molar absorbance of **2** in *n*-octane at 30 °C is $\epsilon_M^{2067}(\mathbf{2}) = 4383.2$ cm$^2$ mmol$^{-1}$. Initial rates were calculated from the measured absorbances in the first few minutes. The rates are reproducible to within 7%.

**Kinetic Experiments of the Reaction of Tricarbonyl (2-Acetyl-$\eta^3$-3,3-dimethylallyl)cobalt (2ac) with 3-Methyl-1,2-butadiene (A).** The reaction was followed in two independent ways. (a) The reaction was monitored by applying infrared spectroscopy and measuring the decrease of the absorbance of the reaction mixture at 2068 cm$^{-1}$ using the above apparatus. The molar absorbance of **2ac** in *n*-octane at 30 °C is $\epsilon_M^{2068}$ (**2ac**) = 4966.8 cm$^2$ mmol$^{-1}$. Initial rates were calculated from the measured absorbances in the first few minutes. In a typical experiment at 30 °C, [**2ac**] = 0.553 × $10^{-2}$ M, [**A**] = 2.913 × $10^{-2}$ M, and [CO] = 1.052 × $10^{-2}$ M, and the initial rate $r_{\mathbf{2ac}}$ of 8.84 × $10^{-7}$ M s$^{-1}$ was measured. The calculated rate constant for this measurement $k_{\mathbf{2ac}}$ (30 °C) = $r_{\mathbf{2ac}}$[CO]/[**2ac**][**A**] = 5.77 × $10^{-5}$ s$^{-1}$. (b) By using $^1$H NMR technique, the rate data were collected by measuring the decrease of the 3-methyl-1,2-butadiene multiplet between 4.51 and 4.53 ppm of the reaction mixtures. In a typical experiment at 30 °C, [**2ac**] = 5.94 × $10^{-2}$ M, [**A**] = 10.08 × $10^{-2}$ M, [CO] = 1.052 × $10^{-2}$ the initial rate $r_{\mathbf{2ac}}$ = 3.08 × $10^{-5}$ M s$^{-1}$ was measured. The calculated rate constant for this measurement is $k_{\mathbf{2ac}}$ (30 °C) =

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[21] Prepared from ketene and hydridotetracarbonylcobalt according to ref 22.

[22] Ungváry, F. *J. Organomet. Chem.* **1986**, *303*, 251−255.

[23] Prepared from allyl bromide and sodium tetracarbonylcobaltate according to refs 17 and 24.

[24] Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097−1102.

**Table 4.** Pertinent Crystallographic Information for Complexes **1** and **2**

| | **1** | **2** |
|---|---|---|
| empcl form | $C_{17}H_{16}O_7Co_2$ | $C_{22}H_{24}O_7Co_2$ |
| form wt | 450.18 | 518.29 |
| space group | $P\bar{1}$ | $P2_1/a$ |
| $a$, Å | 7.093(1) | 17.732(1) |
| $b$, Å | 9.897(1) | 7.0943(7) |
| $c$, Å | 13.790(1) | 20.284(3) |
| $\alpha$, deg | 86.99(1) | 90.0 |
| $\beta$, deg | 85.97(1) | 109.246(8) |
| $\gamma$, deg | 79.57(1) | 90.0 |
| $V$, Å$^3$ | 949.0(2) | 2408.9(4) |
| Z | 2 | 4 |
| radiation | Cu($\bar{\alpha}$) | Cu($\bar{\alpha}$) |
| $D_{\mathrm{calc}}$, g/cm$^3$ | 1.575 | 1.429 |
| $\mu$ (Cu K$\alpha$), mm$^{-1}$ | 140.15 | 111.18 |
| R | 0.070 | 0.044 |
| $R_{\mathrm{w}}$ | 0.081 | 0.045 |
| goodness of fit | 4.25 | 2.83 |
| unique reflns measd | 3893 | 5361 |
| no. observns ($I > 3\sigma(I)$) | 1999 | 1288 |
| parameters refined | 236 | 280 |
| refln/param ratio | 8.47 | 4.60 |

**Table 5.** Selected Bond Lengths and Estimated Standard Deviations (in Parentheses) (Å) for Structures **1** and **2**

| structure **1** | | structure **2** | |
|---|---|---|---|
| Co(1)−C(1) | 1.80(1) | Co(1)−C(1) | 1.77(1) |
| Co(1)−C(2) | 1.78(2) | Co(1)−C(2) | 1.81(1) |
| Co(1)−C(3) | 1.77(1) | Co(1)−C(3) | 1.76(1) |
| Co(2)−C(4) | 1.78(1) | Co(2)−C(4) | 1.78(1) |
| Co(2)−C(5) | 1.82(1) | Co(2)−C(5) | 1.78(2) |
| Co(2)−C(6) | 1.79(2) | Co(2)−C(6) | 1.75(1) |
| Co(1)−C(11) | 2.10(1) | Co(1)−C(11) | 2.03(1) |
| Co(1)−C(12) | 1.99(1) | Co(1)−C(12) | 2.00(1) |
| Co(1)−C(13) | 2.17(1) | Co(1)−C(13) | 2.12(1) |
| Co(2)−C(21) | 2.08(1) | Co(2)−C(31) | 2.07(1) |

$r_{\mathbf{2ac}}[\mathrm{CO}]/[\mathbf{2ac}][\mathbf{A}] = 5.41 \times 10^{-5}\ \mathrm{s}^{-1}$. The rates obtained by both methods are reproducible to within 6%.

**Kinetic Experiments of the Reaction of Tricarbonyl (2-Allyl-$\eta^3$-3,3-dimethylallyl)cobalt (2a) with 3-Methyl-1,2-butadiene (A).** The reaction was followed by the above NMR technique. In a typical experiment at 30 °C, $[\mathbf{2a}] = 7.0 \times 10^{-2}$ M, $[\mathbf{A}] = 12.57 \times 10^{-2}$ M, $[\mathrm{CO}] = 1.051 \times 10^{-2}$ M, and the initial rate $r_{\mathbf{2a}} = 4.56 \times 10^{-6}$ M s$^{-1}$ was measured. The calculated rate constant for this measurement is $k_{\mathbf{2a}}$ (30 °C) $= r_{\mathbf{2a}}[\mathrm{CO}]/[\mathbf{2a}][\mathbf{A}] = 5.45 \times 10^{-6}\ \mathrm{s}^{-1}$. The rates are reproducible to within 6%.

**X-ray Diffraction Analysis.** Crystals of **1** and **2** were mounted in glass capillaries and sealed from the atmosphere. Cell dimensions were determined from 25 accurately centered reflections in the range of $15 < \theta < 40°$. Pertinent crystallographic information is supplied in Table 4. Absorption corrections were applied *via* $\Psi$-scan measurements[25] (**1**, transmission range of 47−100%; **2**, transmission range of 74−100%); no significant decomposition of either crystal was observed in the three standard intensity measurements made every 2 h. All structural computations were performed using TEXSAN.[26] Structures were solved through direct methods[27] and refined by full matrix least squares. Hydrogen atom positions were calculated and included in the least squares refinement with fixed parameters. ORTEP[28] diagrams of **1** and **2** are shown in Figures 3 and 4. Selected bond lengths and angles are provided in Tables 5 and 6. One technical difficulty with structure **2** was a nonpositive definite anisotropic temperature factor for atom C(12); the ORTEP diagram was produced using a positive isotropic factor. The likely cause for the nonpositive temperature factor was the relatively low reflection/parameter ratio for **2** leading to Fourier series termination effects.

**Table 6.** Selected Bond Angles (deg) and Estimated Standard Deviations (in Parentheses) for Structures **1** and **2**

| structure **1** | | structure **2** | |
|---|---|---|---|
| C(1)−Co(1)−C(2) | 107.3(6) | C(1)−Co(1)−C(2) | 101.1(6) |
| C(1)−Co(1)−C(3) | 104.4(7) | C(1)−Co(1)−C(3) | 99.5(6) |
| C(2)−Co(1)−C(3) | 96.2(6) | C(2)−Co(1)−C(3) | 103.7(6) |
| C(1)−Co(1)−C(11) | 97.7(6) | C(1)−Co(1)−C(11) | 154.5(5) |
| C(1)−Co(1)−C(12) | 123.2(6) | C(1)−Co(1)−C(12) | 114.0(5) |
| C(1)−Co(1)−C(13) | 103.5(6) | C(1)−Co(1)−C(13) | 92.1(5) |
| C(2)−Co(1)−C(11) | 90.6(6) | C(2)−Co(1)−C(11) | 98.8(5) |
| C(2)−Co(1)−C(12) | 109.0(5) | C(2)−Co(1)−C(12) | 125.2(5) |
| C(2)−Co(1)−C(13) | 146.2(5) | C(2)−Co(1)−C(13) | 103.7(5) |
| C(3)−Co(1)−C(11) | 153.7(5) | C(3)−Co(1)−C(11) | 91.2(5) |
| C(3)−Co(1)−C(12) | 113.3(6) | C(3)−Co(1)−C(12) | 110.0(5) |
| C(3)−Co(1)−C(13) | 89.2(5) | C(3)−Co(1)−C(13) | 147.6(5) |
| C(11)−Co(1)−C(12) | 40.9(4) | C(11)−Co(1)−C(12) | 40.5(4) |
| C(11)−Co(1)−C(13) | 71.7(4) | C(11)−Co(1)−C(13) | 67.7(4) |
| C(12)−Co(1)−C(13) | 40.0(4) | C(12)−Co(1)−C(13) | 38.4(3) |
| C(4)−Co(2)−C(5) | 104.4(6) | C(4)−Co(2)−C(5) | 105.5(6) |
| C(4)−Co(2)−C(6) | 96.1(7) | C(4)−Co(2)−C(6) | 106.3(7) |
| C(5)−Co(2)−C(6) | 105.5(7) | C(5)−Co(2)−C(6) | 96.8(7) |
| C(4)−Co(2)−C(21) | 88.9(6) | C(4)−Co(2)−C(31) | 101.0(5) |
| C(4)−Co(2)−C(22) | 114.1(6) | C(4)−Co(2)−C(32) | 123.7(5) |
| C(4)−Co(2)−C(23) | 154.9(5) | C(4)−Co(2)−C(33) | 99.8(5) |
| C(5)−Co(2)−C(21) | 103.7(6) | C(5)−Co(2)−C(31) | 92.0(6) |
| C(5)−Co(2)−C(22) | 122.7(5) | C(5)−Co(2)−C(32) | 112.2(6) |
| C(5)−Co(2)−C(23) | 94.7(5) | C(5)−Co(2)−C(33) | 149.7(6) |
| C(6)−Co(2)−C(21) | 148.1(6) | C(6)−Co(2)−C(31) | 147.8(5) |
| C(6)−Co(2)−C(22) | 110.5(6) | C(6)−Co(2)−C(32) | 108.9(6) |
| C(6)−Co(2)−C(23) | 94.3(6) | C(6)−Co(2)−C(33) | 91.7(6) |
| C(21)−Co(2)−C(22) | 40.5(4) | C(31)−Co(2)−C(32) | 39.8(4) |
| C(21)−Co(2)−C(23) | 70.6(5) | C(31)−Co(2)−C(33) | 66.7(5) |
| C(22)−Co(2)−C(23) | 40.8(4) | C(32)−Co(2)−C(33) | 38.0(4) |

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**Supporting Information Available:** Crystallographic data for **1** and **2** including experimental details, structure solution and refinement information, and tables of positional and thermal parameters and interatomic distances and angles (24 pages). See any current masthead page for ordering and Internet access instructions.

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