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Kinetics and Mechanism of the Reaction of $HCo(CO)_4$ with 2,3-Dimethyl-1,3-butadiene[1]

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Spectroscopic evidence and the kinetics of CO uptake in the reaction of $HCo(CO)_4$ (1) with 2,3-dimethyl-1,3-butadiene (2) are consistent with a rate-determining concerted 1,4 addition of 1 to the s-cis conformation of 2 forming (2,3-dimethyl-2-butenyl)cobalt tetracarbonyl (3): $k_1^{5 °C} = 1.42 \times 10^{-2}\ M^{-1}\ s^{-1}$ ($k_1^{5 °C} = 1.79 \times 10^{-2}\ M^{-1}\ s^{-1}$ with $DCo(CO)_4$). The intermediate 3 successively (a) rearranges in a first-order reaction to (3,4-dimethyl-3-pentenoyl)cobalt tricarbonyl (4), which in turn adds CO to form (3,4-dimethyl-3-pentenoyl)cobalt tetracarbonyl (5), and (b) reacts with 1 in a bimolecular homolytic displacement reaction leading to 2,3-dimethyl-1-butene where a H atom is abstracted from 1 by the γ-carbon atom of 3 and simultaneously $\cdot Co(CO)_4$ is eliminated. The ratio of the rate constants of these two competing fast reactions is 20.7 M^{-1} (12.5 M^{-1} in the case with $DCo(CO)_4$) at 5 °C.

Introduction

The reaction of $HCo(CO)_4$ with the olefinic double bond is regarded as one of the steps in the cobalt-catalyzed hydroformylation reaction.[2] The stoichiometric reaction between conjugated diolefins and $HCo(CO)_4$ has been studied previously, and the resulting complexes have been described.[3] Simultaneously with complex formation, hydrogenation of diolefin to monoolefin occurs. It was suggested that the monoolefin arises through an η^1 complex formed by the 1,4 addition of $HCo(CO)_4$ to the diolefin and the η^3-allyl type complex is a byproduct rather than an intermediate of monoolefin formation.[4] Later it has been suggested that in the case of 1,3-butadiene the *cis*-η^1-butenyl complex is probably the principal intermediate of 1-butene formation but that also the η^3-methallyl complexes could be precursors to 1-butene and other butenes as well.[5]

Now we report the results of our kinetic study that allows a more detailed description of the reactions between $HCo(CO)_4$ and conjugated diolefins. In our experiments 2,3-dimethyl-1,3-butadiene has been used mainly as a model substrate.

Results

Conjugated diolefins absorbed CO in the presence of $HCo(CO)_4$, but after a rapid CO uptake slow evolution of CO occurred. Table I shows the initial rates of CO uptake (r_{CO}) and CO release (r_{-CO}) and the maximum amounts of CO absorbed (CO_{max}) and then released ($-CO_{max}$) for various conjugated diolefins.

The comparison of the initial CO absorption rates in Table I shows that the straight-chain trans diolefins were more reactive than the cis ones and that two substituents in the 1,4-positions were unfavorable but not so if they were in the 2,3-positions. High reactivity was found for cyclic diolefins.

The data in Table I show also that added $Co_2(CO)_8$ had practically no influence[6] on r_{CO}, CO_{max}, and r_{-CO}. The very slow CO evolution in the experiments when no $HCo(CO)_4$ was present at the beginning was due to the formation of some (η^4-2,3-dimethyl-1,3-butadiene)dicobalt hexacarbonyl that could be detected in the infrared spectrum of the reaction mixture by its characteristic bridging ν(CO) band at 1839 cm^{-1}.[7]

With use of $DCo(CO)_4$ instead of $HCo(CO)_4$, higher values of r_{CO} and CO_{max} could be observed. Changing the solvent *n*-heptane for Nujol resulted in lower values of r_{CO}, r_{-CO}, and CO_{max}.

The characteristic changes of the terminal ν(CO) bands in the infrared spectrum of the reaction mixture (after removal of $Co_2(CO)_8$ by crystallization at −79 °C) in the case of isoprene and 2,3-dimethyl-1,3-butadiene are shown in Figure 1. At the end of CO absorption a mixture of acyl- and alkylcobalt tetracarbonyls was present[8] (Figure 1a). The ratio of these compounds could be roughly estimated from the spectra by assuming the same molar absorbancies for the highest (A_1) ν(CO) bands of the acyl- and alkyl compounds. In this way acyl/alkyl ratios of 1/1, 4/1, 9/1, and 15/1 were calculated in the products obtained from isoprene, 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene, and 1,3-cyclohexadiene, respectively. The successive transformation of these complexes into η^3-allyl-type cobalt tricarbonyls was the reason for the slow CO evolution that followed. During this process the acyl/alkyl ratio remained unchanged (Figure 1b). At the end of CO evolution the amount of released CO and the infrared

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(1) Presented in part at the 22nd ICCC, Budapest, 1982; Abstract Fr P 62.

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(8) Typical infrared spectra of acylcobalt tetracarbonyls[9] show four and those of alkylcobalt tetracarbonyls[9,10] three terminal ν(CO) bands. The highest band for the acyl appears at somewhat higher wavenumbers[11] than for the related alkyl, and the two bands are usually well resolved even in the case of acyl–alkyl mixtures.[12] In our case these bands appeared in *n*-heptane solution at 2103 and 2091 cm^{-1} starting from 2,3-dimethyl-1,3-butadiene and at 2103.4 and 2093.3 cm^{-1} starting from isoprene.

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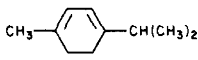
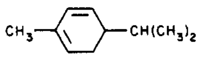
Table I. Initial Rates and the Maxima of CO Uptake and Release in the Reaction of $HCo(CO)_4$ (0.0208 M) with Conjugated Diolefins (0.140 M) in *n*-Heptane Solution at 10 °C under CO at Atmospheric Pressure

	$10^6 r_{CO}$, M s^{-1}	CO_{max}[a]	$10^6 r_{-CO}$, M s^{-1}	$-CO_{max}$[a]
trans-1,3-pentadiene	81	0.50 (0.09)	5.3	0.56 (36)
cis-1,3-pentadiene	73	0.41 (0.08)	4.0	
trans,trans-2,4-hexadiene	1.0	(1)[b]		
cis,trans-2,4-hexadiene	0.4	(3)[b]		
isoprene	28.8	0.37 (0.20)	1.7	0.99 (10)
	29.1[c]	0.37[c] (0.20)	1.8[c]	
	37.0[d]	0.38[d] (0.18)	1.52[d]	0.97 (20)
2,3-dimethyl-1,3-butadiene			0.02[e]	
	61.2	0.37 (0.10)	0.89	0.64 (26)
	60.7[c]	0.37[c] (0.10)	0.92[c]	
	82.2[d]	0.46[d] (0.09)	0.89[d]	
	29.2[f]	0.31[f] (0.20)	0.57[f]	
1,3-cyclohexadiene	73.2	0.48 (0.14)	2.0	0.49 (9)
	70.1[c]	0.48[c] (0.14)	2.1[c]	
	107.0[d]	0.52[d] (0.10)	1.5[d]	0.54[d] (10)
1,3-cyclopentadiene	4.9	0.09 (0.40)		
 [g]	1.6	0.03 (0.30)		
 [h]	32.1	0.14 (0.05)	2.7	
	33.6[c]	0.14[c] (0.05)	2.7[c]	

[a] mol of CO/mol of $HCo(CO)_4$, time necessary (hours). [b] >50% $HCo(CO)_4$ unreacted. [c] In the presence of initially added $[Co_2(CO)_8]$ = 0.0344 M. [d] With $DCo(CO)_4$. [e] In the presence of initially added $[Co_2(CO)_8]$ = 0.0344 M but without adding $HCo(CO)_4$. [f] In Nujol solution. [g] α-Terpinene. [h] (*R*)-(−)-α-Phellandrene.

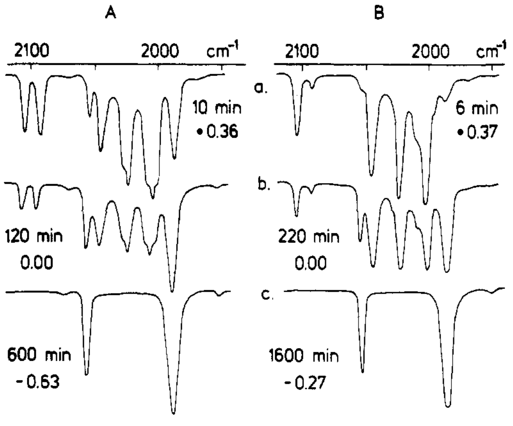


Figure 1. Characteristic changes of the terminal ν(CO) bands in the infrared spectrum of reaction mixtures of $HCo(CO)_4$ with isoprene (A) or with 2,3-dimethyl-1,3-butadiene (B), after $Co_2(CO)_8$ was frozen out at −79 °C. Reaction conditions: 10 °C; 1 bar of CO. Initial concentrations: $[HCo(CO)_4]$ = 0.0208 M and [diene] = 0.140 M in *n*-heptane solution. Reaction time (min) and amount of CO absorbed (+) or released (−) as mol of CO/mol of $HCo(CO)_4$ are indicated.

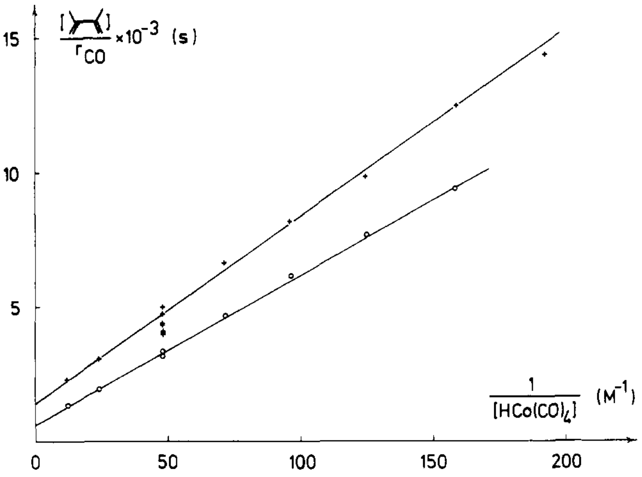


Figure 2. [2]/r_{CO} against 1/$[HCo(CO)_4]$ for the reaction of 2,3-dimethyl-1,3-butadiene with $HCo(CO)_4$ under atmospheric pressure of CO at 5 °C in *n*-heptane solution: o, experiments using $DCo(CO)_4$.

spectra (Figure 1c) showed the quantitative transformation of all acyl and alkyl complexes into η^3-allyl-type cobalt tricarbonyls.[13] The CO evolution could not be reversed with 80 bar of CO at 25 °C in 10 h.[14]

The products and the rates of their formation were investigated in detail in the case of 2,3-dimethyl-1,3-butadiene as the substrate.

The products formed from $HCo(CO)_4$ and 2,3-dimethyl-1,3-butadiene under CO depended on the concentration of the reactants (Table II). At high concentrations of $HCo(CO)_4$ only small amounts of CO were absorbed and $HCo(CO)_4$ was consumed mainly in hydrogenation reactions. The major hydrogenated product was 2,3-dimethyl-1-butene accompanied by minor amounts of 2,3-dimethyl-2-butene as could be checked by GC and ^1H NMR[16] analyses. Increasing CO pressure from 1 to 80 bar, the amount and the composition of hydrogenated products

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[13] Kemmitt, R. D. W.; Russel, D. R. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 5, pp 211–222.

[14] To achieve CO uptake in (η^3-allyl)$Co(CO)_3$, in frozen CO matrix, irradiation is necessary.[15]

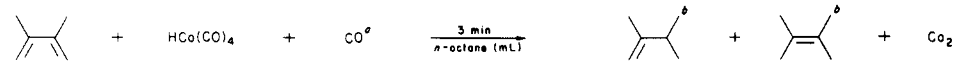
[15] Rest, A. J., Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1291.

[16] Performing the reaction in an NMR tube by mixing $HCo(CO)_4$ and 2,3-dimethyl-1,3-butadiene in 1:1 molar ratio at −79 °C in CH_2Cl_2 solution and recording the spectra between 0.5 and 3 ppm (δ) repeatedly every 20 s in a way similar to that described in ref 17, the growing signals assigned to 2,3-dimethyl-1-butene [δ 0.98 (6 H, d), 1.70 (3 H, s)] and 2,3-dimethyl-2-butene [δ 1.62 (12 H, s)] could be observed. In contrary to observations with 1,1-diphenylethylene[17] and styrene,[18] these signals did not show anomalous intensities. The ratio of 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene remained constant within one experiment, but values of 11 and 5 were observed if the concentrations of **1** were 0.6 and 0.01 M and those of **2** 0.3 and 0.2 M, respectively. At the end of the reaction only traces of aldehydes [δ 9.64 (CHO)] could be detected in the spectra.

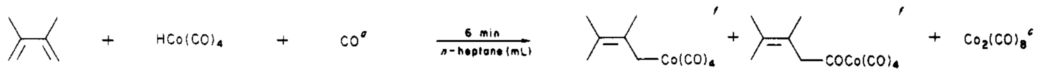
[17] Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222.

[18] Bockman, T. M.; Garst, J. F.; King, R. B.; Markó, L.; Ungváry, F., unpublished CIDNP observations in the reaction of styrene with $HCo(CO)_4$: the hydrogenated product ethylbenzene shows an emission at δ 1.16 (t) and an enhanced absorption at δ 2.56 (q); among the carbonylated products phenyl methyl ketene shows an enhanced absorption at δ 2.00 (s).

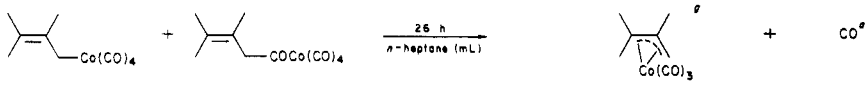
Table II. Effect of Concentrations on Product Composition in the Reaction of $HCo(CO)_4$ with 2,3-Dimethyl-1,3-butadiene under CO at Atmospheric Pressure at 10 °C



mmol	0.70	1.20	0.04	(2)	0.54	0.05	0.59
mmol	0.70	1.20	*d*	(2)	0.53	0.05	0.58
mmol	0.70	1.20[e]	0.07	(2)	0.53	0.05	0.58
mmol	0.70	1.20	0.06	(10)	0.49	0.05	0.50
mmol	0.70	1.20[e]	0.11	(10)	0.49	0.05	0.53



mmol	1.9	0.28	0.10	(13)	0.02	0.08	0.09
mmol	7.5	0.15	0.09	(29)	0.02	0.08	0.025
mmol	7.5	0.15[e]	0.10	(29)	0.02	0.09	0.02



mmol	0.02	0.08	(13)	0.10	0.18

[a] Measured gasometrically. [b] Determined by gas chromatography using *n*-nonane as internal standard. [c] Determined by an infrared spectrographic method using the known molar absorbance of $Co_2(CO)_8$: Spindler, F.; Bor, G.; Dietler, U. K.; Pino, P. *J. Organomet. Chem.* **1981**, *213*, 303. [d] Reaction performed under 80 bar of CO pressure; CO uptake was not measured. [e] $DCo(CO)_4$. [f] Sums of $RCo(CO)_4$ and $RCOCo(CO)_4$ were calculated from the differences between the total cobalt and $Co_2(CO)_8$ concentrations. $RCo(CO)_4$ and $RCOCo(CO)_4$ ratios were estimated by assuming the same molar absorbancies for the A_1 ν(CO) bands of the alkyl and acyl complexes. [g] Based on infrared spectrum, calculated from the total cobalt.

did not change. At low concentrations of $HCo(CO)_4$ and high concentrations of 2,3-dimethyl-1,3-butadiene, CO absorptions up to 0.69 mol/mol of $HCo(CO)_4$ occurred and besides minor amounts of hydrogenated products, mainly, an acyl-type[9] and an alkyl-type[10] cobalt tetracarbonyl, could be detected in the reaction mixture by IR spectroscopy. These complexes decomposed on standing at 10 °C quantitatively into (2,3-dimethyl-η^3-butenyl)cobalt tricarbonyl, giving off the calculated amount of CO. The material balances (Table II), ^1H NMR spectra,[16] and IR spectra[19] showed only very little aldehyde formation during CO uptake.

When Ph_3P or 2,4-dinitrophenylhydrazine was added to the reaction mixture after CO uptake, (3,4-dimethyl-3-pentenoyl)cobalt tricarbonyl triphenylphosphine[20] (in 40% yield based on $HCo(CO)_4$) or a mixture of (2,4-dinitrophenylhydrazones of unsaturated C_7 aldehyde isomers[21] (in less than 1% yield based on $HCo(CO)_4$) was isolated. The Ph_3P-substituted derivative of the alkylcobalt carbonyl could not be observed in the IR spectrum even immediately after Ph_3P addition.

The reaction between 2,3-dimethyl-1,3-butadiene and $HCo(CO)_4$ under CO was followed by measuring the rate of CO uptake. Table III compiles the results of these kinetic measurements. The initial rates of CO uptake were approximately first order in diene and zero order in CO. The order in $HCo(CO)_4$ was between zero and one. The amount of absorbed CO increased by raising the initial concentration of the diene or by lowering the initial concentration of $HCo(CO)_4$. The rate of CO evolution (r_{-CO}) during (2,3-dimethyl-η^3-butenyl)cobalt tricarbonyl formation showed a negative dependence on CO concentration.

Table III. Initial Rates of CO Uptake (r_{CO}) and the Maxima of CO Absorption (CO_{max}) in the Reaction of $HCo(CO)_4$ (1) with 2,3-Dimethyl-1,3-butadiene (2) in *n*-Heptane Solution under Various Conditions

temp, °C	$10^2[1]$, M	$10^2[2]$, M	$10^2[CO]$,[a] M	$10^6 r_{CO}$, M s^{-1}	CO_{max},[b] mol/mol of 1
5	2.08	56.0	0.97	111	0.52
5	0.52	28.0	0.98	19.5	0.68
5	0.63	28.0	0.98	22.3	0.65
5	0.63[c]	28.0	1.00	29.6	0.68
5	0.80	28.0	0.98	28.4	0.62
5	0.80[c]	28.0	1.00	36.2	0.65
5	1.04	28.0	0.98	33.8	0.55
5	1.04[c]	28.0	1.00	45.0	0.62
5	1.40	28.0	0.98	41.6	0.50
5	1.40[c]	28.0	1.00	59.6	0.59
5	2.08	28.0	0.99	58.9	0.44
5	2.08[c]	28.0	0.99	83.7	0.53
5	4.16	28.0	0.98	91.7	0.34
5	4.16[c]	28.0	1.00	140.8	0.43
5	8.32	28.0	0.98	121.3	0.21
5	8.32[c]	28.0	0.99	202.6	0.30
5	2.08	14.0	0.99	32.3	0.37[d]
5	2.08	14.0	2.29	34.7	0.39[e]
5	2.08	14.0	3.01	35.0	0.39
5	2.08[c]	14.0	0.99	44.0	0.47
5	2.08	7.0	0.99	15.9	0.31
5	2.08	3.5	0.98	8.1	0.24
5	2.08	3.5	2.26	8.7	0.28
10	0.53	25.0	1.02	25.5	0.62
10	1.04	3.5	1.03	12.0	0.33
10	2.08	3.5	1.02	16.0	0.22
10	2.08	7.0	1.02	32.0	0.30
10	4.16	7.0	1.03	47.7	0.19

[a] Calculated from p_{CO} and the solubility of CO in *n*-heptane (Gjaldbaek, J. C. *Acta Chem. Scand.* **1952**, *6*, 623; Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363). [b] After the CO uptake ceased a slow CO evolution began. The initial rate of this CO evolution (r_{-CO}) is given in two cases in order to show its dependence on CO concentration: [d] $r_{-CO} = 0.6 \times 10^{-6}$ M s^{-1}; [e] $r_{-CO} = 0.3 \times 10^{-6}$ M s^{-1}. [e] $DCo(CO)_4$.

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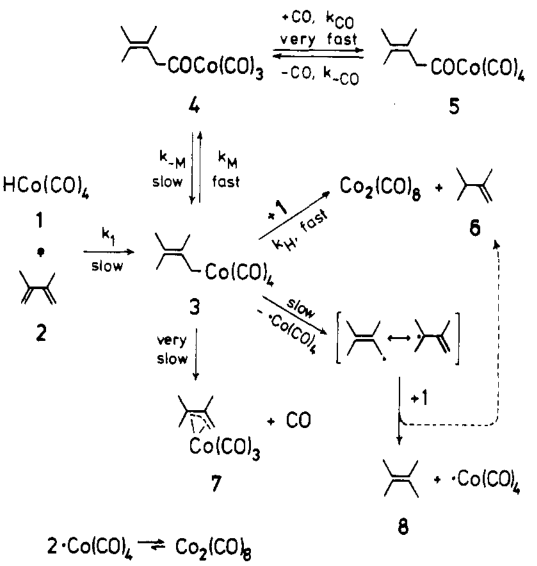
(19) The aldehyde formed in the reaction showed a ν(CO) band at 1718 cm^{-1} in heptane solution. With use of $DCo(CO)_4$ in the reaction this band appeared at 1707 cm^{-1}.

(20) The preparation of this compound was described in ref 3e, although its structure was only assumed. This turned out to be correct as shown by its ^1H NMR spectrum [δ (C_6D_6) 1.52 (3 H, s, 3-CH_3), 1.67 (3 H, s, 4-CH_3 (*Z*)), 1.73 (3 H, s, 4-CH_3 (*E*)), 4.05 (2 H, s, CH_2), 6.92 (9 H, m, *o,p*-C_6H_5), 7.38 (6 H, m, *m*-C_6H_5)]. With use of $DCo(CO)_4$ in the preparation the ^1H NMR spectrum was identical with the exception that at δ 1.67 only 2 H appeared according to the monodeuterization of the 4-CH_3 (*Z*).

(21) TLC chromatography on silica gel showed the presence of three isomers having the same M^+ 292 in their mass spectra.

Scheme I



Discussion

The experimental results can be explained by assuming the rate-determining formation of an intermediate from the diene and HCo(CO)$_4$, followed by competing reactions leading to the products **5**, **6**, **7**, and **8** (Scheme I).

The formation of **7** under 1 bar of CO is very slow in comparison to that of **5**, **6**, and **8**. Since **8** is formed only in minor amounts, the main competition in the early stages of the reaction is between the formation of **4** and **6**. Because the equilibrium between **4** and **5** is nearer to the side of **5**, the observed rate of CO uptake (r_{CO}) is the same as the rate of formation of **4** from **3** by alkyl migration.

With the assumption of steady-state concentration for the intermediate **3**, r_{CO} can be described under these simplified conditions by eq 1 or after rearrangement (eq 2).

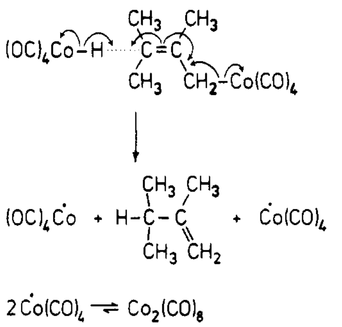
$$r_{CO} = -dCO/dt = k_1 k_M[1][2]/(k_M + k_H[1]) \qquad (1)$$

$$[2]/r_{CO} = 1/k_1[1] + k_H/k_1 k_M \qquad (2)$$

Rate equation (2) describes the experimentally observed orders for **1**, CO, and **2**. With use of the data obtained at 5 °C (Table III) and a plot of $[2]/r_{CO}$ against $1/[1]$, the experimental points give straight lines (Figure 2), where k_1 and the ratio k_H/k_M can be calculated from the slope and the intercept. For HCo(CO)$_4$ and DCo(CO)$_4$ we obtain $k_1 = 1.42 \times 10^{-2}$ and 1.79×10^{-2} M^{-1} s^{-1} and $k_H/k_M = 20.7$ and 12.5 M^{-1}, respectively. These data show an inverse kinetic isotope effect for the rate-determining step and a normal one for the hydrogenation if we assume that there is no effect on k_M.

The inverse kinetic isotope effect is similar to that of the reaction between HCo(CO)$_4$ and 1,1-diphenylethylene[22] or styrene[23] where the intermediate formation of radical pairs was proven unambiguously by CIDP experiments[17,18] and a solvent viscosity effect.[24] No CIDNP effect has been found in the present system, and so there is no support for radical pair intermediates in the reaction of **1** and **2**. Some conclusions regarding the mechanism of this step can be drawn, however, from the influence of the diolefin structure on the rate of the reaction (Table I). These rates can be rationalized by assuming a rate-determining 1,4 addition of the H–Co bond to the diene in the s-cis conformation. Indeed, in the case of cyclic dienes, where the two double bonds are fixed in the s-cis conformation, significantly higher reactivities were found. On the other hand the reactivity of open chain dienes depended on the equilibrium constant for the conformational interconversion. As known from the Diels–Alder reaction, a cis 1-substituent favors the s-trans form and thus causes lower reactivity than a trans 1-substituent, whereas a 2-substituent or 2,3-substituents favor the s-cis form and lead to enhanced reactivities in comparison to the unsubstituted or less substituted diene. A similar pattern of reactivities has been reported recently[25] in the reaction of HFe(CO)$_4$SiCl$_3$ with conjugated dienes. On the basis of these observations, we suggest that the 1,4 addition of HCo(CO)$_4$ to conjugated dienes is a concerted reaction.

Scheme II



The formation of **6** does not depend on CO and shows a normal kinetic isotope effect. These facts are in sharp contrast to the observations made with the HCo(CO)$_4$ + heptene reaction[6] and the reduction of (ethoxycarbonyl)methylcobalt tetracarbonyl by **1**,[26] where negative dependencies on CO and practically no kinetic isotope effects were found with DCo(CO)$_4$. These differences strongly suggest that the formation of **6** from **3** and **1** proceeds by another way. As the main pathway we propose a homolytic displacement reaction[27] in which a H atom is abstracted from **1** by the γ-carbon atom of **3** and simultaneously ·Co(CO)$_4$ is eliminated (Scheme II).

The small amount of 2,3-dimethyl-2-butene (**8**) is certainly not the result of a subsequent isomerization of **6** because the ratio of butenes during their formation is constant and independent of CO pressure. The ratio **6**/**8** is, however, higher if the ratio of **1**/**2** is higher or the reaction of **1** with **2** occurs in a more concentrated solution.[16] This fact points to a different mechanism for the formation of **8**. Probably homolytic decomposition of the (η^1-alkenyl)cobalt carbonyl **3** furnishes 2,3-dimethylbutenyl radicals and these react with **1** (Scheme I). Due to the delocalized character of the 2,3-dimethylbutenyl radical a small fraction of **6** may be formed by this route too.

Experimental Section

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer. NMR spectra were recorded with a Tesla BS 487/C 80-MHz spectrometer using Me$_4$Si as the internal standard. Mass spectral analyses were carried out with a JEOL B 300 spectrometer fitted with a JMA 2000β system. Analysis of the volatile compounds was performed on an analytical Carlo Erba Fractovap Model C gas chromatograph using a 3-m column with 10% β-oxydipropiononitrile on 60–80

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mesh Chromosorb P stationary phase at 40 °C, 40 mL of N H_2/min., HWD. All manipulations involving air-sensitive organometallic compounds were carried out by using the usual anaerobic technique.[28] Reactions under 80 bar of CO were performed with 6-mL samples in a 20-mL stainless-steel rocking autoclave.

Materials. The solvents were dried in the usual way and stored under CO. Commercial dienes were freshly distilled under CO. Stock solutions of $HCo(CO)_4$ were prepared in *n*-octane from $Co_2(CO)_8$, DMF, and concentrated HCl.[23] $DCo(CO)_4$ was prepared from $HCo(CO)_4$ solutions by H–D exchange with a 50-fold molar excess of D_2O.[29] Isotopic purity was >95% as calculated from mass spectrometric measurements of its decomposition products. Dicobalt octacarbonyl was doubly recrystallized first from CH_2Cl_2 and then from *n*-heptane under CO.

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette. A 5-L buffer flask was connected to the levelling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermostated (±0.05 °C). The actual total pressure was determined in millimeters of Hg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The reaction was started by injecting the diene into the vigorously stirred solutions of $HCo(CO)_4$. The initial rate of CO uptake and the initial rate of CO release were calculated from the change of gas volume with time.

Preparation of Aldehyde 2,4-Dinitrophenylhydrazones. To a solution of 0.33 mL of 2,3-dimethyl-1,3-butadiene (2.65 mmol) in 9 mL of *n*-heptane under CO at 10 °C was added 4.6 mL of a 0.65 M solution of $HCo(CO)_4$ in *n*-octane (3.0 mmol) dropwise in 50 min. During this time 0.8 mmol of CO was absorbed. The reaction mixture was stored on dry ice overnight and was filtered in the cold to separate crystalline $Co_2(CO)_8$. A solution of 198 mg (1 mmol) of 2,4-dinitrophenylhydrazine and 0.15 mL of concentrated HCl in 5 mL of methanol was added to the filtrate and the mixture evaporated to dryness in vacuo. The hydrazone was extracted with CH_2Cl_2, and after evaporation of the solvent it was recrystallized twice from benzene. A 50-mg (0.17-mmol) sample of yellow crystalline product resulted. TLC chromatography on Silicagel G (benzene–petroleum ether = 5:1) showed the presence of three isomers, all of which had the expected M^+ 292 in their mass spectra.

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Registry No. 1, 16842-03-8; 2, 513-81-5; *trans*-1,3-pentadiene, 2004-70-8; *cis*-1,3-pentadiene, 1574-41-0; *trans,trans*-2,4-hexadiene, 5194-51-4; *cis,trans*-2,4-hexadiene, 5194-50-3; isoprene, 78-79-5; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclopentadiene, 542-92-7; α-terpinene, 99-86-5; (*R*)-α-phellandrene, 4221-98-1; D_2, 7782-39-0.

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Zirconocene–η^4-1,3-Pentadiene Complex and Its Higher Homologues. A New Synthetic Method Involving σ–π Rearrangement of the Hydrido-2,4-pentadienylzirconium Species

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The (1,3-pentadiene)zirconocene complex and its higher homologues of the type $(\eta^5\text{-}C_5H_5)_2Zr(CR^1(CH_3){=}CR^2CR^3{=}CR^4H)$ were prepared by reaction of $(\eta^5\text{-}C_5H_5)_2ZrHCl$ with alkyl-substituted or nonsubstituted pentadienyl anions through novel σ–π rearrangement of hydrido-2,4-pentadienylzirconium species. The ^1H NMR studies on these complexes revealed that the 1,3-pentadiene and 2,4-hexadiene complexes are composed of ca. 1:1 mixture of s-cis and s-trans isomers while each of the complexes containing 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 1-(trimethylsilyl)-1,3-pentadiene, and 1,5-bis(trimethylsilyl)-1,3-pentadiene ligands consists of a single isomer of s-cis structure. The process of hydrogen transfer was elucidated on the basis of the analysis of the stoichiometric reaction between $(\eta^5\text{-}C_5H_5)_2ZrDCl$ and (2-methylpentadienyl)potassium. The reaction of $(\eta^5\text{-}C_5H_5)_2Zr$(2,4-hexadiene) with 1-alkenes or 2-butyne showed that the coordinated diene is easily expelled to give zirconacyclopentanes or a zirconacyclopentadiene derivative, respectively. The addition of butanal or 3-pentanone resulted in double insertion into the 2,4-hexadiene moiety to selectively afford 3-hexene-1,6-diols through hydrolysis.

Introduction

Chemistry of diene complexes of group 4A early transition metals has received considerable attention in recent years because of their unique structural pattern coupled with their unusually high selectivity observed in the reaction with various electrophiles. For example, *s-trans*-η^4-diene coordination to mononuclear metal species was first discovered in the case of zirconocene complexes,[1,2] and the extremely high regioselective dienylation of saturated or unsaturated carbonyl compounds has been achieved with these complexes.[3,4] The following four procedures have been known for the preparation of a series of zirconium–diene complexes: (1) reaction of Cp_2ZrCl_2 (Cp =

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