REACTIONS OF TRIS(TRIPHENYLPHOSPHINE)DINITROGENCOBALT HYDRIDE WITH ETHYL VINYL ETHER, VINYL ACETATE AND METHYL ACRYLATE AND GENERAL REMARKS ON ITS REACTION WITH TERMINAL OLEFINS

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SUMMARY

Tris(triphenylphosphine)dinitrogencobalt hydride (I) reacts with vinyl ethyl ether and vinyl acetate to yield products of hydrogenation. A diamagnetic binuclear cobalt complex is formed in the reaction with vinyl acetate and a paramagnetic binuclear cobalt complex with vinyl ethyl ether. Methyl acrylate reacts with (I) to give methyl α-(d, l)-methylpropionylacetate, dimethyl α-d,l-methylglutarate, methyl adipate and dimethyl cyclobutane-1,2-dicarboxylate. In this reaction a paramagnetic cobalt complex is also formed and interaction of the unpaired electron with ^{1}H is observed. The nature of the cobalt complexes in solution is discussed. Changes in the direction of reaction of (I) with substituted olefins $R-CH=CH_2$, when R is varied, are also discussed.

INTRODUCTION

Tris(triphenylphosphine)dinitrogencobalt hydride (I) reacts with styrene to give a binuclear paramagnetic cobalt complex (II)[1]. Under the reaction conditions when (I) has reacted completely a substantial quantity of a diamagnetic cobalt complex[1] is formed in addition to (II).
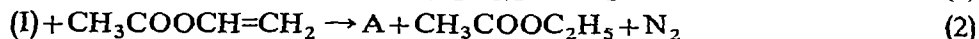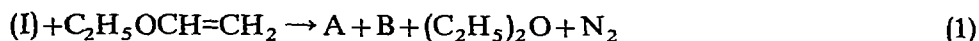
The double bonds in aliphatic olefins are known to migrate in the presence of the catalyst for which (I) is a direct precursor[2,3]. Ethyl vinyl ketone is hydrogenated to a saturated ketone by (I)[4], and conjugated aldehydes undergo decarbonylation with simultaneous formation of a stable Co–C bond[4].

As an extension to the study of the reactions of (I) with terminal olefins $RCH=CH_2$ we have examined the reaction of (I) with vinyl ethyl ether, vinyl acetate and methyl acrylate.

RESULTS

Reactions of vinyl ethyl ether and vinyl acetate with (I)

Vinyl ethyl ether and vinyl acetate react with (I) according to eqns. (1) and (2):

$$(I)+C_2H_5OCH=CH_2 \rightarrow A+B+(C_2H_5)_2O+N_2 \tag{1}$$

$$(I)+CH_3COOCH=CH_2 \rightarrow A+CH_3COOC_2H_5+N_2 \tag{2}$$

Saturated products can be removed by distillation *in vacuo*. During the reaction, a violent evolution of nitrogen, in quantity corresponding to removal of all the nitrogen present in the parent complex, occurs.

A and B contain cobalt but in neither case were they isolated. A and B are soluble in benzene and THF. Use of ethyl ether or saturated hydrocarbons gave rise to oily products. The substances decompose at *ca. 60°*, are involatile even under a high vacuum, and are very sensitive to water and oxygen.

UV spectrum of a reaction mixture containing A and B in benzene or THF resembles essentially the spectrum of the reaction product of (I) with 1-pentene[3]. There is no distinct absorption band in the region 32×10^3 to 18×10^3 cm^{-1} and thus UV spectroscopy is of little use in elucidating the structure of A and of B. Neither do IR spectra of the reaction solutions with a molar ratio (I)/olefin = 1/1.2 reveal any characteristic features useful in the determination of A and B. B represents the paramagnetic component of the mixture resulting from the reaction of (I) with vinyl ethyl
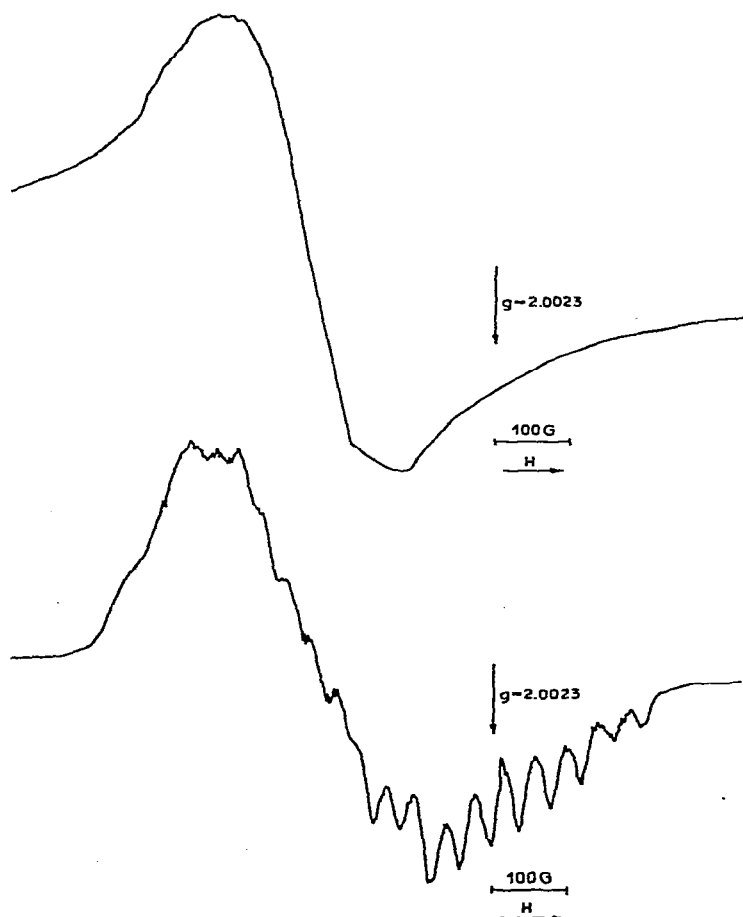
Fig. 1. ESR spectrum of the reaction mixture: (I) + vinyl ethyl ether = 1/2; c_{Co} = 0.015 *M*; temp. *25°*; cavity temperature: upper curve ≈ 20°, lower curve −140°; solvent: benzene.

ether and exhibits an ESR signal (Fig. 1). A benzene solution of the reaction mixture involving vinyl acetate shows no ESR absorption. The NMR and IR spectra in this case are characteristic of a saturated ester.

Reaction of methyl acrylate with (I)

Reaction of (I) with methyl acrylate takes place according to eqn. (3):

$$(I) + CH_2=CHCOOCH_3 \rightarrow A' + C + \text{organic products} + N_2 \tag{3}$$
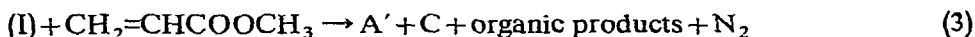
A′ represents a diamagnetic cobalt-containing compound; C is a paramagnetic cobalt complex whose ESR spectrum is shown in Fig. 2.

The behaviour of A′ and C during attempted isolation was the same as A and B. We have therefore studied the influence of different reactants on the ESR spectrum of C.

When allyl chloride or CCl_4 are added, the ESR signal disappears if the molar ratio, total Co/allyl chloride, is at least 1/0.15. This suggests the quantity of paramagnetic cobalt atoms is $\approx 7\%$ of the total cobalt present.

Organic acids and acetylacetone lead to rapid disappearance of the signal when the ratio, total cobalt/$H^+ = 1/0.2$.

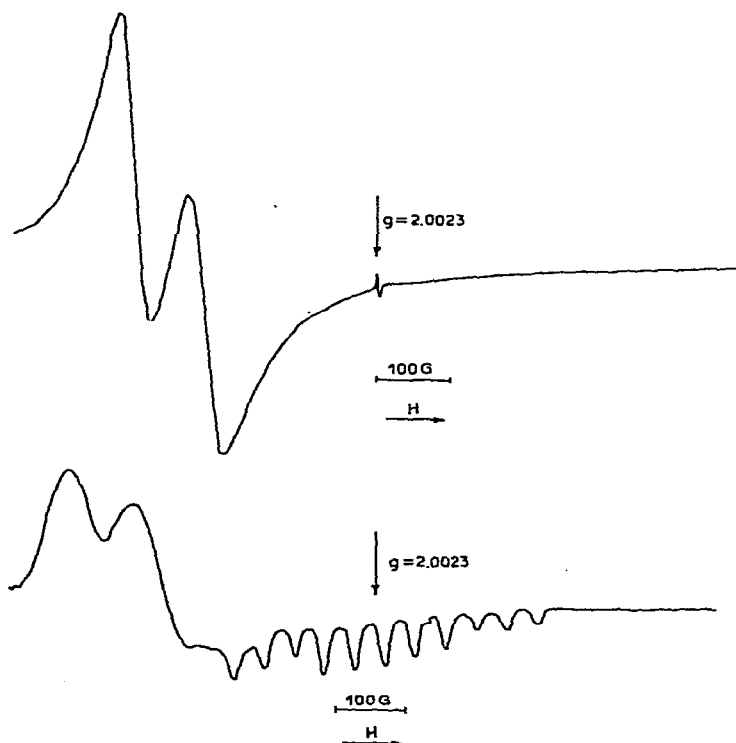Olefins such as styrene, 1-pentene, isoprene, and cyclooctene do not influence

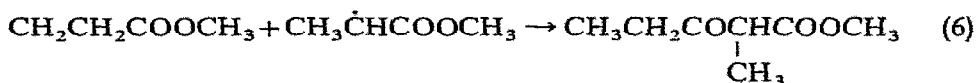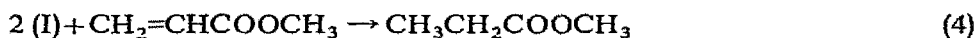Fig. 2. ESR spectrum of the reaction mixture: (I) + methyl acrylate = 1/2; c_{Co} = 0.015 M; temp. 25°; cavity temperature: upper curve $\approx 20°$; lower curve $-140°$; solvent: benzene.

the signal, neither do phenols up to a molar ratio of total Co/phenol = 1/1. Similar behaviour was observed in the ESR spectrum of substance B, however, in order to destroy the spectrum it was necessary to use a molar ratio, total cobalt/allyl chloride = 1/0.6. This shows that paramagnetic cobalt atoms make up ca. 30% of the total cobalt (assuming that allyl chloride reacts at a comparable rate with the paramagnetic and diamagnetic cobalt complexe components of the mixture). The following substances were identified as organic products (listed in the elution sequence from a gas chroma‑ tograph) under the conditions given in the experimental section: methyl α-(d,l)-me‑ thylpropionylacetate (32%), dimethyl α-d,l-methylglutarate (37%), dimethyl adipate (5%) and dimethyl cyclobutane-1,2-dicarboxylate (20%). In addition, five substances are present, to a total extent of 6%, which could not be separated or analysed. The organic products in reaction (3) are formed even in the absence of air (with which they come into contact in any case during manipulation prior to gas chromatography). This fact was confirmed by a high vacuum distillation of the reaction mixture which yielded identical products. Another observation which strongly supports the above conclusion was the analysis of the oxidative degradation products of reaction mixture (3) with CCl_4. These organic products were the same as those obtained by the proce‑ dure in which the reaction mixture (3) is separated using column and gas chromato‑ graphy.

Column chromatography proved to be the most convenient method for separating the organic products listed and gave the elution sequence: triphenyl‑ phosphine, organic products, triphenylphosphine oxide, cobalt compounds (eluted only by acetic acid). The organic products in question were then further separated by preparative gas chromatography.

Reaction of (I) with methyl acrylate in the presence of methyl propionate

Identification of a methyl ester of α-(d,l)-methylpropionylacetic acid is evi‑ dence for the following reaction sequence:

$$2\,(I) + CH_2{=}CHCOOCH_3 \rightarrow CH_3CH_2COOCH_3 \qquad (4)$$

$$(I) + CH_2{=}CHCOOCH_3 \rightarrow CH_3\dot{C}HCOOCH_3 \qquad (5)$$

$$CH_2CH_2COOCH_3 + CH_3\dot{C}HCOOCH_3 \rightarrow CH_3CH_2COCHCOOCH_3 \qquad (6)$$
$$\underset{CH_3}{|}$$

Reaction (6) is probably assisted by the complex in that it takes place within the coordination sphere of a cobalt atom.

The reaction of (I) with methyl acrylate, performed in the presence of methyl propionate, should give rise to more of the methyl ester of α-(d,l)-methylpropionyl‑ acetic acid. Indeed, the yield of this product in the reaction carried out with molar ratio (I)/methyl propionate/methyl acrylate = 1/4/3 is 75% and is accompanied by 24% of methyl adipate. Other products, formed in trace quantities, indicating that the first stage of the reaction of (I) with methyl acrylate leads to a saturated ester. The radicals $CH_3\dot{C}HCOOCH_3$ and $\dot{C}H_2CH_2COOCH_3$ are then formed in the proportion 3/1. In the presence of methyl propionate cyclization is suppressed which suggests coordination of a saturated ester at a cyclization centre (probably a hydrogen-free cobalt atom).

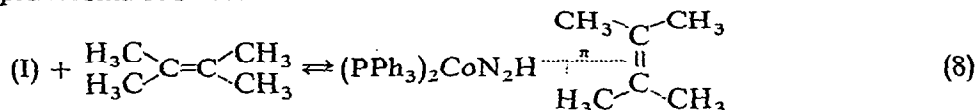*Reactions of methyl acrylate with nitrile complexes derived from (I)*

It is known[10] that coordinated nitrogen in (I) is easily exchanged for nitriles:

$$(PPh_3)_3CoN_2H + RC\equiv N \rightarrow (PPh_3)_3Co(RC\equiv N)H + N_2 \qquad (7)$$

Nitrile complexes also react with methyl acrylate and give rise to the same products as does the nitrogen complex. The yields of methyl adipate and methyl α-(d,l)-methyl-propionylacetate are higher, but the cyclization product is present in trace quantities. When (I) reacts with acetophenone and then methyl acrylate is added, no reaction with the conjugated ester occurs.

Reaction of (I) with 2,3-dimethyl-2-butene

When 2,3-dimethyl-2-butene is added to a benzene solution of (I) in molar ratios 1/1 to 1/20 neither a colour change nor nitrogen evolution occurs. The IR spectra of the reaction mixture shows v_{N_2} at 2088 cm^{-1}, as in the unreacted complex. The solution exhibits no ESR absorption in the temperature range -140–50°. Analysis shows only the presence of subtrate and no trace of any other product. The presence of 2,3-dimethyl-2-butene does not influence the reactivity of (I) with methyl acrylate, vinyl ethers or vinyl acetate. From these observations, it follows that either (I) does not react at all with 2,3-dimethyl-2-butene or, alternatively, only a very weak π complex formation occurs:

$$(I) + \begin{array}{c} H_3C \\ H_3C \end{array}\!\!>\!C=C<\!\!\begin{array}{c} CH_3 \\ CH_3 \end{array} \rightleftharpoons (PPh_3)_2CoN_2H \cdots \overset{\pi}{\underset{}{\Big|}} \begin{array}{c} CH_3\!\!-\!C\!\!-\!CH_3 \\ \| \\ H_3C\!\!-\!C\!\!-\!CH_3 \end{array} \qquad (8)$$

Further study of the reaction (I) with styrene

The reaction mixture of (I) with styrene when analysed after several seconds reveals the presence of ethylbenzene. After several hours the coupling products: Ph(CH$_3$)CHCH(CH$_3$)Ph and Ph(CH$_2$)$_4$Ph were also detected in the ratio 3/7. About 10% of styrene gives rise to coupling products after 10 h of reaction.

After oxidative degradation of the reaction mixture in one case, and with omission of this procedure in the other, both of the above products were detected using column chromatography on silica gel. The cobalt degradation product is (PPh$_3$)$_2$CoCl$_2$.

We attempted to determine more exactly the nature of the paramagnetic, binuclear cobalt complex formed during the reaction (I) with styrene. Two structures were considered possible:
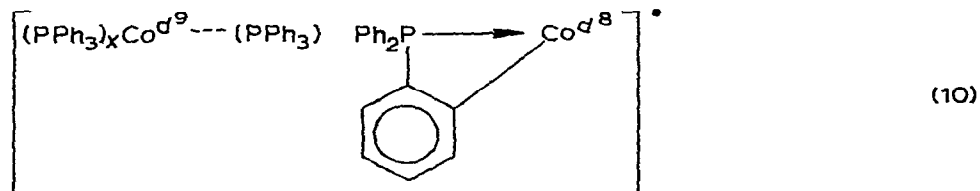
$$\left[(PPh_3)_xCo^{d^9} \cdots (PPh_3)_xCo^{d^8} \!\!-\!\! \underset{\underset{CH_3}{|}}{CHPh} \right]^\bullet \qquad (9)$$

and

$$(10)$$
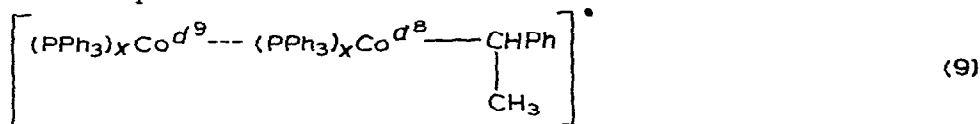
TABLE 1

PRODUCTS OF THE REACTIONS OF (I) WITH OLEFINS RCH=CH$_2$

No	Olefin	Cobalt product	Organic product	Mechanism		Literature
				Proved	Postulated	
1	CH$_2$=CH$_2$	Diamagnetic complexes in a catalytic cycle (PPh$_3$)$_3$CoH (PPh$_3$)$_3$CoC$_2$H$_5$ (PPh$_3$)$_3$CoC$_4$H$_7$	Dimerization product C$_2$H$_5$CH=CH$_2$ separable by vacuum distillation		1) Nitrogen/ethylene exchange 2) Insertion into Co–H bond 3) Insertion of a second C$_2$H$_4$ into Co–C bond 4) $\sigma \to \pi$ rearrangement with release of butene	9
2	RHC=CH$_2$ R = C$_3$H$_7$	Diamagnetic (PPh$_3$)$_2$CoN$_2$H⁻(RCH=CH$_2$) catalyst of the isomerization reaction Diamagnetic (PPh$_3$)$_2$CoH⁻(RCH=CH$_2$)$_2$	Isomerized olefin Dehydrogenation products Separated by vacuum distillation	1) PPh$_3$/olefin exchange 2) Insertion into Co–H bond 3) Formation of Co–C bond 4) $\sigma \to \pi$ rearrangement 5) Olefin exchange		3
3	CH=CH$_2$ CH=CH$_2$	Diamagnetic (π-C$_4$H$_7$)(π-C$_4$H$_6$)(PPh$_3$)Co	Olefin is firmly bound to cobalt Not separable by vacuum distillation		1) PPh$_3$/butadiene exchange 2) H abstraction 3) Chelation of allylic ligand 4) Chelation of butadiene	5
4	ArCH=CH$_2$ Ar=Ph p-C$_6$H$_4$CH$_3$, p-C$_6$H$_4$OCH$_3$.	Paramagnetic [L$_x$Co^{+1}-L$_x$Co^0]‡ or, [L$_x$Co^{-1}-L$_x$Co^0]‡ ≈15–20% of total cobalt ___ Diamagnetic [A]	ArCH$_2$CH$_3$ and small quantities of Ar(CH$_3$)CHCH(CH$_3$)Ar Ar(CH$_2$)$_4$Ar separable by vacuum distillation or chromatography		1) PPh$_3$/styrene exchange 2) Homolytic rupture of Co–H bond with N$_2$ release 3) Reaction with second mole of (I) with synchronous formation of Co–Co bond and organic product	1 and present work

No.	Substrate	Magnetic property	Product / separation	Mechanism	Ref.
5	$C_2H_5O-CH=CH_2$	Paramagnetic [B] ≈30% of total cobalt Diamagnetic [A]	Saturated ether separable by vacuum distillation	1) PPh₃/ether exchange 2) Heterolytic rupture of Co–H bond 3) Reaction with second molecule of (I) with formation of Co–Co and organic product 3) Cyclization at the hydrogen tree cobalt atom	Present work
6	$CH_3OCOCH=CH_2$	Paramagnetic [C] ≈7% of total cobalt	Organic products arising from radical dimerization $CH_3CH_2COCHCOOCH_3$	1) PPh₃/ester exchange 2) Hydrogenation of olefinic bond with N₂ release	Present work
		Diamagnetic [A]	$\overset{\underset{\displaystyle CH_3}{\shortmid}}{}$ $CH_2CH_2COOCH_3$ $CH_3CHCOOCH_3$ $[CH_2CH_2COOCH_3]_2$ $\overset{\displaystyle C-C-COOCH_3}{\underset{\displaystyle C-C-COOCH_3}{\shortmid}}$ Separable by chromatography	Radical formation and coupling	
7	$CH_3COOCI=CH_2$	Diamagnetic [A]	Saturated ester separable by vacuum distillation	1) PPh₃/ester exchange 2) Heterolytic rupture of Co–H bond with N₂ release 3) Reaction with second molecule of (I) with formation of Co–Co bond	Present work
8	$CH_3COCH=CH_2$	Diamagnetic [A]	Saturated ketone separable by vacuum distillation	1) PPh₃/ketone exchange 2) Heterolytic rupture of Co–H bond with N₂ release 3) Reaction with second molecule of (I) with formation of Co–Co bond	4
9	$HCOCH=CH_2$	Diamagnetic cobalt complex containing the $[\overset{\sigma}{Co}-C_2H_5]$ structural unit	Organic product is firmly bound to cobalt and cannot be distilled off Separable after oxidative degradation with CCl₄, as C_2H_5Cl	1) PPh₃/aldehyde exchange 2) Synchronous decarbonylation N₂ release and aldehydic H migration 3) Hydrogenation with Co–H	4
10	$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}C=C\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{}}$	No reaction			Present work

However, both can be rejected, because of the absence of chlorinated products, 1-chloro-1-phenylethane and (*o*-chlorophenyl)diphenylphosphine, after oxidative degradation with CCl_4.

The exact structure of the paramagnetic complex remains unknown.

DISCUSSION

Table 1 summarizes the reactions of (I) with various olefins.

Structures of the complexes in solution

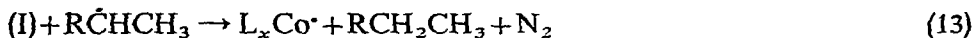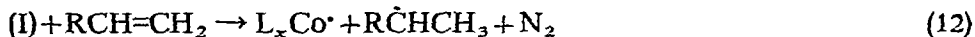It is postulated that substance A is a diamagnetic dimeric cobalt complex:

$$[L_x Co^{d^8}-L_x Co^{d^8}] \tag{11}$$

Such a formulation is supported by the following observations:

(1). During the reaction all the nitrogen is lost from the cobalt complex.

(2). The number of Co–H bonds present in the mixture after the reaction of (I) with olefins is either small or negligible. The number of Co–H bonds was deduced from the amount of $CHCl_3$ produced during oxidative degradation with CCl_4. Diamagnetic substance A is still present in a much greater quantity than the hydridic hydrogen. There are no Co–H bonds in reaction mixture (2) since no $CHCl_3$ was detected as a result of the oxidative degradation.

(3). Formation of a substance having a structure $[L_x Co^{d^8}-L_x Co^{d^8}]$ can be achieved equally well via a homolytic or a heterolytic path:

(*a*). For homolysis:

$$(I)+RCH=CH_2 \rightarrow L_x Co^{\cdot}+R\overset{\cdot}{C}HCH_3+N_2 \tag{12}$$

$$(I)+R\overset{\cdot}{C}HCH_3 \rightarrow L_x Co^{\cdot}+RCH_2CH_3+N_2 \tag{13}$$

$$2 L_x Co^{\cdot} \rightarrow [L_x Co^{d^8}-L_x Co^{d^8}] \tag{14}$$

The possibility of forming a stable $L_x Co-C(CH_3)HR$ is excluded because of the volatility of the resulting hydrogenated product. Formation of a highly reactive $L_x Co-C(CH_3)HR$ species is still possible. This substance will react further:

$$(I)+L_x CoC(CH_3)HR \rightarrow [L_x Co^{d^8}-L_x Co^{d^8}]+RCH_2CH_3+N_2 \tag{15}$$
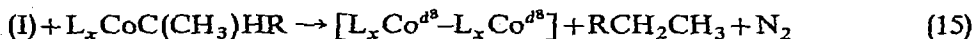
If the reaction was terminated with the formation of $L_x Co^{\cdot}$ radicals, this substance should be detected by ESR: however, no signal attributable to such a species was observed over a wide range of temperatures.

(*b*). For heterolysis;

$$(I)+RCH=CH_2 \rightarrow [L_x Co^{d^{10}}]^-+RCH_2CH_2^++N_2 \tag{16}$$
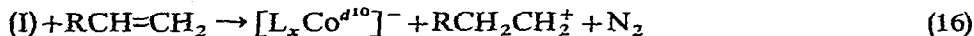
In order to ensure the existence of a "distillable" RCH_2CH_3, abstraction of a second hydrogen, as H^-, must take place:

$$(I)+RCH_2CH_3^+ \rightarrow [L_x Co^{d^8}]^++RCH_2CH_3+N_2 \tag{17}$$
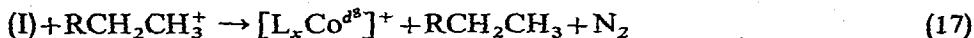
Therefore, at the end of the reaction there are species having the formulae $[L_x Co^{d^{10}}]^-$ and $[L_x Co^{d^8}]^+$, and their dimerization is highly probable. Hence one must conclude that whatever the mechanism of reaction, occurring in the solution, a binuclear cobalt
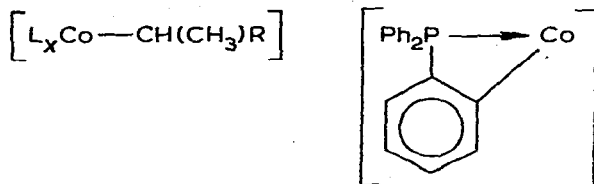
complex must result.

(4). Oxidative degradation of reaction mixtures with CCl_4 does not afford chlorinated products of the type $RCH(Cl)CH_3$,

RCH_2CH_2Cl , Ph_2P —⟨benzene ring with Cl⟩
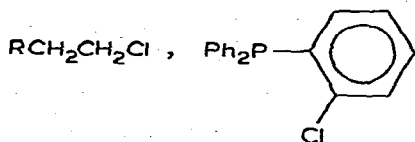
This also points to a lack of substances of the type:

$$\left[L_xCo\!-\!CH(CH_3)R\right] \qquad \left[Ph_2P \longrightarrow Co \text{ (benzene ring)}\right]$$

in the mixtures (1) and (2).

During the reaction with CCl_4, cobalt gives rise to air-stable complexes. For reactions (1) and (2) no organic moiety arising from vinyl ethyl ether or vinyl acetate is attached to the cobalt in the resulting complexes.

This fact is demonstrated by the absence of bands attributable to aliphatic type vibrations in the IR spectra. For reaction (3) an organic moiety exists (arising from methyl acrylate) firmly bound to the cobalt. On this basis we conclude that the main diamagnetic cobalt containing component of the reaction mixture (3) represented by A' is different from A. Either methyl acrylate or compounds arising from it are firmly bound to cobalt in A'.

The structure of the reaction products with CCl_4 and the structure of A' will be reported elsewhere.

The paramagnetic substances B and C are binuclear cobalt complexes. Low temperature spectra reveal hyperfine structures composed of more than 8 lines (8 lines should arise from the interaction of an electron with one cobalt nucleus $I_{Co}=\frac{7}{2}$). It has already been stated[1], that the asymmetric line shape arises because line widths of the individual components of a multiplet are functions of the quantum number m_j. Substance B is postulated to have a structure $[L_xCo\!-\!L_xCo]^{\cdot}$. The reaction mixture (1), when reacted with CCl_4 affords $CHCl_3$ in trace quantities, therefore Co–H bonds cannot be present either in A or in B.

In the case of C, the observed doublet is ascribed to hyperfine splitting caused by [1]H. This type of spectrum was observed by Henrici-Olivé[11] and was ascribed to a cobalt complex:
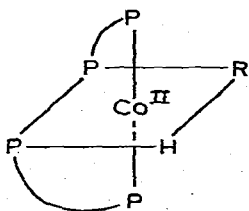
which was the product of the reaction: $(Ph_2PCH_2CH_2PPh_2)CoCl_2+CH_3MgI$. However, this substance was not isolated. In our case the hyperfine splitting amounts to 307 MHz whilst for Henrici-Olivé's complex a value of 220 MHz was reported. The structure of C is:

$$[L_xCo^{d^8}(H)-L_xCo^{d^9}]^{\cdot}$$
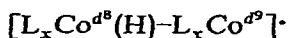
Reaction mixture (3), when quenched with CCl_4, yields $CHCl_3$ in an amount corresponding to the quantity of paramagnetic cobalt as judged from experiments where the signal is made to disappear.

An alternative structure for B and C, with total spin $>\frac{1}{2}$ should give rise to a spectrum with zero field splitting. This would be highly asymmetric and the g factor of these lines would differ considerably from the $g \approx 2$, the value observed in both cases.

Dependence of the direction of reaction upon olefin structure

The observed presence of coupling products and paramagnetic cobalt complexes means that for styrene, methyl acrylate and vinyl ether the reaction follows a free radical path.

The ability of an olefin to accept hydrogen as a radical (a proton or hydridic anion) depends to a certain extent on the position of the antibonding π^* level in the olefin[6]. The olefins studied can be arranged in a sequence of increasing π^* level energies (Fig. 3). The sequence corresponds directly to the ease of the polarographic reduction of the vinyl compounds as stated by Fueno *et al.*[7]
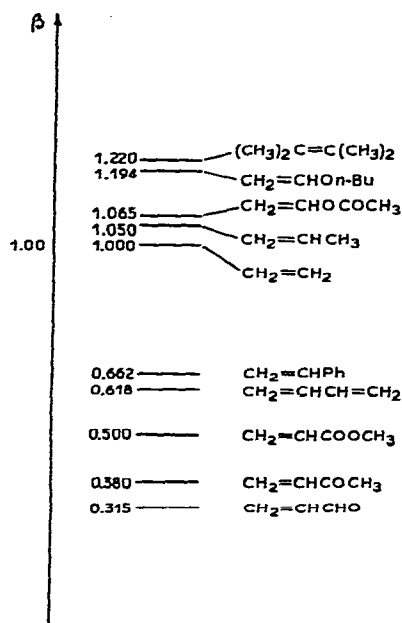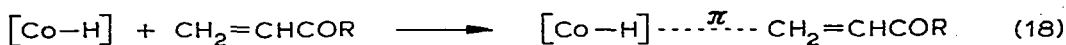

Fig. 3. The positions of π^* orbital in substituted olefins RCH=CH$_2$ (in units of β).

Conjugated carbonyl compounds do not give paramagnetic complexes. For these substances the low energy of the π^* level as well as the strong polarity of the C=C bond[8]:

$$(+ \longrightarrow -) - COR$$

leads us to conclude that the first steps of the reaction are:

$$[Co-H] + CH_2=CHCOR \longrightarrow [Co-H] \cdots \pi \cdots CH_2=CHCOR \qquad (18)$$

$$[Co-H] \cdots \pi \cdots CH_2=CHCOR \longrightarrow [Co^{d^8}]^+ + [H-(+ \longrightarrow -)-COR]^- \qquad (19)$$

For the vinyl ethers where the substituent is of the $-I^+$ type, the situation is reversed:

$$[Co-H] \cdots \pi \cdots CH_2=CHOR \longrightarrow [Co^{d^{10}}]^- + [H-(- \longrightarrow +)-OR]^+ \qquad (20)$$
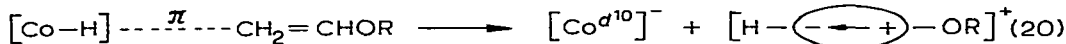
Only olefins $CH_2=CHR$ having π^* in the middle of the range and a not very polar $C=C$ bond, undergo radical rupture of a Co–H bond. Aliphatic olefins with an intermediate value of π^* and with no great difference in the polarity of the carbon atoms do not bring about the rupture of the Co–H bond.

In such a case catalysis of isomerization due to a continuous hydrogen "dance" occurs.

$$[Co-H] \cdots \begin{matrix} CH_2 \\ \| \\ CHR \end{matrix} \begin{matrix} \sigma \\ \rightleftarrows \\ \pi \end{matrix} [COCH_2CH_2R] \qquad (21)$$
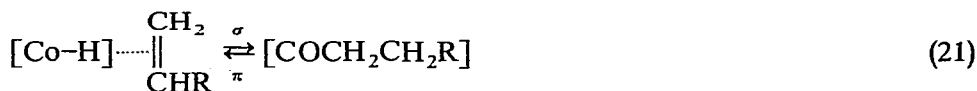
The hydrogenation reaction, after which chelation of the hydrogenated ligand was observed, takes place only with butadiene. The driving forces for this type of the reaction are:

(1) The formation of a σ bond C–H;

(2). The formation of a three centre allylic system with a non-bonding molecular orbital $\psi_{A_2} = 2^{-\frac{1}{2}} \cdot (\Phi_1 - \Phi_3)$.

The hydrogen abstraction step of the reaction then proceeds as follows:

$$H_2C=CH-CH=CH_2 + H^{\cdot}(H^-) \rightarrow H_2C\underline{-CH-CH}-CH_3 \qquad (22)$$

$$3e^- \, (4e^-)$$
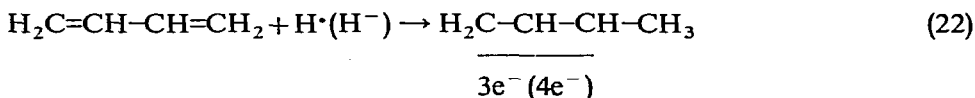
A molecular orbital diagram representing the transition from the conjugated system of double bonds (for a hydrocarbon or for a carbonyl compound) to the allylic system is illustrated in Fig. 4.

In a hypothetical allyl system formed from a conjugated carbonyl compound there would be an occupied orbital n derived from an oxygen atomic orbital. Its energy is certainly in the region suitable for interaction with the cobalt atom. However, in this case there should be a net flow of charge from the ligand to cobalt. In view of the high probability that cobalt acts as a Lewis base in this type of reaction[3] such a property is responsible for the non-formation of allyl complexes of conjugated carbonyl compounds.

EXPERIMENTAL

All operations were performed under N_2 purified over BTS catalyst. Solvents
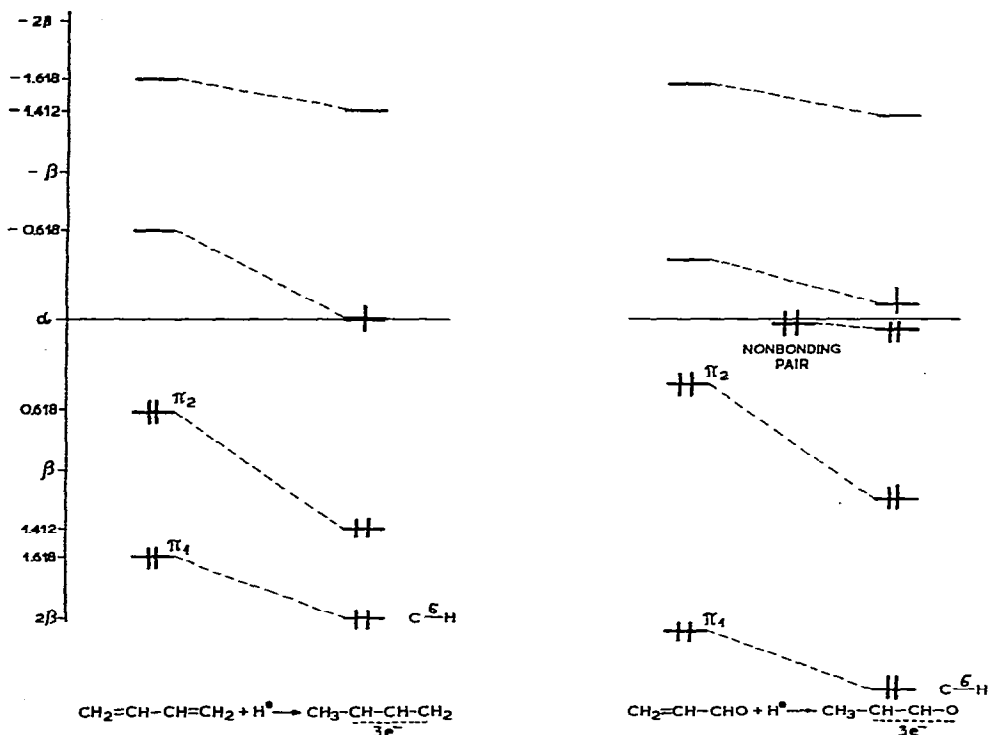
Fig. 4. Comparison of energy changes of the different orbitals in conjugated hydrocarbon and conjugated carbonyl compounds during the formation of an allylic system by reaction with $H \cdot (H^-)$.

were distilled over sodium wire and deoxygenated before use. IR spectra were measured on a Unicam SP 200, ESR spectra on a JEOL ESR JM 3X and electronic spectra on a Unicam SP 700 instrument. Mass spectra were obtained on a LKAB 9000 and the NMR spectra on a JEOL 100 MHz apparatus.

Reactions of (I) with olefins were performed as follows: organic substrates were added to a solution of 4 g of (I) in 40 ml of deoxygenated benzene at room temperature. The molar ratio was 1/2 with ethylvinyl ether and vinyl acetate and 1/4 with methyl acrylate. Volatile substances removed by evaporation at 20 mmHg pressure using a rotary evaporator; the vapours were condensed at $-70°$ and analyzed by gas chromatography. With methyl acrylate only an excess of substrate was detected. In the remaining cases, saturated products were detected in quantities corresponding to a nearly quantitative reaction of the Co–H bonds.

The oily residues, after evaporation, were subjected to column chromatography on silica gel. The organometallic mixture was introduced as a benzene solution. For methyl acrylate, benzene elutes PPh_3, while ether elutes the organic products as a mixture. More polar solvents elute small quantities of triphenylphosphine oxide.

An identical procedure applied to reaction mixtures (1) and (2) gives only PPh_3 and triphenylphosphine oxide. The cobalt compound can be removed from the column only by acetic acid.

Preparative gas chromatography was performed on the mixture of organic

products using a Giede 18.4.3 apparatus. Conditions were as follows: 5 m column (10% SE 30 on Chromosorb P, acid washed); nitrogen flow, 60 ml/min, temp. 150°; 20 portions each of 50 μl were introduced. The fractions were condensed in standard Varian receivers.

*Identification of methyl α-(d,l)-methylpropionylacetate*

(Found: C, 58.00; H, 8.14. $C_7H_{12}O_3$ calcd.: C, 58.33; H, 8.33%.) IR: ν(C=O ketone) 1722; ν(C=O ester) 1750 cm^{-1}. NMR (CCl$_4$, δ ppm): COCH$_2$C$\underline{H}_3$ 2.10 (t, J 13 Hz, 3 H); COC(C$\underline{H}_3$)HCOOCH$_3$ 2.60 (d, J 13 Hz, 3 H); COC$\underline{H}_2$CH$_3$ 4.68 to 5.50 (m, 2 H); COC(CH$_3$)$\underline{H}$COOCH$_3$: 6.85 (q, J 13 Hz, 1 H); COC(CH$_3$)HCOOC$\underline{H}_3$ 8.00 (s, 3 H).

Mass spectrometry (m/e): M^+ = 144 (1.2%); $[M-C_2H_5]$ = 115 (3%); $[M-OCH_3]$ = 113 (2.8%); $[CH_3CH_2COOCH_3]$ = 88 (8%); $[CH_3CHCOOCH_3]$ = 87 (4.7%); $[CH_3CH_2COCHCH_3]$ = 83 (2.8%); $[CH_3CH_2CO]$ = 57 (100%).
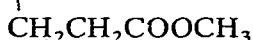
Identification of dimethyl α-(d,l)-methylglutarate

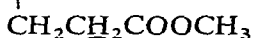(Found: C, 55.16; H, 7.58. $C_8H_{14}O_4$ calcd.: C, 55.2; H, 8.05%.) IR: ν(C=O) 1737 cm^{-1}.

NMR (CCl$_4$, δ ppm):

C$\underline{H}_3^1$–CH^2–COOCH$_3^3$: 1.20 (d; J = 7 Hz; 3 H)
      |
    CH$_2^4$CH$_2^5$COOCH$_3^6$
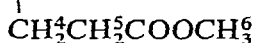
CH$_3$–C$\underline{H}$–COOCH$_3$: 1.55 to 2.18 (m; 2 H)
     |
    C$\underline{H}_2$CH$_2$COOCH$_3$

CH$_3$C$\underline{H}$COOCH$_3$: 2.18 to 2.70 (m; 3 H)
    |
    CH$_2$C$\underline{H}_2$COOCH$_3$

CH$_3$CHCOOC$\underline{H}_3$: 3.70; 3.75 (two s; 6 H)
    |
    CH$_2$CH$_2$COOC$\underline{H}_3$
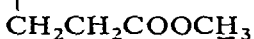
Mass spectrometry (m/e): there is no molecular ion; $[M-OCH_3]$ = 143 (7%); $[M-CH_3COOH]$ = 114 (42%); $[CH_3CH=C-OCH_3]$ = 88 (14%); $[M-CH_3COO-$
                     |
                    OH
H–CH$_3$O] = 83 (18%); $[COOCH_3]$ = 59 (74%); 55 (100%).

The samples for MS were introduced by gas chromatography on Chromosorb P, 3 m, temp. 150°, helium flow 40 ml/min.

Methyl adipate and cyclobutane dimethyl 1,2-dicarboxylate were identified by gas chromatographic comparison with authentic samples. Two columns were used: 3 m of 15% carbowax 20000 on Chromosorb P, acid washed, temp. 150°, N_2 flow 40 ml/min and 5 m of 10% SE 30 on chromosorb P, acid washed, temp. 150°; N_2 flow 40 ml/min. In both cases a flame ionization detector was used.

ESR measurements. Benzene solutions containing reaction products of appropriate concentrations were introduced into ESR tubes without the use of syringes in order to prevent any contact with the atmosphere.

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