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The Codimerization of Butadiene and Ethylene Catalyzed by Cobaltous Chloride-Ditertiary Phosphine Complexes-Grignard Reagent-ROH. Effects of Ditertiary Phosphine Ligands and Alcohols

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Butadiene-ethylene codimerization is accomplished by means of the catalyst derived from the reactions of $CoCl_2(Ph_2P(CH_2)_nPPh_2)_m$ with a Grignard reagent and then with appropriate amounts of alcohols to obtain 1,4-*cis*-hexadiene selectively. The yield of 1,4-hexadiene depends on the number of ditertiary phosphine ligands (m), the methylene-chain length of the ligand (n), and the kind of alcohol. A hydride complex, $HCo(Ph_2P(CH_2)_2PPh_2)_2$ also has codimerization activity in the presence of both n-PrMgCl and alcohols. It is considered that the resulting alkoxymagnesium chloride activates the catalyst.

A number of transition-metal catalyst systems in the codimerization of ethylene and 1,3-butadiene have been investigated by many worker.[1a–j] These catalysts usually consist of a transition-metal salt or complex and organoaluminum compounds as the reducing agents, similar to the Ziegler-type polymerization catalysts,[2] and low valent organo-transition metal complexes have been suggested as the active intermediates. Codimerization catalyst systems, in which Grignard reagents are contained as reducing agents, have, however, been much less studied. It has been found in a patent[3] that 1,4-hexadiene can be prepared by the reaction of ethylene and butadiene in the presence of Fe (II) and a Grignard reagent. Greco and Carbonaro[4] reported that the $FeCl_3$–i-PrMgCl system was an active catalyst of butadiene dimerization and of butadiene-norbornadiene codimerization.

In earlier papers dealing with ethylene-butadiene codimerization reactions catalyzed by $CoCl_2(Ph_2P(CH_2)_nPPh_2)$–$AlEt_3$[5] and $NiCl_2$–$Ph_2P(CH_2)_nPPh_2$–

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[1] a) D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963). b) G. Hata, *J. Amer. Chem. Soc.*, **86**, 3903 (1964). c) T. Alderson, E. L. Jenner, and R. V. Lidsey, Jr., *ibid.*, **87**, 5638 (1965). d) M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, **31**, 4290 (1966). e) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 1633 (1967). f) R. G. Miller, T. J. Kealy, and A. L. Barney, *ibid.*, **89**, 3756 (1967). g) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, **1967**, 2037. h) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **70**, 1221, 1505 (1967). M. Iwamoto and S. Yuguchi, *ibid.*, **71**, 133, 233, 237 (1968), M. Iwamoto and S. Yuguchi, This Bulletin, **41**, 150, (1968). i) G. Hata, This Bulletin, **41**, 2443, 2762 (1968). j) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6777 (1970).

[2] 1) b, d, f, h, and i.

[3] T. Yoshida and S. Yuguchi, Japan. 25964 (1968); *Chem. Abstr.*, **71**, 30037n (1969).

[4] a) A. Greco, A. Carbonaro, and G. Dall'Asta, *J. Org. Chem.*, **35**, 271 (1970). b) A. Carbonaro and A. Greco, *J. Organometal. Chem.*, **25**, 477 (1970).

[5] T. Kagawa, Y. Inoue, and H. Hashimoto, This Bulletin, **43**, 1250 (1970).

AlEt$_3$,[6] the present authors described how the ditertiary phosphine ligand affects product distribution in a striking manner.

In the present investigation, it will now be shown that, in the codimerization of ethylene and butadiene by CoCl$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_m$, Grignard reagent can be used as the reducing agent instead of organoaluminum compounds, provided that an appropriate amount of alcohol or acetone is present, and that 1,4-hexadiene is formed selectively by these catalyst systems. The effects of alcohols and ligands on the 1,4-hexadiene formation have also been studied.

Experimental

Reagents. Ethereal solutions of *n*-propylmagnesium chloride and phenylmagnesium bromide were prepared from Mg chips and *n*-propyl chloride, and from bromobenzene, respectively and were used after filtration. The concentrations of both Grignard reagents were determined by acid-base titration (1.5—2.0 mmol/g solution). Anhydrous cobaltous chloride and triphenylphosphine were obtained commercially, while ditertiary phosphines (Ph$_2$P(CH$_2$)$_n$PPh$_2$, n=2,3,4, and 6)[7] were prepared by the method described by Hewertson and Watson[8] and their purity confirmed by elementary analysis and a melting-point determination. DPE: mp 140—141°C (143—144°C),[8] Found: C, 78.25; H, 6.21%. Calcd: C, 78.39; H, 6.07%. DPP: mp 63.3—65.3°C (61—62°C),[9] Found: C, 78.66; H, 6.08%. Calcd: C, 78.62; H, 6.36%. DPB: mp 134°C (137—139°C),[10] Found: C, 78.78; H, 6.81%. Calcd: C, 78.85; H, 6.62%. DPH: mp 126—127°C, Found: C, 78.50; H, 6.86%. Calcd: C, 79.26; H, 7.11%. The cobalt complexes with the above ditertiary phosphines were prepared according to the reported methods.[11]

A hydride complex, HCo(DPE)$_2$, was obtained by the reduction of CoCl$_2$(DPE)$_2$ with NaBH$_4$ in ethanol and was used after the recrystallization of a benzene solution.[12] IR $\nu_{\text{Co-H}}$ 1884 cm^{-1} (KBr). Elementary analysis; Found: C, 72.79; H, 5.59%. Calcd: C, 72.89; H, 5.78%.

1,3-Butadiene (Nippon Petroleum Chem. Co., Ltd.) was dehydrated by passing it through anhydrous calcium chloride and molecular-sieve columns and was condensed in a measuring vessel in order to measure its volume. Ethylene (of the grade for polyethylene) was used with no further purification. The toluene, ether, alcohols, and acetone were purified by conventional methods, and were distilled and stocked in an atmosphere of nitrogen.

Procedure. Every operation was carried out under a vacuum or in an atmosphere of nitrogen.

Catalyst Preparation. Some typical experiments were carried out as follows. CoCl$_2$DPP-*n*-PrMgCl–ROH System. A 108 mg, (0.20 mmol) of CoCl$_2$DPP was suspended in 8 m*l* of toluene, and then 1.52 g portion of an ethereal solution of *n*-PrMgCl (2.91 mmol, Mg/Co=14.5) was added by a syringe; this solution was stirred with a magnetic stirrer at room temperature until reduction had proceeded completely to form a black solution. A calculated amount of an ethanol–toluene solution (0.572 g, 2.51 mmol of EtOH, EtOH/Co=12.5) was then added with agitation, whereupon an exothermic reaction occurred. This solution was used as the catalyst. Some other catalysts were made in a similar way.

HCo(DPE)$_2$–n-PrMgCl–ROH System. 0.943 g of an *n*-PrMgCl ether solution (1.92 mmol, Mg/Co=17.8) and 0.943 g of a *t*-butyl alcohol–toluene (1.92 mmol of *t*-BuOH, *t*-BuOH/Co=17.8) were added to a toluene suspension of 92 mg (0.11 mmol) of HCo(DPE)$_2$ (in this order), and this mixture was warmed to 40—50°C. The color stayed red throughout the reaction.

Oligomerization Reaction. A 100-m*l* stainless steel autoclave equipped with a magnetic stirrer was charged with the above catalyst solution and a calculated amount of butadiene (in this order). The temperature was then raised to 90—100°C, ethylene was injected to a pressure of approximately 50 kg/cm^2, and the reaction was carried out with agitation under a constant ethylene pressure. After 2.5 hr, the autoclave was cooled to room temperature and the catalyst was quenched by adding 2 m*l* of a methanol–HCl solution. The reaction solution was then washed with distilled water and dried on anhydrous sodium sulfate. After distillation, the products were analyzed by glc. The main product was 1,4-*cis*-hexadiene, which was identified by IR and NMR.

Isolation and Identification of HCo(DPB)$_2$. An ethereal solution of *n*-PrMgCl (6.72 mmol) was added at room temperature, to a stirred suspension of CoCl$_2$DPB (1.11 g, 2.00 mmol) and DPB (0.856 g, 2.01 mmol) in toluene (10 m*l*). The solution gradually became red. After filtration, *n*-hexane was added to the filtrate in order to precipitate the crystals. The resulting crystals were filtered off, dried, and recrystallised from the toluene solution by adding *n*-hexane. The dark-red crystalline compound was dried *in vacuo* at 40—50°C. Mp 158—159°C; Found: C, 73.99; H, 6.33%. Calcd for C$_{56}$H$_{57}$P$_4$Co: C, 73.76; H, 6.18%. Its proton magnetic spectrum in benzene shows a chemical shift at τ=27.2 assigned to the hydridic hydrogen of HCo(DPB)$_2$, which consists of a quintet with an intensity ratio of 1:4:6:4:1 and with a J_{PH} value of 28 Hz. However, its IR spectrum does not show any clearly-defined absorptions due to the cobalt-hydrogen stretching vibrations.

Result and Discussion

Butadiene-ethylene codimerization was catalyzed by adding appropriate amounts of alcohols to the reaction mixture of CoCl$_2$–(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_m$ (n=2, 3, and 4; m=1, 2) with ethereal *n*-propylmagnesium chloride in toluene, thus forming 1,4-hexadiene. In most cases, the selectivity of 1,4-hexadiene is so significantly high that the catalytic activity can be evaluated by means of the yield of 1,4-hexadiene based on the charged butadiene.

CoCl$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_m$–n-PrMgCl–Alcohol Systems. When *n*-propylmagnesium chloride was allowed to react with a cobaltous chloride-suspended toluene solution, the solution gradually turned black and a black precipitate was formed. This solution had no catalytic activity for 1,4-hexadiene formation. The reduction of cobaltous chloride with a Grignard reagent

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6) Y. Inoue, T. Kagawa, and H. Hashimoto, *Tetrahedron Lett.*, **1970**, 1099.

7) Abbreviations: DPE, 1,2-bis(diphenylphosphino)ethane; DPP, 1,3-bis(diphenylphosphino)propane; DPB, 1,4-bis(diphenylphosphino)butane; DPH, 1,6-bis(diphenylphosphino)hexane.

8) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

9) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 19 (1966).

10) L. Sacconi and Gelsomini, *ibid.*, **7**, 291 (1968).

11) a) W. D. Horrocks, Jr., G. R. Van Hecke, and D. D. Hall, *ibid.*, **6**, 694 (1967). b) 10).

12) A. Sacco and R. Ugo, *J. Chem. Soc.*, **1964**, 3274.

has been known as the outset of a Kharasch reaction[13] and has been considered to proceed as follows;

$$2RMgX + CoX_2 \longrightarrow R_2Co + 2MgX_2$$

$$R_2Co \longrightarrow Co + 2R\cdot$$

In this reaction sequence, the formations of organocobalt and of metallic cobalt are assumed as intermediate steps, but it has also been suggested by several workers[14] that a magnesium-coordinated intermediate with a different composition depending upon the molar ratio of Mg/Co is formed.

The addition of an *n*-PrMgCl ether solution to CoCl$_2$DPP in toluene at room temperature brought about a rapid reaction, and the mixture became black. This solution had only a low activity (*ca.* 5% yield of 1,4-hexadiene). On the other hand, when an appropriate amount of alcohol or acetone was added to the above solution, the catalytic activity was drastically increased and the yield of 1,4-hexadiene rose to 70% or more. This behavior is shown in Fig. 1, in which the effect of the amounts of alcohols and acetone at a constant *n*-PrMgCl concentration is illustrated. Among alcohols, ethyl alcohol has a high activity over a wide range of EtOH/Co molar ratios. As can be seen from Fig. 1, the highest activity of 1,4-hexadiene formation is revealed at almost the same amount of alcohol as in the Grignard reagent, while at lower and higher molar ratios of alcohol/Co, the catalyst was deactivated. Acetone was effective in the same manner. Further, in the system of CoCl$_2$DPP–*n*-PrMgCl–large excess *t*-BuOH(*n*-PrMgCl/Co=2.2, *t*-BuOH/Co=34), the codimerization reaction proceeded only slightly. The above facts show that the remaining *n*-PrMgCl reacts with the added alcohol or acetone to give alkoxymagnesium chloride; the catalyst may be activated by the resulting ROMgCl, not by the added alcohol itself.

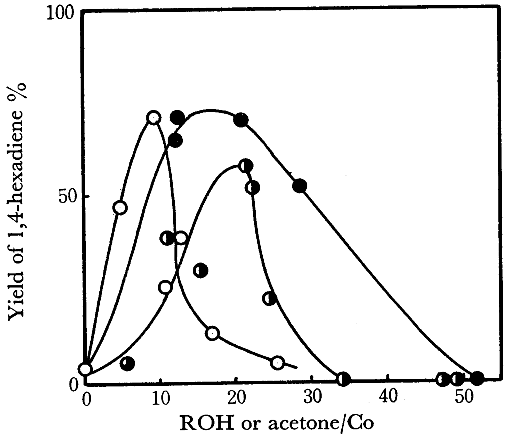

Fig. 1. Effect of molar ratio of ROH/Co or acetone/Co on yield of 1,4-hexadiene at constant concentration of *n*-PrMgCl CoCl$_2$DPP: 0.20 mmol. Reaction temperature: 90—100°C Reaction time: 2—2.5 hr
○ MeOH (*n*-PrMgCl/Co=11)
● EtOH (*n*-PrMgCl/Co=15)
◑ acetone (*n*-PrMgCl/Co=21)

On the other hand, using a mixture of a CoCl$_2$DPP-*n*-PrMgCl (1:2) reaction solution and *t*-BuOMgCl prepared previously from *t*-BuOH and *n*-PrMgCl as the catalyst, the yield of 1,4-hexadiene was found to be 14% (*t*-BuOMgCl/Co=12), but at a higher molar ratio (*t*-BuOMgCl/Co=20) the products were viscous liquids and higher oligomerization compounds were probably formed. The mixing order of catalyst components seems to be important in obtaining a highly active catalyst for butadiene-ethylene codimerization.

The temperature dependency of the codimerization reaction catalyzed by CoCl$_2$DPP–*n*-PrMgCl–*t*-BuOH system was studied and significant activity was revealed over 90°C; this tendency is similar to the case of the CoCl$_2$(DPE)$_2$–AlEt$_3$ system.[15]

The effects of the ligand, that is, the number of ditertiary phosphine ligands, "*m*", that of the methylene chain length between two phosphorus atoms, "*n*", and the kind of added alcohols (ROH; R=Me, Et, *i*-Pr and *t*-Bu) on the yield of 1,4-hexadiene in the system of CoCl$_2$(Ph$_2$P(CH$_2$)$_n$PPh$_2$)$_m$–*n*-PrMgCl–ROH are given in Table 1. The length of the methylene chain, "*n*", slightly affected the formation of 1,4-hexadiene except in the case of DPH, which had no catalytic activity; the following orders are obtained;

TABLE 1. EFFECT OF DITERTIARY PHOSPHINE LIGANDS AND ALCOHOLS IN CoCl$_2$L$_{(2)}$–*n*-PrMgCl–ROH SYSTEMS

Complex	ROH	*n*-PrMgCl/Co	ROH/Co	Yield of 1,4-hexadiene[a] (%)
CoCl$_2$DPE	MeOH	11.2	9.6	36
	EtOH	12.4	10.4	61
	EtOH	12.6	22.7	45
	i-PrOH	12.8	11.1	53
	t-BuOH	13.0	11.3	58
CoCl$_2$(DPE)$_2$	MeOH	12.5	10.5	18
	EtOH	12.2	10.2	67
	EtOH	12.2	22.0	58
	i-PrOH	13.8	12.1	70
	t-BuOH	14.8	12.8	78
CoCl$_2$DPP	MeOH	11.2	9.4	71
	EtOH	14.5	12.5	71
	EtOH	15.2	20.9	70
	i-PrOH	13.3	11.5	50
	t-BuOH	13.9	11.7	63
CoCl$_2$DPP[b]	MeOH	12.8	11.2	11
+ DPP	*t*-BuOH	13.1	11.4	72
CoCl$_2$DPB	MeOH	10.9	8.6	59
	EtOH	14.5	12.5	71
CoCl$_2$DPB[b]	MeOH	15.2	13.2	trace
+ DPB	*t*-BuOH	15.0	12.9	65
CoCl$_2$DPH	EtOH	12.1	10.1	—

CoCl$_2$L$_{(2)}$=0.20 mmol. Reaction temperature: 90—100°C. Reaction time: 2.5 hr.

a) Based on charged butadiene
b) CoCl$_2$L: L=1:1

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[13] Mechanism of Kharasch reaction is reviewed in Ref. 14 b.

[14] a) G. Costa, G. Mestroni, and G. Boscarato, *Ric. Sci. Rend., Sez. A*, **7**, 315 (1964) *Chem. Abstr.*, **63**, 18145h. b) M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 1, 497 (1968).

[15] M. Iwamoto and S. Yuguchi, This Bulletin, **41**, 150 (1968).

$$CoCl_2DPP(n=3) \approx CoCl_2DPB(n=4) \gtrsim CoCl_2DPE(n=2) \gg CoCl_2DPH(n=6)$$

$$CoCl_2(DPE)_2 \gtrsim CoCl_2DPP + DPP \gtrsim CoCl_2DPB + DPB$$

The first order is the same as in the reported $CoCl_2(Ph_2P(CH_2)_nPPh_2)$–$AlEt_3$ system.[15] It shows that these ditertiary phosphine ligands (n=2, 3, and 4) stabilize the active intermediate by the formation of a chelate ring. The number of ditertiary phosphine ligands, "m", was closely related to the kinds of alcohol in activating the catalyst; the catalysts of $CoCl_2(DPE)_2$ and $CoCl_2L+L$ (L=DPP and DPB) (m=2) had a highly active character in combination with *t*-BuOH, but with MeOH only a small amount of 1,4-hexadiene was produced, while in the case of $CoCl_2L$ (L=DPE, DPP, and DPB) (m=1) the activity was roughly independent of the king of alcohol. In other words, the resulting *t*-BuOMgCl is a better co-catalyst than MeOMgCl in the $CoCl_2L_2$ and $CoCl_2L+L$ systems.

These results suggest that this catalytic codimerization reaction consists of two steps: one is the reduction of Co(II) complexes by the Grignard reagent, and the other is the activation of the resulting low-valent cobalt complex by alkoxymagnesium chloride. Therefore, a further investigation of butadiene-ethylene codimerizations catalyzed by low-valent cobalt complexes would be useful in accounting for these two steps.

Codimerization Reaction Catalyzed by a Hydride Complex $HCo(DPE)_2$. As low-valent cobalt complexes coordinated by the ditertiary phosphine, $HCo(DPE)_2$[16] and $Co(DPE)_2$[17] have been known. The hydride complex $HCo(DPE)_2$ shows codimerization activity only in the presence of both *n*-PrMgCl and alcohols, as is shown in Table 2. The order of activation is as follows:

$$t\text{-BuOH} > i\text{-PrOH} \approx \text{EtOH} > \text{MeOH}$$

This behavior is the same as in the $CoCl_2L_2$ (or $CoCl_2L+L$)+ *n*-PrMgCl system described above, and the possibility of hydride-complex formation seems to be present in the later system.

On the other hand, a number of σ-bonded organo-transition-metal complexes stabilized by phosphine ligands[18] have been obtained in reactions of transition-metal complexes with Grignard reagents containing no β-hydrogen. With Grignard reagents having β-hydrogen, the σ-alkylmetal complexes formed may decompose to hydride-metal complexes because of their instability. In the reaction of $CoCl_2(DPE)_2$ or $CoCl_2L+L$ (L=DPP and DPB) with *n*-PrMgCl also, low-valent cobalt complexes must be formed. In fact, a new hydride complex, $HCo(DPB)_2$, was isolated from the reaction mixture of $CoCl_2DPB$, DPB and *n*-PrMgCl in a toluene–ether solvent at room temperature; it was later identified. In the case of $CoCl_2L$ (m=1), which has a ligand-deficient structure, there may be present another type of low-valent complex, which may be coordinated by a magnesium compound or a solvent.

TABLE 2. ETHYLENE-BUTADIENE CODIMERIZATION REACTION CATALYZED BY $HCo(DPE)_2$–*n*-PrMgCl–ROH

ROH	*n*-PrMgCl/Co	ROH/Co	Yield of 1,4-hexadiene (%)
MeOH	—	30.5	none
	17.1	17.2	trace
EtOH	—	21.7	none
	17.0	17.3	34
	17.8	21.8	34
i-PrOH	18.8	18.7	33
t-BuOH	17.8	17.8	53

$HCo(DPE)_2$=0.1 mmol.
Reaction condition: see footnote in Table 1.

The facts that $HCo(DPE)_2$ itself has no activity for codimerization reaction and that there is no influence on its activity by adding *t*-BuOH alone, while in the presence of both *n*-PrMgCl and *t*-BuOH a high activity is obtained (Table 2), show that the resulting ROMgCl also plays an important role in this system. It is said that a vacant coordination site is a major factor in influencing catalytic behavior in a homogeneous transition-metal catalyst. Iwamoto and his co-workers[19] reported that $HCo(DPE)_2$ reveals catalytic activity in the presence of some kinds of phenol, and they assumed an interaction between phosphorus atoms and phenol to make a vacant coordination site. Recently, Tolman[20] described how a nickel hydride $HNi(P(OEt)_3)^+_4$ catalyzed an ethylene-butadiene codimerization to give 1,4-hexadiene and that the rate-determining step in this system was ligand dissociation from $HNiL_4^+$ ($L=P(OEt)_3$). Therefore, alkoxymagnesium chloride may cause ligand dissociation in these cobalt-based catalysts.

$CoCl_2(Ph_2P(CH_2)_nPPh_2)_m$–PhMgBr–ROH Systems. When phenylmagnesium bromide was used as the reducing agent instead of *n*-propylmagnesium chloride, the 1,4-hexadiene formation reaction proceeded in the same way, but the yield was lower than that of the *n*-PrMgCl system. The results are listed in Table 3.

TABLE 3. $CoCl_2L_{(2)}$–PhMgBr–ROH CATALYST SYSTEM

Complex	ROH	PhMgBr/Co	ROH/Co	Yield of 1,4-hexadiene (%)
$CoCl_2DPE_2$	EtOH	11.9	9.9	15
$CoCl_2(DPE)_2$	EtOH	8.7	7.6	45
$CoCl_2DPP$	EtOH	11.7	9.7	65
$CoCl_2DPP$ + DPP	EtOH	11.4	9.4	53
$CoCl_2DPB$	EtOH	10.6	9.2	15
$CoCl_2DPB$	EtOH	11.2	9.4	trace
+ DPB	*t*-BuOH	11.1	9.1	trace

$CoCl_2L_{(2)}$=0.20 mmol.
Reaction condition: see footnote in Table 1.

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16) a) F. Zingales, F. Canziani, and A. Chiesa, *Inorg. Chem.*, **2**, 1303. b) 12).

17) A. Sacco and R. Rossi, *Chem. Commun.*, **1965**, 602.

18) G. W. Parshall and J. J. Mrowca, "Advances in Organometallic Chemistry" ed. by F. G. A. Stone and R. West, Academic Press Inc. New York, Vol. 7, (1968), p. 157.

19) Y. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **71**, 233 (1968).

20) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 4217, 6777 (1970).

A diphenyl-complex may be formed in this catalyst system, since Chatt and his associates[21] isolated a diaryl-complex from the reaction solution of $CoBr_2(PEt_2Ph)_2$ with mesitylmagnesium bromide. No further details of the mechanism of 1,4-hexadiene formation are yet clear in these systems.

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[21] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1961**, 285.