

Preparation and Properties of a But-2-enyl Butadiene Complex of Cobalt and of an Analogous Complex from Isoprene

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Reaction of butadiene with cobalt(II) chloride in the presence of metallic zinc, ethanol, and triphenylphosphine gives the complex *anti*- π -but-2-enylbutadiene(triphenylphosphine)cobalt, $(C_4H_7)(C_4H_8)CoPPh_3$. This is readily isomerized to the *syn*-isomer by action of PPh_3 , dimethyl sulphoxide, or pyridine. From isoprene an analogous complex $(C_5H_9)(C_5H_8)CoPPh_3$ is obtained. The co-ordinated diolefin is displaced from these complexes by carbon monoxide to give the corresponding dicarbonyl derivatives. N.m.r. data for all of the complexes isolated are reported. Reaction of the complexes $(C_4H_7)(C_4H_8)CoPPh_3$ and $(C_5H_9)(C_5H_8)CoPPh_3$ with allene, 3-methylbuta-1,2-diene, and acetylene gives highly crystalline linear polymers.

THERE has been much interest in the reaction of butadiene with transition metal complexes, due to the very different kinds of products that can be obtained. These

include metal-olefin^{1,2} or but-2-enyl derivatives,^{2,3} oligomerized butadiene-complexes,^{4,7} cyclic or linear oligomers,^{4,5,6} and polymers.^{8,9} We have examined

¹ A. Carbonaro and A. Greco, *J. Organometallic Chem.*, 1970, **25**, 477.

² See H. W. Quinn and J. H. Tsai, *Adv. Inorg. Chem. Radiochem.*, vol. 12, p. 217.

³ S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

⁴ G. Wilke, *Angew. Chem.*, 1963, **2**, 105.

⁵ G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

⁶ G. Natta, U. Giannini, P. Pino, and A. Cassata, *Chimica e Industria*, 1965, **47**, 524.

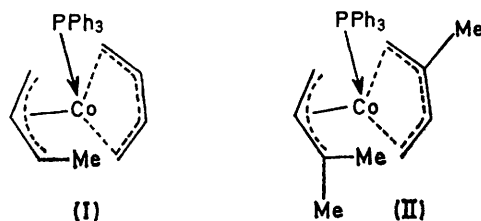
⁷ J. K. Nicholson and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 807.

⁸ R. E. Rinehart, H. P. Smith, J. S. Witt, and H. Romeyn, *J. Amer. Chem. Soc.*, 1961, **83**, 4864.

⁹ A. J. Canale, W. A. Hewett, T. M. Shryne, and E. A. Youngman, *Chem. and Ind.*, 1960, 1304.

the reaction of cobalt(II) chloride with butadiene in the presence of metallic zinc, ethanol, and triphenylphosphine and have isolated a but-2-enyl-butadiene complex of cobalt. An analogous complex has been obtained from the reaction with isoprene.

We now describe the preparation and some reactions of these complexes; we have already reported briefly on the complex from butadiene.¹⁰



In the preparation of complex (I) crystals of formula $C_{26}H_{28}CoP$, are obtained by low-temperature crystallization. At room temperature the formation of

to give metallic cobalt is less so that higher temperatures can be used.

The complexes have been identified on the basis of their chemical behaviour and their n.m.r. spectra, and, for complex (I) by X-ray examination.

Reaction of (I) with aqueous hydrochloric acid gives butadiene and butenes (a mixture of the three isomers) in *ca.* 1:1 ratio. Similarly, (II) gives isoprene and a mixture of methylbutenes. This suggests that (I) and (II) contain a molecule of diolefin π -bonded to cobalt and a butenyl group. These conclusions are in agreement with the n.m.r. spectra of the complexes (see the Table). The spectra of both (I) and (II) show the resonance pattern characteristic of π -but-2-enyl complexes, with $J_{gem} = 0$, $J_{anti} = 10$, $J_{syn} = 7$. For complex (I) the value of the coupling constant J_{ab} is 6 Hz, and that of J_{bd} is 11 Hz, while no coupling is observed between the geminal protons H^d and H^c . These findings are consistent with an *anti* configuration

TABLE

N.m.r. data ^a for the but-2-enylbutadiene, 3-methylbut-2-enyl-2-methylbutadiene, and but-2-enyldicarbonyl complexes of cobalt

Complex <i>anti</i> -(PPh ₃)CoC ₈ H ₁₃ ^b Compound (I)	a 4.23m <i>J</i> _{Me} ^b 6 <i>J</i> _b ^b 6	b 3.00m <i>J</i> _c ^b 7 <i>J</i> _d ^b 11	c 4.98d	d 8.43t <i>J</i> _F ^b 11	Me 6.97d	g 2.55m <i>J</i> _k ^b 7 <i>J</i> _i ^b 11.5	g 2.55m <i>J</i> _t ^b 7 <i>J</i> _e ^b 11	or _k ^t 5.15d	or _k ^k 4.80d	or _i ^e 7.57t <i>J</i> _F ^b 11.5	or _e ⁱ 6.54t <i>J</i> _F ^b 9.3
<i>syn</i> -(PPh ₃)CoC ₈ H ₁₃ ^c Compound (III)	6.40m <i>J</i> _{Me} ^c 5 <i>J</i> _b ^c 10 <i>J</i> _F ^c 15	2.93m <i>J</i> _c ^c 7 <i>J</i> _d ^c 11	5.28d	6.93dd <i>J</i> _F ^c 14	6.22d	2.70m <i>J</i> _k ^c 7 <i>J</i> _i ^c 11	2.70m <i>J</i> _t ^c 7 <i>J</i> _e ^c 11	5.43d	4.95d	8.0t <i>J</i> _F ^c 9.3	7.90t <i>J</i> _F ^c 11.9
<i>anti</i> -(PPh ₃)(CO) ₂ CoC ₄ H ₇ ^d	3.83q <i>J</i> _b ^d 6.5 <i>J</i> _{Me} ^d 6.5	2.95t <i>J</i> _c ^d 6 <i>J</i> _b ^d 11	4.88t <i>J</i> _F ^d 6	4.64d	6.31t <i>J</i> _F ^d 5						
<i>syn</i> -(PPh ₃)(CO) ₂ CoC ₄ H ₇ ^d	4.5m <i>J</i> _b ^e 10 <i>J</i> _{Me} ^e 5	3.2m <i>J</i> _c ^e 6 <i>J</i> _b ^e 10	5.18t <i>J</i> _F ^e 14	5.58d	5.86t <i>J</i> _F ^e 4						
(PPh ₃)CoC ₁₀ H ₁₇ ^e Compound (II)	Me' 5.84s	b 2.9m <i>J</i> _c ^f 8 <i>J</i> _d ^f 11.5	c 5.52 ^e	d 6.97t <i>J</i> _F ^f 11.5	Me 6.89d <i>J</i> _F ^f 2.1	g 2.80m <i>J</i> _{Me'} ^{g'} 3.2 <i>J</i> _k ^{g'} 7.6 <i>J</i> _i ^{g'} 10.45	Me 5.53d	f 5.31s	k 5.19d	e 8.64d <i>J</i> _F ^g 13.8	i 7.59t <i>J</i> _F ^g 10.45

^a The chemical shifts are in p.p.m. with respect to internal benzene. ^b In [2H₆]benzene. ^c In [2H₈]toluene. ^d In [2H₆]acetone. ^e Observed only by integration and decoupling.

noticeable amounts of metallic cobalt is observed, but this can be greatly reduced by operating initially at -30° , and subsequently gradually warming the mixture to *ca.* 20° . Under these conditions the reaction is completed in about four days, with a yield of *ca.* 80% based on the cobalt chloride. Longer reaction times cause the formation of oils derived from oligomerization of butadiene which made the isolation of (I) laborious. The analogous reaction with isoprene gives red-orange crystals $C_{28}H_{32}CoP$, (II), with a yield of *ca.* 50%. The reaction is slower than with butadiene but the tendency

of the but-2-enyl group. The abnormal upfield shift observed for the *anti* protons of butadiene (H^e and H^i) suggests a partial σ character for the bonds between cobalt and the terminal C-atoms of the co-ordinated butadiene.

The low chemical-shift of H^g and $H^{g'}$ supports this observation and suggests that the C(2)-C(3) bond of the butadiene is of olefinic character.

It is interesting to observe that ³¹P is coupled only

¹⁰ L. Porri, G. Vitulli, M. Zocchi, and G. Allegra, *Chem. Comm.*, 1969, 276.

with protons in the *anti*-position, which suggests a pyramidal structure for the molecule, in which the *anti*-hydrogens are much closer to P than the *syn*-ones.

In the spectrum of (II) one observes that there is no coupling between the protons of the allylic unit and the methyl groups, which indicates that these are both on the terminal C-atom of the allylic ligand. On the basis of these findings complex (I) is to be formulated as *anti*- π -but-2-enylbutadiene(triphenylphosphine)cobalt, and complex (II) as 3-methylbut-2-enylisoprene(triphenylphosphine)cobalt. For complex (I) the structure has been confirmed by X-ray analysis on single crystals; the geometry of the molecule has been reported in a preliminary note.¹⁰

For complex (I) *syn-anti* isomerism is expected. The *anti*-isomer is stable at room temperature in pentane or benzene and does not change configuration upon recrystallization from these boiling solvents. However, it is rapidly transformed into the *syn*-isomer by the action of PPh₃, pyridine, dimethyl sulphoxide, even at room temperature. The fact that the isomerization is caused by co-ordinating compounds suggests that it occurs through a σ - π intermediate with free rotation around the metal-carbon bond. The n.m.r. spectrum of (III) (see Table) is very similar to that of (I) except for a very strong upfield shift of the proton geminal to the methyl group, H^a. For this complex the value of J_{ab} is 10 Hz and that of J_{bc} is 7 Hz, in accord with a *syn*-configuration. A less significant difference between the spectra of (I) and (III) is that the resonances of the co-ordinated butadiene are more symmetrical in the spectrum of (III). In the latter complex, only the *anti* protons are coupled with ³¹P, as observed for complex (I), which suggests that the steric structure of (I) and (III) is essentially the same.

The formation reaction of (I) represents one of the few cases in which an *anti*-isomer is obtained practically free of the *syn*-isomer. In fact, the reactions leading to π -butenyl complexes usually give the *syn*-isomer or a mixture of the two, with predominance of the *syn*, which is thermodynamically the more stable.¹¹⁻¹⁴ We can say little about the mode of formation of (I), but most probably the butenyl group is formed by reaction of a co-ordinated butadiene on a Co-H bond. The formation of an *anti*-configuration is presumably due to the specific conformation of the co-ordinated butadiene in the intermediate complex.

Complexes (I)–(III) are diamagnetic and are soluble in the common organic solvents, but are insoluble in water.

In chlorinated solvents they decompose readily to give cobalt(II) chloride. In solution they also react with some inorganic chlorine compounds, e.g. ZnCl₂,

SiCl₄, SnCl₄. Thus compounds (I)–(III) react with ethanolic solutions of ZnCl₂ to give an unidentified green precipitate containing cobalt, zinc, and chlorine. If PPh₃ is present in the solution, the known compound chlorotris(triphenylphosphine)cobalt can be isolated.¹⁵ This exchange reaction affects the preparative yields of compounds (I) and (II). The red filtrate obtained after the separation of the metallic zinc contains zinc chloride, and if the solution is set aside at room temperature, the red colour gradually fades with the formation of a green precipitate. This can be prevented by crystallizing (I) and (II) as rapidly as possible.

The reactions of compounds (I)–(III) with hydrogen, carbon monoxide, and some unsaturated compounds have been examined. The complexes react rapidly with hydrogen at room temperature and atmospheric pressure to give brown solutions from which no definite compound could be isolated. When the reaction is carried out in the presence of PPh₃, the known diamagnetic compound (PPh₃)₃CoH₃ was isolated.^{16,17}

Treatment of complexes (I)–(III) with carbon monoxide causes the displacement of the co-ordinated diolefin, but the ease of displacement varies with the complex. (I) Reacts under very mild conditions (*i.e.* upon bubbling carbon monoxide through a solution of (I) in pentane at room temperature) to give *anti*- π -but-2-enyldicarbonyl(triphenylphosphine)cobalt (IV). Complex (III) reacts under more severe conditions (*i.e.* at 40° and *ca.* 10 atm.) to give *syn*- π -but-2-enyldicarbonyl(triphenylphosphine)cobalt (V). The configurations of (IV) and (V) were determined from their n.m.r. spectra which show the typical pattern of the π -but-2-enyl group, with resonances at 2.95, 3.83, 4.64, 4.88, 6.31, and 3.2, 4.54, 5.18, 5.58, 5.86 p.p.m. from benzene.

The values of $J_{ab} = 7$ for complex (IV) and $J_{ab} = 11$ for (V) are in accord with the assigned configurations. Complex (V) appears identical with that obtained by action of PPh₃ on π -but-2-enyltricarbonylcobalt.¹⁸ Complex (IV) is slowly isomerized to (V) in acetone solution, more rapidly in hydrocarbon solutions in the presence of PPh₃, or dimethyl sulphonide or pyridine. In both these compounds ³¹P is coupled only with the *syn*-hydrogens and not with those *anti*; moreover H^a is strongly deshielded on respect to the corresponding hydrogen in (I) and (III) (3.83 *vs.* 4.22, and 4.5 *vs.* 6.40). Both these observations suggest the possibility that the steric disposition of the butenyl unit with respect to the P atom is different in compounds (IV) and (V) from that in (I), (II), and (III). Complex (II) also reacts with carbon monoxide, with displacement of isoprene, to give 3-methylbut-2-enyldicarbonyl(triphenylphosphine)cobalt (VI). The reaction occurs easily at

¹¹ J. A. Bertrand, H. B. Jonassen, and D. W. Koore, *Inorg. Chem.*, 1963, **3**, 601.

¹² J. M. Rowe and D. A. White, *J. Chem. Soc. (A)*, 1967, 1451.

¹³ J. Lukas, S. Coren, and J. E. Blom, *Chem. Comm.*, 1969, 1303.

¹⁴ C. W. Fong and W. Kitching, *Austral. J. Chem.*, 1969, **22**, 477.

¹⁵ M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1969, **3**, 227.

¹⁶ A. Sacco and M. Rossi, *Chem. Comm.*, 1967, 316.

¹⁷ A. Sacco and M. Rossi, *Inorg. Chim. Acta*, 1968, **2**, 96.

¹⁸ R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 1097.

room temperature, upon bubbling carbon monoxide into a pentane solution of (II).

Benzene solutions of (I)–(III) react at room temperature with allene and 3-methylbuta-1,2-diene to give, with high yields, crystalline polymers having a regular 1,2-structure. From acetylene, crystalline linear polyacetylene is obtained. These polymers appear identical with those obtained, from the same monomers, with other organometallic catalysts.^{19–21}

Polymers, but with lower yields, were also obtained from ethylene, butadiene, isoprene, and hexa-1,5-diene.

EXPERIMENTAL

All reactions and manipulations were carried out in an atmosphere of pure dry nitrogen. Solvents were used after dehydration and distillation. N.m.r. spectra were obtained on a Varian HA 100 spectrometer, i.r. spectra on a 221 Perkin-Elmer instrument.

anti-But-2-enylbuta-1,3-diene(triphenylphosphine)cobalt.—Butadiene (40 ml, 26 g), ethanol (7 ml), n-hexane (40 ml), triphenylphosphine (3.3 g), anhydrous cobalt(II) chloride (1.7 g), and zinc powder (10 g) were introduced, in that order, into a glass container. The suspension was kept at -30° for one day, then at 0° for two days, and finally at room temperature for an additional day, with occasional shaking during this period. The colour changed gradually from green to orange, then to red. The suspension was filtered at *ca.* -10° with rigorous exclusion of air; the filtrate was concentrated to *ca.* 60 ml *in vacuo* and set aside at -30° to give, after *ca.* two days, red-orange diamagnetic crystals (2.4 g) (I) which decompose at 110°C . These were filtered off and recrystallized from n-pentane (Found: C, 72.2; H, 6.4; Co, 14. $\text{C}_{26}\text{H}_{28}\text{CoP}$ requires C, 72.57; H, 6.5; Co, 13.7%). An additional 1.9 g of complex was obtained upon extraction of the solid residue with n-pentane; the red solution obtained was filtered, concentrated, and cooled to -30° . N.m.r. examination (see the Table) showed (I) to have the *anti*-configuration. It is insoluble in water, but is readily soluble in benzene, pentane, tetrahydrofuran, and ethanol giving orange-red solutions. Recrystallization from benzene gives crystals containing half a molecule of occluded benzene per atom of cobalt (Found: C, 74.7; H, 6.2; Co, 12.4. $\text{C}_{26}\text{H}_{31}\text{CoP}$ requires C, 74.3; H, 6.6; Co, 12.5%). X-Ray examination of single crystals confirmed the presence of benzene in the amount indicated by analysis. Recrystallization of the benzene-containing crystals from n-pentane gave (I).

3-Methylbut-2-enyl-2-methylbuta-1,3-diene(triphenylphosphine)cobalt.—Zinc powder (34 g) was added to a suspension, cooled to -10° , of ethanol (20 ml), benzene (60 ml), isoprene (80 ml), triphenylphosphine (3.3 g), and cobalt(II) chloride (1.7 g). The mixture was set aside for two days at -10° , then four days at room temperature, and shaken occasionally. The solid phase was filtered off and the filtrate was concentrated under reduced pressure to *ca.* 10 ml; n-pentane was added to it. The precipitate which formed was filtered off and the filtrate was set aside at *ca.* -30° for two days to give orange-yellow crystals (2.8 g) of complex (II), which were recrystallized from n-pentane (Found: C, 73.91; H, 7.36; Co, 13.2. $\text{C}_{28}\text{H}_{32}\text{CoP}$ requires C, 73.3; H, 7.0; Co, 12.9%).

¹⁹ S. Otsuka, K. Mori, T. Suminoe, and F. Imaizumi, *European Polymer J.*, 1967, **3**, 73.

syn-But-2-enylbuta-1,3-diene(triphenylphosphine)cobalt.—(a) Complex (I) (1.1 g) was dissolved in dry dimethyl sulphoxide (3 ml) at 30° (at higher temperatures some decomposition occurs). The solution was filtered and set aside to give, after a few days, red diamagnetic crystals of complex (III), having the same elemental analysis as the starting material (for n.m.r. data see the Table).

(b) To a solution of complex (I) (1 g) in benzene (10 ml), triphenylphosphine (0.5 g) was added; the mixture was kept at 40° for 1 h. After removal of the solvent under reduced pressure, the residue was dissolved in n-pentane (10 ml) and filtered. The filtrate was cooled to -30° to give crystals of (III).

Reaction of Complex (I) with HCl.—To a solution of complex (I) (0.2 g) in diethyl ether (5 ml), cooled to -5° , conc. HCl (2 ml) was added, and the mixture was shaken for a few minutes. G.l.c. of the ether layer showed the presence of butadiene and butenes in the ratio *ca.* 1 : 1.

The analogous reaction with complex (II) gave isoprene and a mixture of isoprenes in *ca.* 1 : 1 ratio.

Reaction of the Complexes (I)–(III) with Hydrogen.—A solution of the complex (I) (1.2 g) and triphenylphosphine (1.4 g) in benzene (15 ml) was kept in a hydrogen atmosphere at room temperature and atmospheric pressure for 48 h.

After this time, the solution was concentrated to a small volume and n-pentane was added to it. The product precipitated by cooling the mixture to 0°C was recrystallized from methanol-tetrahydrofuran (1 : 1 by vol.), under an atmosphere of argon, to give green-yellow crystals (*ca.* 2 g). (Found: C, 75.8; H, 5.6. Calc. for $\text{C}_{18}\text{H}_{18}\text{CoP}$: C, 76.4; H, 5.66).

The product was found to be identical with an authentic sample^{16,17} of $[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{CoH}_3$.

When the recrystallization was carried out under an atmosphere of nitrogen, the known^{16,17} complex $[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{CoH}\cdot\text{N}_2$ was obtained.

Analogous reactions with complexes (II) and (III) gave the same product as obtained from (I).

But-2-enyldicarbonyl(triphenylphosphine)cobalt.—*anti*-*Isomer*. Carbon monoxide was bubbled through a solution of complex (I) (0.5 g) in n-hexane (80 ml) for *ca.* 6 h at room temperature. The solution was concentrated under reduced pressure to *ca.* 30 ml, and then cooled to -20° to give orange-red crystals (0.7 g), decomp. 90° (Found: C, 66.7; H, 5.45; Co, 12.8. Calc. for $\text{C}_{24}\text{H}_{22}\text{CoOP}_2$: C, 66.65; H, 5.15; Co, 13.5%). For the n.m.r. spectrum see the Table; ν_{max} (KBr): 3062w, 2995m, 2970w, 2945w, 2900w, 1980vs, 1925vs, 1895m, 1585w, 1480s, 1432s, 1385m, 1358w, 1305w, 1195w, 1190w, 1160w, 1090s, 1030m, 1023m, 985m, 910w, 860w, 742w, 700s, and 695s.

syn-*Isomer*. A solution of the complex (III) (0.5 g) in benzene (15 ml) was treated with carbon monoxide at 40° and 10 atm. for 24 h. The benzene was evaporated, n-hexane was added, and the solution was then cooled to -30° to give crystals (0.4 g) whose elemental analysis was identical to that of the compound obtained from complex (I). The n.m.r. spectrum (see the Table) showed that the complex obtained had a *syn* configuration; ν_{max} (KBr): 3062w, 3000w, 2960w, 2940w, 2920w, 2850w, 1975vs, 1920vs, 1910vs, 1582w, 1478s, 1432s, 1370s, 1305w, 1232w, 1180m, 1118w, 1090s, 1068vw, 1025m, 995m, 840m, 741s, 698s, and 690s.

²⁰ G. Natta, G. Mazzanti, and P. Corradini, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1958, **25**, 3.

²¹ L. B. Luttinger, *J. Org. Chem.*, 1962, **27**, 1591.

3-Methylbut-2-enyldicarbonyl(triphenylphosphine)cobalt.—Carbon monoxide was bubbled, at room temperature, through a solution of (II) (0.5 g) in n-hexane (40 ml) for 6 h. After concentration to a small volume, orange-red crystals (0.4 g) were obtained on cooling (Found: C, 67.1; H, 5.4; Co, 12.9. $C_{25}H_{24}CoO_2P$ requires C, 66.7; H, 5.35; Co, 13.1%). ν_{max} (KBr): 3060w, 2960m, 2923w, 2959w, 1980s, 1922s, 1585w, 1478w, 1426m, 1370w, 1260s, 1180m, 1110s, 1095s, 1025s, 860w, 795s, 740m, 718w, and 690s.

Reaction of Complex (I) with Allenes and Acetylene.—A sample of complex (I) (30 mg) was added to a solution of allene (3 g) in toluene (20 ml) and the resulting mixture was set aside at room temperature. After a few hours an insoluble polymer began to precipitate. The reaction was terminated after 40 h by pouring the reaction mixture into a large excess of methanol (ca. 100 ml). The polymer (2.6 g) was purified by repeated washing with methanol and then dried under reduced pressure. The i.r. spectrum (film by hot pressing) and X-ray pattern showed it to be crystalline and identical with the polymer already described in the literature.¹⁹ The reactions with 3-methylbuta-1,2-diene and with complexes (II) and (III) were analogous.

Dry acetylene was bubbled at room temperature through a solution of complex (I) (50 mg) in benzene (15 ml) for 8 h. A crystalline, insoluble polymer (0.8 g) was obtained, which was found (i.r. and X-ray) to be identical to polyacetylene obtained with other organometallic catalysts.^{20,21}

Reaction with Ethylene.—Dry ethylene was bubbled at room temperature into a solution of complex (I) (50 mg) in benzene (20 ml) for 18 h. The precipitate formed (0.1 g) was separated by decantation repeatedly washed with methanol. X-Ray and i.r. examinations showed it to be crystalline linear polyethylene.

Reaction with Diolefins.—Complex (I) (0.1 g) was introduced into a solution of butadiene (12 g) in benzene (20 ml) and the mixture was kept at room temperature for 4 days. The solvent and unchanged butadiene were removed under reduced pressure, leaving a polybutadiene (ca. 1 g) of the following composition: *trans*-1,4 units (40%), *cis*-1,4 (40%) and 1,2 (20%).

Analogous reaction with isoprene, penta-1,3-diene and hexa-1,5-diene also gave polymers which were not examined.

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