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The Insertion of Diene Hydrocarbons in a Transition Metal - Ligand Bond

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Reactions involving the insertion of diene hydrocarbons in transition metal - ligand bonds, leading to the formation of σ- or π-allyl complexes, are examined and their possible mechanisms are discussed.
The bibliography includes 242 references.

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I. INTRODUCTION

Progress in polymerisation catalysis achieved in recent years has been largely due to the involvement of organometallic compounds in research. The use of catalytic systems based on aluminium and transition metal compounds made it possible to carry out specific syntheses of many olefin and diene polymers and to organise the industrial production of polyethylene, polypropylene, and stereoregular rubbers, including isoprene rubber.

Among many pathways leading to the reaction of unsaturated hydrocarbons under the influence of organometallic compounds, the addition of the latter to multiple carbon–carbon bonds is of particular interest. Active metal–carbon bonds, capable of involvement in further chemical reactions, persist in the resulting adducts. Numerous repetition of the addition steps, achieved in many instances, leads to the formation of long hydrocarbon chains, i.e. telomer or polymer molecules.

Studies on the addition of organic derivatives of metals to conjugated multiple carbon–carbon bond systems have yielded extremely valuable information for the development of organometallic and organic chemistry. The wide variability of the structures of the adducts formed and their dependence on the nature of the reactants made it possible to outline various approaches to the study of the mechanisms of the reactions of unsaturated compounds.

In contrast to the addition of organometallic compounds to mono-olefins, in the case of conjugated diene systems adducts are formed with a metal atom in the β-position relative to the double bond. When there are coordination vacancies in the metal, such σ-compounds can be converted into thermodynamically more favourable π-allyl complexes in which the bond with the metal is formed with participation of three carbon atoms. In the presence of substituents at the terminal carbon atoms of the π-allyl group, the "non-classical" structure of the π-allyl complexes is responsible for the non-equivalence of the bonds of the metal with the first and third carbon atoms and also for the existence of complexes in two isomeric forms (*syn*- and *anti*-). All these facts must be taken into account in determining the mode of addition of transition metal derivatives to diene hydrocarbons.

The synthesis of diene polymers under the influence of metal complex catalysts is carried out by inserting the monomer molecules in metal–carbon bonds. The study of the simplest reactions of this type is therefore of undoubted interest for the development of ideas concerning the mechanisms of the elementary stages in the polymerisation of diene hydrocarbons, which are practically important processes.

An attempt was made in the present review to survey all the available experimental data on the reactions involving the insertion of diene hydrocarbons in active metal–ligand (hydride, alkyl, acyl, allyl, and acido-groups), which can be regarded as model reactions leading to the formation of active centres in various organic synthetic and polymerisation processes with participation of diene hydrocarbons. The insertion of dienes in metal–ligand bonds is also used widely as one of the preparative procedures for the synthesis of allyl complexes of transition metals[1,2].

II. INSERTION IN TRANSITION METAL–HYDROGEN BONDS

1. Buta-1,3-diene

Transition metal hydrides add to butadiene with formation of both σ- and π-crotyl 1 : 1 adducts, the insertion in the latter case being accompanied by the displacement of one monodentate ligand from the coordination sphere of the metal.

At moderate temperatures hydridopentacarbonylmanganese adds to butadiene in the 1,4-positions[3,4]. The reaction products contain 85% of the *cis*-σ-crotyl complex and 15% of the *trans*-isomer. Hydridocyclopentadienyldicarbonyliron reacts similarly under these conditions[5]. At 80–100°C in the former case and under ultraviolet irradiation in the latter, mainly *syn*-π-crotyl complexes are formed. Mild decarbonylation and a mixture of *cis*- and *trans*-σ-crotylmanganese pentacarbonyls with the aid of bis(diphenylphosphinoethane)iridium chloride takes place with retention of the geometrical configuration of the crotyl ligand[6].

The π-crotyl structure has been established for butadiene adducts and all the remaining hydrides listed in Table 1. It is therefore impossible to determine the mode of addition (in the 1,2- and 1,4-positions). Table 2 presents the known examples of reactions involving the

insertion of butadiene in transition metal–hydrogen bonds formed when compounds of these metals are reduced in the presence of butadiene.

Table 1. The insertion of butadiene in transition metal–hydrogen bonds.

Initial compound	Reaction product	References
$HMn(CO)_5$	*cis-* and *trans-* $CH_3CH{=}CHCH_2{-}Mn(CO)_5$	3
$HFe(C_5H_5)(CO)_2$	*cis-* and *trans-* $CH_3CH{=}CHCH_2{-}Fe(C_5H_5)(CO)_2$	5
$HFe(NO)(CO)_3$	$C_4H_7Fe(NO)(CO)_2$	7,8
$HFe(CO)_4SiCl_3$	*anti-* $C_4H_7Fe(CO)_3SiCl_3$	9
$HCo(CO)_4$	*syn-* and *anti-*$C_4H_7Co(CO)_3$	3,10–13
$HCo(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_n$ ($n = 2,3$)	$C_4H_7Co(CO)_{4-n}[P(n\text{-}C_4H_9)_3]_{n-1}$	14
$HCo(N_2)[P(C_6H_5)_3]_3$	*syn-*$C_4H_7Co(C_4H_6)P(C_6H_5)_3$	15
$HCo(PF_3)[P(C_6H_5)_3]_3$	*anti-* $C_4H_7Co(C_4H_6)PF_3$	16
$\{HNi[P(OCH_3)_3]_4\}^+HSO_4^-$	*syn-* and *anti* -$\{C_4H_7Ni[P(OCH_3)_3]_3\}^+HSO_4^-$	17,18
$[HTi(C_5H_5)_2]_2$	$C_4H_7Ti(C_5H_5)_2$	19,20
$HV(CO)_6$	*syn-* and *anti-* $C_4H_7V(CO)_5$	21,22
$HRh(CO)[P(C_6H_5)_3]_3$	$C_4H_7Rh(CO)[P(C_6H_5)_3]_2$	23
$HRh[P(C_6H_5)_3]_4$	*syn-* and *anti* -$C_4H_7Rh[P(C_6H_5)_3]_2$	24
$HRh(PF_3)_4$	*syn-* and *anti* -$C_4H_7Rh(PF_3)_3$	25,26
$(CH_3)_5C_5{-}M(Cl)(\mu\text{-}H)(\mu\text{-}Cl)M(Cl){-}C_5(CH_3)_5$ ($M = Rh, Ir$)	*syn-*$C_4H_7M(Cl)[C_5(CH_3)_5]$	27–29
$\{HIr[C_5(CH_3)_5]X\}_2$ ($X = Cl, Br, I$)	*syn-*$C_4H_7Ir(X)[C_5(CH_3)_5]$	30
$HIr(CO)_2[P(C_6H_5)_3]_2$	$C_4H_7Ir(CO)[P(C_6H_5)_3]_2$	23
$HPt(NO_3)[P(C_2H_5)_3]_2 + NaB(C_6H_5)_4$	$\{C_4H_7Pt[(P(C_2H_5)_3]_2\}^+B(C_6H_5)_4^-$	31,32
$[HPt(PR_3)_2(CH_3COCH_3]^+PF_6^-$ PR_3 = $P(C_6H_5)_{3-n}(CH_3)_n$ ($n = 1,2$)	$[anti\text{-}C_4H_7Pt(PR_3)_2]^+PF_6^-$	33,34
$HPt(ClO_4)[P(C_6H_5)_3]_2$	$[anti\text{-}C_4H_7Pt[P(C_6H_5)_3]_2\}^+ClO_4^-$	34
$[HMo(C_5H_5)_2L]_2 + NH_4PF_6$ ($L = \mu\text{-}C_6H_{11}MgBr_2Mg[O(C_2H_5)_2]$)	$[C_4H_7Mo(C_5H_5)_2]^+PF_6^-$	35,36
$[H_3Mo(C_5H_5)_2]^+PF_6^-$	$[C_4H_7Mo(C_5H_5)_2]^+PF_6^-$	37
$[HM(C_5H_5)_2Li]_4$ ($M = Mo, W$)	$[C_4H_7M(C_5H_5)_2]^+PF_6^-$	37,38

π-Crotyl(cyclo-octa-1,5-diene)rhodium is the product of the addition to butadiene of the intermediate hydride formed from (π-cyclohexenyl)(cyclo-octal-1,5-diene)-rhodium via the reaction[56]

$$(1.5\text{-}C_8H_{12})Rh(\pi\text{-}C_6H_9) \rightleftharpoons [(1.5\text{-}C_8H_{12})\underset{\underset{H}{|}}{Rh}(\pi\text{-}C_6H_8)] \xrightarrow[+C_4H_6]{-C_6H_8} (1.5\text{-}C_8H_{12})Rh(C_4H_7)\ .$$

The intermediate nickel hydride complexes arising in the reduction of $NiCl_2$ by tri-isobutylaluminium react in succession with several butadiene molecules, giving rise to allyl complexes of nickel with the oligomeric π-allyl ligand[57]. The reactions involving the addition of hydride complexes of transition metals to butadiene with formation of intermediate π- or σ-crotyl complexes take place in the hydrogenation of butadiene under the influence of the pentacyanocobalt ion[58–69] and also in the codimerisation of butadiene with α-olefins in the presence of transition metal compounds capable of forming active metal–hydrogen bonds under the conditions of the synthesis[70–84].

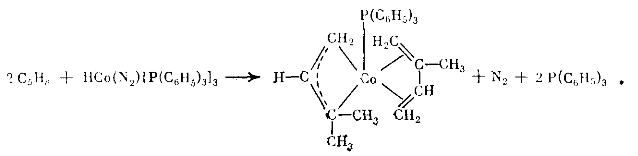
2. Isoprene and Chloroprene

Hydridopentacarbonylmanganese reacts with isoprene and chloroprene to form 1,4-σ-adducts close to room temperature[3]:

$$H_2C{=}\underset{\underset{X}{|}}{C}{-}CH{=}CH_2 + HMn(CO)_5 \rightarrow H_3C{-}\underset{\underset{X}{|}}{C}{=}CH{-}CH_2Mn(CO)_5 \quad X{=}CH_3,\ Cl\ .$$

The iron hydride $HFe(CO)_4SiCl_3$ reacts similarly with isoprene[9].

According to ^1H NMR data, the only product of the interaction of isoprene with the ion $[HCo(CN)_5]^{3-}$ under the conditions of the hydrogenation reaction is the α-3-methylbut-2-enyl complex $[(CH_3)_2C{=}CHCH_2Co(CN)_5]^{3-}$.[88] This structure of the σ-allyl adducts of manganese, iron, and cobalt agrees satisfactorily with the 1,1-dimethyl-π-allyl structure of the complexes formed directly from the diene and the metal hydride under conditions promoting the elimination of one of the ligands. The interaction of isoprene with $HMn(CO)_5$ and $HFe(CO)_4SiCl_3$ at 95 °C yields immediately 1,1-dimethyl-π-allyl complexes[3,9]. The iron and cobalt hydrides $HFe(NO)(CO)_3$[7,8] and $HCo(CO)_4$[13] add similarly. It has been shown[85] that $HCo(N_2)[P(C_6H_5)_3]_3$ reacts with two isoprene molecules, one of which is inserted in the Co–H bond and the other is coordinated to cobalt, displacing a nitrogen molecule and two triphenylphosphine molecules:



This complex can also be obtained by the interaction of isoprene with cobalt hydride formed *in situ* (in the reduction of an ethanol solution of $CoCl_2$ by metallic zinc in the presence of triphenylphosphine)[42,86].

Table 2. The insertion of butadiene in transition metal–hydrogen bonds at the instant of their formation on reduction of metal compounds in the presence of butadiene.

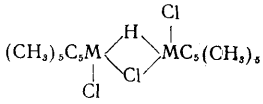
Initial compounds	Reaction product	References
$CoCl_2 + NaBH_4 + C_2H_5OH$	$C_8H_{13}CoC_4H_6$	39–41
$CoCl_2 + Zn + P(C_6H_5)_3 + C_2H_5OH$	*anti-* $C_4H_7Co(C_4H_6)P(C_6H_5)_3$	42,43
Cathodic reduction of $CoCl_2 + P(n\text{-}C_4H_9)_3$	$C_4H_7Co(C_4H_8)P(n\text{-}C_4H_9)_3$	44
$CoBr_2L_2 + NaBH_4 + NaX + CH_3OH$ *	$[(syn\text{-}C_4H_7)_2CoL_2]^+X^-$	45
$CoCl_2\cdot6H_2O + L_2 + NaBH_4 + NaX + CH_3OH$ *	$[(syn\text{-}C_4H_7)(anti\text{-}C_4H_7)CoL_2]^+X^-$	46
$NiCl_2 + Zn + P(C_6H_5)_3 + C_2H_5OH + C_6H_6$	$\{syn\text{-}C_4H_7Ni[P(C_6H_5)_3]_2\}^+ZnCl_3^-$	47
$[P(C_6H_5)_3]_4Ni + HCl$	$(syn\text{-}C_4H_7Ni[P(C_6H_5)_3]Cl$	48
$RhCl_3 + C_2H_5OH$	$(syn\text{-}C_4H_7RhCl_2)_2C_4H_6$	49–51
$[(C_2H_4)_2RhCl]_2 + HCl + C_2H_5OH$	$(syn\text{-}C_4H_7RhCl_2)_2C_4H_6$	52
$RhCl_3\cdot3H_2O + Zn + C_2H_5OH$	$[syn\text{-}C_4H_7RhCl_2(H_2O)]_2$	53
$[(CH_3)_5C_5MCl_2]_2 + Na_2CO_3 + C_2H_5OH$ ($M = Rh, Ir$)	$syn\text{-}C_4H_7MCl[C_5(CH_3)_5]$	54
$H_2IrCl_6 + C_2H_5OH$	$(syn\text{-}C_4H_7IrCl_2)_2C_4H_6$	55

*L_2 = 2,2′-bipyridyl or 1,10-phenanthroline; X = ClO_4 or PF_6.

According to Kruck et al.[87], the hydride $HCo(PF_3)_4$ adds to isoprene with formation of a 1,1-dimethyl-π-allyl adduct. Nixon and coworkers[88] observed that cobalt and rhodium complexes of this type readily undergo a skeletal isomerisation to 1,2-dimethyl-π-allyl complexes[26,89]. It is of interest that ***anti***-1,2-dimethyl-π-allyltrifluorophosphine complexes of cobalt and rhodium are isomerisation intermediates. However, the ***anti***-isomer of the rhodium complex is rapidly converted into the *syn*-isomer. On the other hand, the hydride $HRh(PF_3)_4$ adds to isoprene

with the immediate formation of the *anti*- and *syn*-1,2-dimethyl-π-allyl adducts[28]; the ratio of the *anti*- and *syn*-isomers depends on the temperature conditions in the reactions.

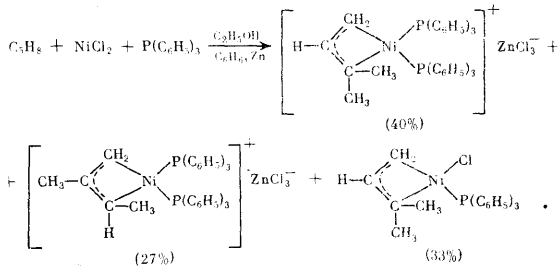
The iridium compound $HIr(CO)_2[P(C_6H_5)_3]_2$,[23] the titanium compound $[HTi(C_5H_5)_2]_2$,[20] the vanadium compound $HV(CO)_6$,[21,22] the palladium compounds $[HPdL_2]^+PF_6^-$ (L_2 = diphenylphosphinoethane or diphenylarsinoethane),[90,91] and the rhodium and iridium complexes



[29] react with isoprene like the rhodium complexes. On the other hand, the vanadium hydride complexes $HV(CO)_4L_2$ (L_2 = bisdiphenylarsinomethane or 1-diphenylarsino-2-diphenylphosphinoethane) add to isoprene with the preferential formation of 1,1-dimethyl-π-allyl complexes[92].

A mixture of adducts of the nickel hydride $\{HNi.[P(OCH_3)_3]_4\}^+HSO_4^-$ and isoprene contains mainly the *anti*-1,2-dimethyl-π-allyl complexes[18]. The fraction of 1,1-dimethyl-π-allyl adducts does not exceed 20%. Under these conditions, chloroprene forms exclusively $\{syn$-1-methyl-2-chloro-π-allyl-Ni$[P(OCH_3)_3]_3\}^+HSO_4^-$.

The mode of reaction of isoprene with nickel hydride complexes, formed in the reduction of nickel chloride by metallic zinc in the presence of bases, differs significantly from that observed by Tolman[18]. The amount of 1,1-dimethyl-π-allyl complexes is in this case much greater[47]:



On the other hand, when this reaction is carried out in acetonitrile, the only product is the 1,1-dimethyl-π-allyl adduct.

The codimerisation of isoprene with ethylene (in the presence of a catalyst comprising a nickel halide complex of trialkylphosphine + dialkylaluminium chloride) leads to the formation of *cis*-4-methylhexa-1,4-diene,[78] which indicates the occurrence of the reaction via an intermediate *anti*-1,2-dimethyl-π-allyl adduct of nickel hydride and isoprene. When a rhodium catalyst is used, the product is the *syn*-1,2-dimethyl-π-allyl complex, responsible for the formation of *trans*-4-methylhexa-1,4-diene from isoprene and ethylene[52]. The reactions involving the insertion of isoprene in the metal–hydride bond with formation of allyl complexes also occur when it [isoprene] is reduced by potassium iron carbonylate[93], in carbonylation under the influence of palladium catalysts[94], and in polymerisation in the presence of rhodium nitrate[95].

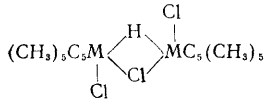
3. Penta-1,3-diene, Its Homologues, and Penta-1,4-diene

Penta-1,3-diene combines with transition metal hydrides, forming preferentially 1,3-dimethyl-π-allyl complexes regardless of the nature of the transition metal.

Among the adducts of hydridotetracarbonylcobalt and penta-1,3-diene, both *syn,anti*-, and *syn,syn*-1,3-dimethyl-π-allylcobalt tricarbonyls (with the latter predominating) were found[13,96-98]. The cobalt hydride, obtained by the reduction of $CoCl_2$ with zinc, reacts with penta-1,3-diene similarly[88].

The relative contents of the *syn,syn*- and *syn,anti*-structures depend primarily on the reaction temperature. The reaction of $HRh(PF_3)_4$ with penta-1,3-diene at 0°C leads to the formation of both isomers in nearly equimolar proportions. An increase of temperature promotes an increase of the yield of the *syn,syn*-1,3-dimethyl-π-allyl adducts. The influence of temperature has been demonstrated particularly clearly by Tolman[18], who showed that the addition of $\{HNi[P(OCH_3)_3]_4\}^+HSO_4^-$ to penta-1,3-diene at 0°C leads to $\{syn,anti$-1,3-dimethyl-π-allyl-Ni$.[P(OCH_3)_3]_3\}^+HSO_4^-$, whereas at 50°C 80% of the total amount of the 1,3-dimethyl-π-allyl complexes are in the *syn,syn*-configuration.

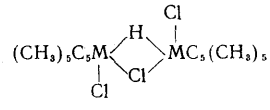
Only the *syn,syn*-1,3-dimethyl-π-allyl ligands were present in the complexes $C_5H_9Ti(C_5H_5)_2$[19,20,99-102] and $[C_5H_9PdL_2]^+PF_6^-$ (L_2 = diphenylphosphinoethane or diphenylarsinoethane)[90,91], synthesised by the reaction of penta-1,3-diene with the corresponding titanium and palladium hydrides. The *syn,syn*-1,3-dimethyl-π-allyl complexes of rhodium and iridium are the main products of the interaction of penta-1,3-diene with the complexes



[29] but in these instances only 15% of the complexes with the 1-ethyl-π-allyl ligand are formed. Reactions involving the insertion of penta-1,3-diene in metal–hydride bonds also occur when it polymerises under the influence of rhodium chloride[103] and is hydrogenated in the presence of $RuCl_2[P(C_6H_5)_3]_3$.[104]

The influence of the position of the methyl substituents at the double bonds in penta-1,3-diene homologues on the rate and mode of reaction with the nickel hydride $\{HNi[P(OCH_3)_3]_4\}^+HSO_4^-$ was investigated by Tolman[18]. Table 3 shows that dienes with inner double bonds (hexa-2,4-diene and 2,5-dimethylhexa-2,4-diene) exhibit the lowest reactivity. 2-Methylpenta-1,3-diene is five times less reactive than penta-1,3-diene; the presence of substituents at the inner double bond makes the difference between the rates less significant.

The titanium hydride $[HTi(C_5H_5)_2]_2$ reacts with 3-methylpenta-1,3-diene similarly to nickel hydride[20]. On the other hand, the mode of reaction of the iridium hydride $HIr(CO)_2[P(C_6H_5)_3]_2$ with 2,4-dimethylpenta-1,3-diene differs from that indicated in Table 3 for nickel hydride—the product is 1-isopropyl-2-methyl-π-allyldicarbonyltriphenylphosphineiridium[23]. Rhodium and iridium complexes of the type



react with 2-methylpenta-1,3-diene and 2,5-dimethylhexa-2,4-diene to form compounds with 1,1,3-trimethyl- and 3-isopropyl-1,1-dimethyl-π-allyl ligands[29]. However, when the former diene reacts with the rhodium complex, approximately 20% of *syn*-1-ethyl-2-methyl-π-allyl-RhCl$.[C_5(CH_3)_5]$ is also formed.

Only $HCo(CO)_4$ adds to penta-1,4-diene; in this instance a mixture of *syn*- and *anti*-1-ethyl-π-allylcobalt tricarbonyls with an admixture of the 1,3-dimethyl-π-allyl complexes was isolated[96-98]. Under the influence of the

rhodium hydride $HRh(PF_3)_4$,[28] the titanium hydride $[HTi(C_5H_5)_2]_2$,[20], and the nickel hydride $HNi[P(OCH_3)_3]_4 \cdot HSO_4$,[18] penta-1,4-diene initially isomerises to penta-1,3-diene. Subsequently the reaction proceeds via the pathway indicated above.

Table 3. Reactions of $HNi[P(OCH_3)_3]_4HSO_4$ with dienes[18].

Diene	Structure of π-allyl ligand in reaction products	$\tau^*_{1/2}$, h (t, °C)
Penta-1,3-diene (mixture of *cis*- and *trans*-forms)	*syn, anti*-1,3-dimethyl-π-allyl *syn, syn*-1,3-dimethyl-π-allyl	0.3 (0)
trans-3-Methylpenta-1,3-diene	*syn, anti*-1,2,3-trimethyl-π-allyl *syn, syn*-1,2,3-trimethyl-π-allyl	0.5 (0)
trans-2-Methylpenta-1,3-diene	*syn*-1,1,3-trimethyl-π-allyl	1.5 (0) 0.2 (25)
2,4-Dimethylpenta-1,3-diene	1,1,3,3-tetramethyl-π-allyl	0.4 (25)
Hexa-2,4-diene (mixture of *trans, trans*-, *cis, trans*-, and *cis, cis*-forms)	*anti*-1-ethyl-*syn*-3-methyl-π-allyl *syn*-1-ethyl-*syn*-3-methyl-π-allyl	0.5 (25) 0.5 (25)
2,5-Dimethylhexa-2,4-diene	3-isopropyl-1,1-dimethyl-π-allyl	1.5 (25)

*50% reaction time.

The higher rate of reaction of hydrides with conjugated dienes compared with non-conjugated dienes readily explains the finding that in the codimerisation of 1,3-dienes with α-olefins the hydrides react with 1,3-dienes to form π-allyl complexes.

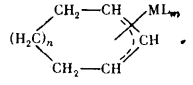
4. 2,3-Dimethylbutadiene

The addition of transition metal hydrides to 2,3-dimethylbutadiene leads to complexes with a 1,1,2-trimethyl-π-allyl ligand. These reactions have been described only for cobalt-group (cobalt[13] as well as rhodium and iridium[29]) hydrides. The iron hydride $HFe(CO)_4SiCl_3$ reacts with 2,3-dimethylbutadiene to form only the σ-adduct[9].

The nickel complexes $\{C_6H_{11}Ni[P(C_6H_5)_3]_2\}^+ ZnCl_3^-$ and $C_6H_{11}Ni[P(C_6H_5)_3]Cl$ have been obtained as a result of the addition to 2,3-dimethylbutadiene of the nickel hydride formed in the reduction of $NiCl_2$ by zinc in the presence of triphenylphosphine[47].

5. Cyclic Diene Hydrocarbons

Table 4 presents the structures of the adducts of transition metal hydrides and cyclic dienes, which are complexes with π-allyl cyclic ligands having the general form



π-Cyclohexenyl-π-cyclo-octa-1,5-dieneiridium[108] and π-cyclo-octenyl-π-cyclo-octa-1,5-dienecobalt[86] were obtained as a result of the addition of the intermediate metal hydrides to cyclohexa-1,3-diene and cyclo-octa-1,5-diene respectively:

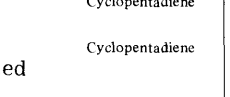
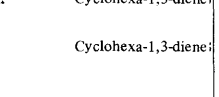
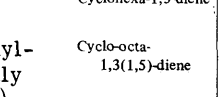
$$(1.5\text{-}C_8H_{12})\,IrCl]_2 + C_6H_8 \xrightarrow[\text{ether, u.v.light}]{\text{iso-}C_3H_7MgBr} \left[\begin{array}{c} H \\ | \\ (1.5\text{-}C_8H_{12})\,Ir\,(C_6H_8) \end{array}\right] \rightarrow (1.5\text{-}C_8H_{12})\,Ir\,(C_6H_9);$$

$$CoCl_2 + 1.5\text{-}C_8H_{12} \xrightarrow[C_5H_5N]{Na,\ THF} [HCo\,(1.5\text{-}C_8H_{12})_2] \rightarrow C_8H_{13}Co\,(1.5\text{-}C_8H_{12}).$$

6. Allene Hydrocarbons

Allene is very readily inserted in a metal–hydrogen bond. The addition of hydrogen leads solely to an *sp*-hybridised carbon atom and π-allyl complexes are formed. The pentacoordinate trigonal-bipyramidal rhodium and iridium complexes $HRh(CO)[P(C_6H_5)_3]_3$ and $HIr(CO)_2[P(C_6H_5)_3]_2$ react with allene to form the complexes $C_3H_5M(CO)[P(C_6H_5)_3]_2$ having the same coordination number[23]. As in the reaction with butadiene, one of the equatorial ligands (triphenylphosphine in the former complex and carbon monoxide in the latter) is displaced. $HRh(PF_3)_4$ and allene give rise to the adduct $C_3H_5Rh(PF_3)_3$;[25,26] $HV(CO)_6$ adds to allene to form π-allylpentacarbonylvanadium[22].

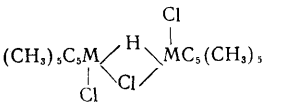
Table 4. Addition of cyclic dienes to transition metal hydrides.

Cyclic diene	Initial hydride complex	Reaction product	Refs.
Cyclopentadiene	$HNi[P(OCH_3)_3]_4HSO_4$	$C_5H_7Ni[P(OCH_3)_3]_3HSO_4$	18
Cyclopentadiene	$HPdL_2PF_6$*	$C_5H_7PdL_2PF_6$*	90,91
Cyclopentadiene	 (M=Rh, Ir)	$C_5H_7M[C_5(CH_3)_5]Cl$	105
Cyclohexa-1,3-diene	$HCo(CO)_4$	$C_6H_9Co(CO)_3$	106
Cyclohexa-1,3-diene	$HRh[P(C_6H_5)_3]_4$	$C_6H_9Rh[P(C_6H_5)_3]_2$	24
Cyclohexa-1,3-diene	$HRh(PF_3)_4$	$C_6H_9Rh(PF_3)_3$	25,26
Cyclohexa-1,3-diene	 (M=Rh, Ir)	$C_6H_9M[C_5(CH_3)_5]Cl$	105
Cyclohexa-1,3-diene	$HPdL_2PF_6$*	$C_6H_9PdL_2PF_6$*	90,91
Cyclohexa-1,3-diene	$H_2Mn_2(CO)_{12}$	$C_7H_{11}Mn(CO)_4$	107
Cyclo-octa-1,3(1,5)-diene	 (M=Rh, Ir)	$C_8H_{13}M[C_5(CH_3)_5]Cl$	27,105
Cyclo-octa-1,3(1,5)-diene	$HPdL_2PF_6$*	$C_8H_{13}PdL_2PF_6$*	90,91
Cyclo-octa-1,3(1,5)-diene	$HPh[P(C_6H_5)_3]_4$	$C_8H_{13}Rh[P(C_6H_5)_3]_2$	24

*L_2 = diphenylphosphinoethane or diphenylarsinoethane.

When allene was allowed to react with a solution of *trans*-$HPt(NO_3)[P(C_2H_5)_3]_2$ and $NaB(C_6H_5)_4$ in methanol, the complex $\{C_3H_5Pt[P(C_2H_5)_3]_2\}^+B(C_6H_5)_4^-$ was isolated[31,32]. The reaction of allene with *trans*-$HPt(CH_3OH)[P(C_6H_{11})_3]_2 \cdot PF_6$ led to an analogous π-allyl complex[109].

The hydride complexes of rhodium and iridium



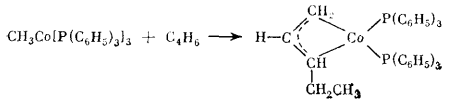
add to 1,1-dimethylallene, forming 1,1-dimethyl-π-allyl complexes[29]. The insertion of the coordinated methylallene in the metal–hydride bond in the intermediate complex, arising in the interaction of π-indenyl-π-dimethylacetylenebis(trimethyl phosphite)molybdenum tetrafluoroborate with $NaBH_4$, leads to an anti-π-crotyl complex of molybdenum[110].

III. INSERTION IN TRANSITION METAL–CARBON σ-BONDS

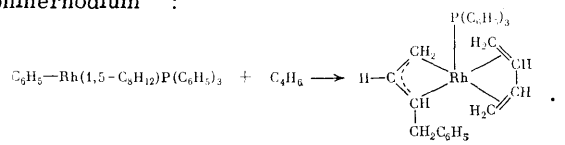
As a rule, alkyl compounds of transition metals are characterised by a low stability which naturally restricts the range of their reactions with unsaturated hydrocarbons.

1. Conjugated Dienes

Only one example of a stoichiometric reaction involving the insertion of butadiene in a transition metal–alkyl bond is known at the present time [111]:

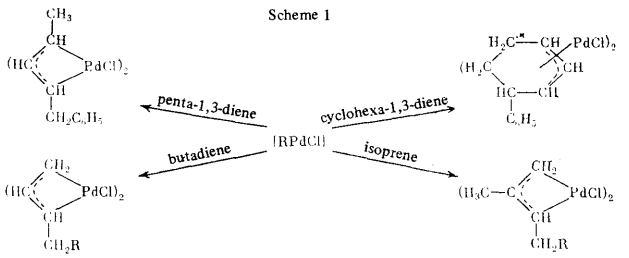


The geometrical configuration of the 1-ethyl-π-allyl ligand in this complex was not established by the authors. Butadiene also adds to phenyl(cycloocta-1,5-diene)triphenylphosphinerhodium [112]:



Alkyl- and allyl-palladium chlorides, obtained from $LiPdCl_3$ and the corresponding mercury, magnesium, or tin compounds, react with conjugated dienes to form π-allyl adducts [113]:

Scheme 1



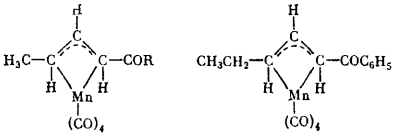
R = CH_3, C_6H_5, *p*-anisyl, or 1-naphthyl

R = C_6H_5 or $C_6H_5CH_2$

The structure of the adducts in Scheme 1 leads to the conclusion that the mode of insertion of isoprene in Pd–C σ-bonds is the same as in its addition to Pd–H and Pd–acido-ligand bonds (see below).

σ-Alkyl and aryl derivatives of manganese, cobalt, and iron carbonyls readily react with 1,3-diene hydrocarbons. The addition reaction is preceded by the conversion of the organometallic compound into an acyl form: the diolefin molecule is inserted in the metal–acyl [M–C(O)–] bond (Tables 5 and 6). The data in Tables 5 and 6 show that the mode of addition of acylmetal carbonyls is determined by the nature of the transition metal in the initial methyl- or acyl-metal carbonyls. Whereas the *cis*-double bond is the most reactive in cobalt complexes and the acyl ligand is attached to the terminal carbon atoms in transoid diolefins, iron complexes react with *cis*-penta-1,3-diene and isoprene to form 1,3- and 1,1-disubstituted π-allyl adducts respectively.

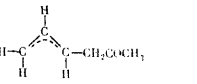
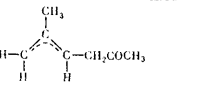
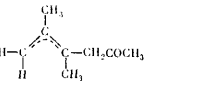
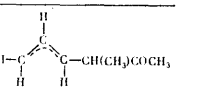
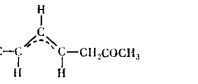
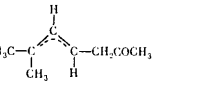
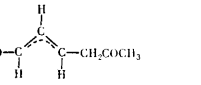
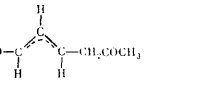
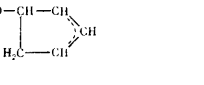
Phenyl- and methyl-manganese pentacarbonyls react with butadiene and *trans*-penta-1,3-diene to form the π-allyl complexes (I) and (II) respectively [118–121]:



(I) (II)

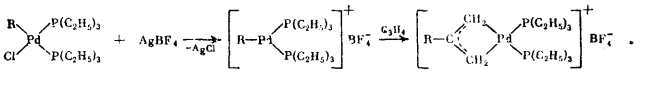
R = CH_3 or C_6H_5 .

Table 5. π-Allylcobalt tricarbonyl formed from dienes and $CH_3Co(CO)_4$ or $CH_3COCo(CO)_4$. [114–117]

Diene	Structure of π-allyl ligand
Butadiene	
Isoprene	
2,3-Dimethylbutadiene	
cis-Penta-1,3-diene	
trans-Penta-1,3-diene	
4-Methylpenta-1,3-diene	
trans-1-Methoxybutadiene	
Methyl sorbate	
Cyclopentadiene	

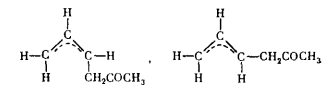
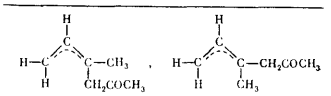
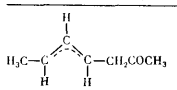
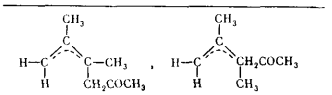
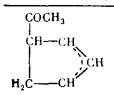
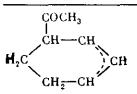
2. Cumulated Dienes

Allene is inserted in the $Pt–CH_3$ bond with formation of 2-methyl-π-allyl complexes [122–124]. The coordination-unsaturated methyl- or phenyl-bis(triphenylphosphine)-palladium tetrafluoroborates add very readily to allene [125]:

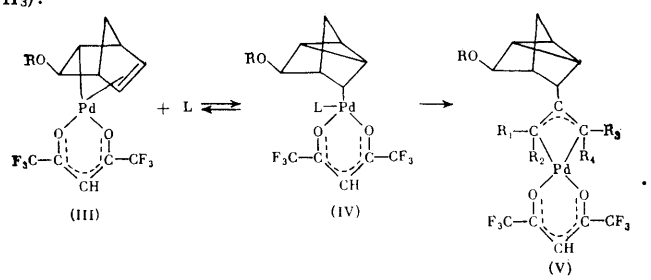


The reactions of cationic vinylplatinum complexes $\{Pt(R^1{=}C{=}CHR^2)[P(OC_2H_5)_3]_2(CH_3COCH_3)\}^+PF_6^-$ (R^1 = CH_3, CF_3, or $COOCH_3$; R^2 = CH_3, CF_3, C_6H_5, $COOCH_3$ or cyclo-C_6H_{11}) react with allene also to form π-allyl products with a 2-alkenyl substituent in the π-allyl ligand [126]. Acyltricarbonylcobalt reacts with allene to form π-allyl complexes containing an acyl group at the central carbon atom of the allyl group [127].

Table 6. The structure of the π-allyl ligands in the iron complexes formed in reactions of $NaFe(NO)(CO)_3$ and CH_3I in the presence of dienes [8].

Diene	Structure of π-allyl ligand
Butadiene	
Isoprene	
cis-Penta-1,3-diene	
2,3-Dimethylbutadiene	
Cyclopentadiene	
Cyclohexa-1,3-diene	

Allene and 1-methyl-, 1,1-dimethyl-, and 1,3-dimethylallenes are inserted in the palladium–nortricyclenyl ligand σ-bond in complexes (IV) (L = 1,2-diene) arising when allenes react with complexes (III) (R = CH_3CH_2CO or C_6H_5CO). This results in the formation of the corresponding π-allyl complexes (V) (R_1, R_2, R_3, R_4 = H or CH_3): [128]



(III) (IV) (V)

Conjugated dienes (butadiene, isoprene, 2,3-dimethylbutadiene, and *cis*- and *trans*-pentadienes) also readily form complexes of type (IV), in which L is a 1,3-diene coordinated as a monodentate species. However, in contrast to allene, they are not inserted in a Pd–C bond.

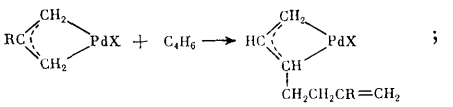
IV. ADDITION OF DIENES TO π-ALLYL METAL–CARBON BONDS

The discovery in 1964 of the catalytic activity of the π-allyl complexes of nickel in the polymerisation of 1,3-diolefins [129,130] initiated the systematic investigation of these reactions. However, in the present review we shall not consider in detail the extensive data accumulated at the present time on the polymerisation of dienes under the influence of π-allyl transition metal complexes, attention being concentrated on studies in which the structures of the products of the addition of the 1,3-dienes to the metal–π-allyl ligand bond were rigorously established.

1. Butadiene

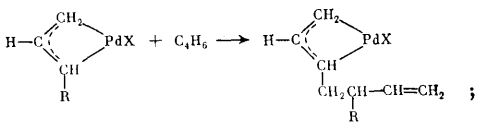
Bis-(π-crotylnickel halides) add stereo- and regioselectively to butadiene [131]. Regardless of the nature of the halogen atom, the addition takes place with participation of only the bond between nickel and the unsubstituted carbon atom of the allyl group. Frequent repetition of such steps leads to the formation of polybuta-1,4-diene. The individual stages of this process were investigated in relation to the reactions of bis-(π-crotylnickel iodide) and its deuterated analogues with butadiene, 1,1,4,4-tetradeuterobutadiene, and perdeuterobutadiene [132–141].

The π-allyl complexes of palladium react with butadiene to form 1 : 1 adducts [142–150]:



R = H, CH_3, Cl, $COOCH_3$, or t-C_4H_9; X = acido-ligand.

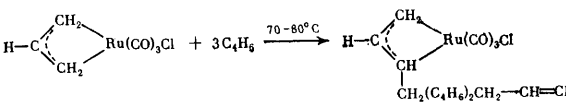
Regardless of the nature of the substituent (R = CH_3, CH_2Cl, Cl, $COOCH_3$, or C_6H_5), in reactions with 1-substituted π-allylpalladium complexes butadiene attacks only the substituted carbon atom of the allyl ligand [143–146,149]:



X = Cl, Br, or hexafluoroacetylacetonate.

When the last two reactions are carried out at a high temperature and a high concentration of the reactants, there is a possibility of the polymerisation of the 1,3-diene [144–146,151–153].

π-Allyltricarbonylruthenium chloride reacts with butadiene to form the product of the insertion of three diene molecules at once [154]:

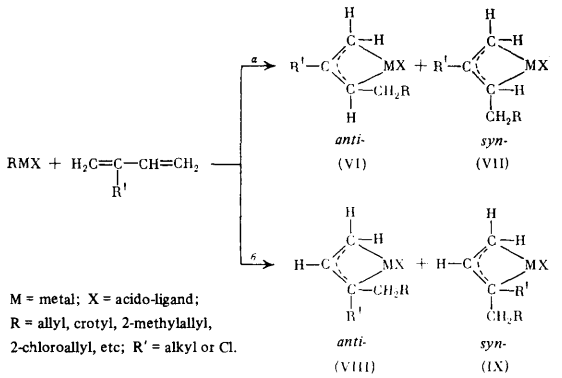


According to infrared spectroscopic data [154], the butadiene units of the complex have the *trans*-1,4-structure.

2. 2-Alkyl-Substituted 1,3-Dienes and Chloroprene

The reactions of these asymmetric dienes with π-allyl complexes of transition metals can lead theoretically to the formation of π-allyl adducts of four types:

Scheme 2

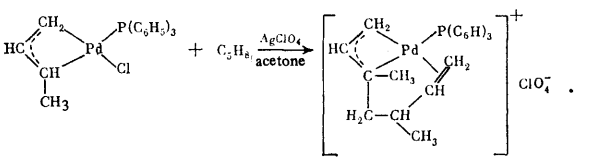


Bis-(π-crotylnickel iodide) reacts with isoprene via both pathways (*a* and *b*). The total fraction of *anti*- and *syn*-1,2-disubstituted complexes (VI) and (VII) is approximately 90%.[155-157] The ratio of these isomers changes during the reaction and tends to a limit, which depends on temperature. During the first period, only the *anti*-complexes (VI) are detected in solution[158,159], but subsequently the latter isomerise to the *syn*-adducts.

The reactions with 2-ethyl-, 2-isopropyl-, and 2-t-butyl-butadienes proceed wholly via pathway *a*.[158-160] The nature of the alkyl substituent has a very significant influence on the ratio of the *anti*- and *syn*-isomers formed. For a long time after the start of the interaction of $(C_4D_7NiI)_2$ with 2-ethyl- and 2-isopropyl-butadienes the concentration of the *anti*-isomers greatly exceeds that of the *syn*-isomers. On the other hand, the adduct of $(C_4D_7NiI)_2$ with 2-t-butylbutadiene exists in the *anti*-configuration (VI) (R′ = t-C_4H_9; R = C_4D_7). The ^{13}C NMR spectra of the 1 : 1 *anti*- and *syn*-adducts of crotylnickel iodide and 2-alkylbutadienes provide an idea about the nature of the distribution of electron density over the π-allyl carbon atoms[161].

In contrast to π-crotylnickel iodide, the π-allyl complexes of palladium react with isoprene only via pathway *b*, yielding 1,1-disubstituted π-allyl complexes (VIII) and (IX) (R′ = CH_3).[143-146,149,162-164] The fraction of the *anti*-isomers (VIII) in the adducts of π-allyl- and π-methylallylpalladium bromides and isoprene is approximately 80%,[146] while bis-(2-chloro-π-allylpalladium chloride)[146,162,163] and 2-chloro-π-allylpalladium hexafluoroacetylacetonate[148] give rise to approximately equal proportions of the *anti*- and *syn*-isomers (VIII) and (IX) (R′ = CH_3, R = CH_2–$CCl=CH_2$). 2-Chloro-π-allylpalladium chloride adds to 2-t-butylbutadiene with formation of a 1,1-disubstituted π-allyl complex in which the chlorobutenyl group is only in the *anti*-position[165].

Structure (X) with a coordinated vinyl group has been proposed for the product of the reaction of π-crotyltriphenylphosphinepalladium chloride with isoprene in the presence of $AgClO_4$, but accurate data for the structure of this compound are not quoted[166]:

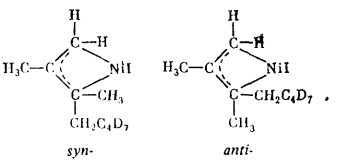


(X)

Chloroprene reacts with π-allyl complexes of palladium like isoprene, forming a mixture of the *syn*- and *anti*-isomers of 1,1-disubstituted π-allyl complexes[146,163].

3. 2,3-Dimethylbutadiene

On interaction with 2,3-dimethylbutadiene, π-allyl complexes of nickel and palladium form adducts containing 1,1,2-trisubstituted π-allyl ligands. The ^1H NMR spectrum of the adduct of $(C_4D_7NiI)_2$ and 2,3-dimethylbutadiene showed the presence in solution of complexes having the *syn*- and *anti*-structures[141,160]:

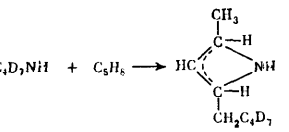


syn- *anti*-

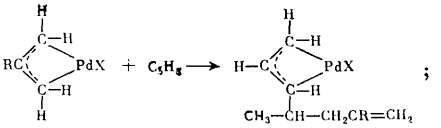
The adducts of the π-allyl complexes of palladium also consisted of a mixture of the *syn*- and *anti*-isomers[149]. In 1-substituted π-allyl complexes of palladium a new carbon–carbon bond is formed between the methylene group of the diene and the substituted carbon atom of the allyl group.

4. Penta-1,3-diene and 4-Methylpenta-1,3-diene

The *cis*- and *trans*-penta-1,3-diene isomers react differently with π-allyl complexes of nickel and palladium. The allyl ligand in the nickel complexes adds to the terminal methylene group of the diene[141,160]:

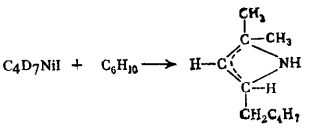


Palladium compounds react with pentadiene, forming 1-substituted π-allyl adducts[146-149]:



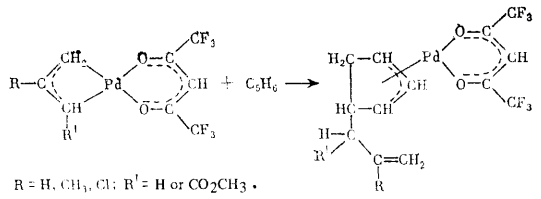
R = H, Cl; X = Cl or hexafluoroacetylacetonate.

[D_7]π-Crotylnickel iodide reacts with 4-methylpenta-1,3-diene to form the 1,3,3-trisubstituted *syn*-π-allyl complex[141,160]:



5. Cyclic 1,3-Dienes

On interaction with π-allyl complexes of palladium, cyclopentadiene forms π-cyclopentenyl compounds[149]:

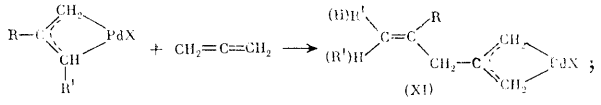


R = H, CH_3, Cl; R' = H or CO_2CH_3.

Palladium 2-chloro-π-allylhexafluoroacetylacetonate adds to cyclohexa-1,3-diene to form the corresponding π-cyclohexenyl complex. Cyclo-octa-1,3-diene is not inserted in the palladium–allyl ligand bond[146,149].

6. Allenes

In contrast to conjugated dienes, allene react with π-allyl complexes of palladium, adding to the less substituted terminal carbon atom of the allyl group[146,148]:

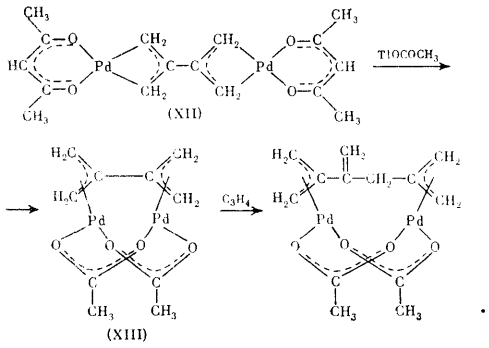


(XI)

R = H, CH_3, or Cl; R' = H, CH_3, Cl, or $COOCH_3$; X = acetylacetonate or Cl.

It is of interest to note that the product of the reaction of bis-(1-chloro-π-allylpalladium chloride) with allene is a mixture of *cis*- (80%) and *trans*-isomers (20%) of compound (XI) (R = H, R' = Cl),[146] which shows that the 1-chloro-π-allyl ligand in the initial complex exists predominantly in the *anti*-configuration.

Interaction of π-allylpalladium acetylacetonate with allene results in the formation of compound (XII) in addition to complex (XI) (R = R' = H).[167] If the acetylacetonate ligand in the former compound is replaced by the acetate ligand, the three-bridge complex (XIII) formed under these conditions can combine with yet another allene molecule[168,169]:



(XII) (XIII)

The reactions involving the insertion of allene in the bond between the nickel atom and the π-allyl ligand take place in the cyclic oligomerisation of allene by nickel[170–174] and rhodium[175] complexes.

Summarising the available experimental data, it is possible to set up activity series for reactions involving the addition of π-allyl complexes of nickel[141,155–160] and palladium[143,146,149] to 1,3-dienes (Table 7). The data in Table 7 show that the mode of addition of π-allyl complexes of nickel and palladium to diolefins is determined by the nature of the transition metal and the acido-ligand links to it. All the addition reactions examined are characterised by high regio- and stereo-selectivity. Isoprene reacts with nickel derivatives faster than does butadiene; in relation to the palladium analogues, butadiene is more reactive. Among π-allylpalladium halides, the chlorides are more reactive than the iodides; allylnickel iodides react more readily with dienes than do the chlorides.

Table 7. The activity series in the formation of 1 : 1 adducts of the π-allyl complexes of nickel and palladium and 1,3-dienes.

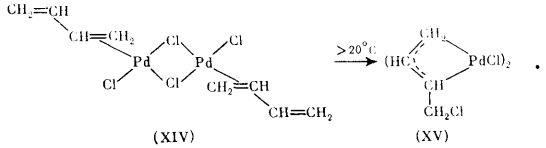
Pd complexes	Ni complexes
Dienes	
Butadiene > isoprene > chloroprene > *trans*-penta-1,3-diene > 2,3-dimethylbutadiene > cyclopentadiene > cyclohexadiene > *cis*-penta-1,3-diene > 2,5-dimethylhexa-2,4-diene	Butadiene < isoprene < 2-ethylbutadiene < 2-isopropylbutadiene < 2-t-butylbutadiene
Substituents in π-allyl ligand	
2-Chloro- > 2-methoxycarbonyl > 1-chloro- > 1-methoxycarbonyl > H > 2-methyl > 1-methyl > 1-phenyl > 2-t-butyl	H > 2-methyl > 2-ethyl > 2-isopropyl ≫ 2-t-butyl
Acido-ligands	
Hexafluoroacetylacetonate > acetylacetonate > Cl > Br > SCN > I	Cl < Br < I

In the palladium complexes a diene molecule attacks the most substituted of the terminal carbon atoms of the π-allyl ligand, while in the reaction of π-crotylnickel halides a new carbon–carbon bond is formed with participation of the unsubstituted carbon atom. Asymmetric 1,3-dienes (isoprene and pentadiene) form adducts with different structures of the π-allyl ligand; palladium forms 1,1-disubstituted and nickel mainly 1,2-disubstituted π-allyl complexes.

V. INSERTION OF DIENES IN TRANSITION METAL–ACIDO-LIGAND BONDS

1. Conjugated Dienes

Addition reactions of this type have been described only for palladium compounds. The interaction of butadiene with the palladium salts $(C_6H_5CN)_2PdCl_2$, $PdCl_2$, and $[(olefin)PdCl_2]_2$ at temperatures below −40°C leads to the quantitative formation of the dimeric complex (XIV):[176]



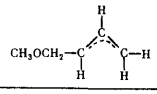
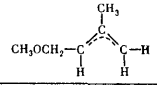
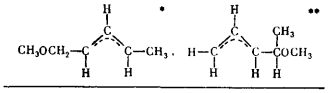
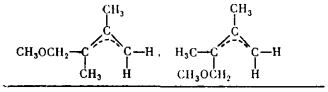
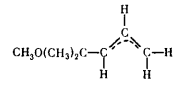
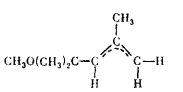
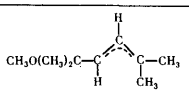
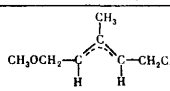
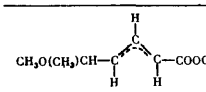
(XIV) (XV)

When the complex (XIV) is heated above 20°C or the interaction of butadiene with the palladium salt is carried out above room temperature, the formation of the π-allyl complex (XV), which is a product of the insertion of the

coordinated butadiene in the Pd–Cl bond, is promoted[176,177]. The addition of palladium chloride to chloroprene takes place with formation of the dimeric 1-chloromethyl-2-chloro-π-allylpalladium chloride[178].

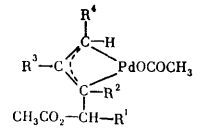
The mechanism of these reactions was studied by Lukas and coworkers[179,180] in relation to the formation of dimeric 1-(1-chloroethyl)-3-methyl-π-allylpalladium chlorides derived from the three isomers of hexa-2,4-diene. If the reaction of the palladium salts with dienes is carried out in an alcoholic medium, then its products are π-allyl complexes with alkoxy-groups. The structures of the π-allyl ligands in the complexes obtained as a result of the interaction of methanol solutions of palladium salts with various dienes are presented in Table 8. Certain cyclic dienes (for example, cyclohexa-1,3-diene) react similarly with palladium salts, giving rise to complexes with cyclic π-allyl ligands containing a methoxy-group in the ring[187]. The stability of these complexes is much lower than that of the corresponding acyclic analogues, which is due to the ease of elimination of the alcohol molecule.

Table 8. The structures of the π-allyl ligands in the complexes formed on interaction of 1,3-dienes with palladium salts in CH_3OH.

Diene	Structure of π-allyl ligand	Refs.
Butadiene		177, 181, 182
Isoprene		181–184
Penta-1,3-diene		184
2,3-Dimethyl-butadiene		181
4-Methylpenta-1,3-diene		181
2,4-Dimethylpenta-1,3-diene		181
2,5-Dimethylhexa-2,4-diene		181
cis- or *trans*-Ocimene		185
Methyl sorbate		186

* Principal product at a reaction temperature of 50–60°C.
** Principal product at a reaction temperature of 0–10°C.

If the interaction of palladium salts with dienes is carried out in acetic acid, complexes with the CH_2OCOCH_3 group at the terminal carbon atom of the allyl group are produced. Butadiene[184,188], isoprene[184,188], and 2,3-dimethylbutadiene[188] react in this way with palladium halides. The π-allyl complexes (XVI) are products of the interaction of palladium acetate with hexa-2,4-dienes ($R^1 = R^4 = CH_3$; $R^2 = R^3 = H$), 2,3-dimethylbutadiene ($R^1 = R^4 = H$; $R^2 = R^3 = CH_3$), and 2-t-butyl-5,5-dimethylhexa-1,3-diene ($R^1 = R^3 = t\text{-}C_4H_9$; $R^2 = R^4 = H$):[189]



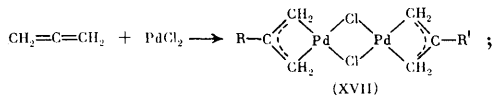
(XVI)

The reactions of diene hydrocarbons with palladium salts in alcoholic media or in acetic acid can be regarded formally as reactions involving the insertion of the diene in the palladium–acido-ligand bond. However, there is good reason to believe at the present time that the nucleophilic methoxide or acetate ions attack directly the diene ligand, resulting in the formation of complexes containing an ether or ester group respectively in the π-allyl ligand[179,183].

The π-allyl complexes with an alkoxy-substituent, generated from butadiene, isoprene, and pentadiene, are intermediates in the carbonylation of these dienes in the presence of palladium chloride[190,191]. The formation of 1-acetoxybutadiene and 1,4-diacetoxybut-2-ene from butadiene and palladium acetate in acetic acid proceeds via the intermediate 1-acetoxy-π-allyl palladium complex[192].

2. Cumulated Dienes

Allene and its homologues (methyl-, dimethyl-, and tetramethyl-allenes) react very readily with palladium chloride, giving rise to π-allyl complexes with various groups at the central carbon atom of the allyl group[182,193–197].



(XVII)

(a) $R = R^1 = Cl$; (b) $R = R^1 = -C(CH_2)CH_2Cl$;

(c) $R = Cl$, $R^1 = -C(CH_2)CH_2Cl$; (d) $R = R^1 = -C(CH_2)CH_2OCH_3$.

The structure of the resulting complex (XVIII) depends on the reaction conditions. If the allene is introduced into a benzene solution of $(C_6H_5CN)_2PdCl_2$, then the product is mainly bis-(2-chloro-π-allylpalladium chloride) (XVIIa). When benzonitrile or methylene chloride is used as the solvent, the complex (XVIIb) is formed; the same compound is produced when allene is passed through a methanol suspension of Na_2PdCl_4. The analogous reaction with $(C_6H_5CN)_2PdCl_2$ leads to approximately equal amounts of complexes (XVIIb) and (XVIId). A dimeric complex with two different π-allyl ligands (XVIIc) is obtained when $(C_6H_5CN)_2PdCl_2$ is introduced into a benzene solution of allene.

The interaction of allene with an acetic acid solution of Na_2PdCl_4 in the presence of sodium acetate leads to bis-(2-acetoxy-π-allylpalladium chloride) (XVII) (R = R′ = CH_3COO).[198] The same complex is a product of the reaction of palladium acetate with allene in benzene in the presence of aqueous NaCl.[199]

The mechanism of reactions of allene with palladium salts, discussed in a number of studies[193,195,197,200], is not altogether clear. Whereas the formation of the complex (XVIIa) apparently involves the simple insertion of allene in the Pd–Cl bond, products containing the dimerised allene can arise via different pathways. At any rate the formation of such complexes does not involve the insertion of a second allene molecule in the Pd–π-allyl bond of complex (XVIIa), because it has been established[197] that this reaction does not occur. Furthermore, such insertion would have resulted in a complex with a different structure of the π-allyl ligand. It has been suggested[197] that the second allene molecule is inserted in the Pd–C bond in the intermediate σ-complex $CH_2=C(CH_2Cl)-Pd$(Cl)<. There is also a possibility of the dimerisation of two allene molecules in the coordination sphere of palladium with subsequent migration of chlorine from palladium to carbon and the formation of compound (XVIIb).

VI. THE MECHANISM OF STEREOREGULATION IN REACTIONS INVOLVING THE INSERTION OF DIENES IN TRANSITION METAL–LIGAND BONDS

The reactions involving the insertion of dienes in transition metal–ligand bonds are characterised by high regio- and stereo-selectivities. This is due primarily to the fact, despite the significant differences in details, the above processes are based on a coordination mechanism. Preliminary coordination of the diolefin to the transition metal is a necessary condition for the subsequent addition. As a result of coordination, the molecule of the unsaturated compound is not only fixed in a particular configuration, which is responsible for the mode of the subsequent interaction, but, by virtue of its unusual energy state in such a complex, it acquires the ability to be inserted in the metal–ligand bond.

Before being inserted in the metal–ligand bond, the diene forms as a rule a π-complex only in the transition state, which hinders the direct experimental detection of such complexes. However, in a few instances it is possible to isolate intermediates (XIV) of this kind[176].

Preliminary coordination of the diene to the transition metal can be observed indirectly by NMR. For example, the coordination of the diolefin to the palladium atom in π-allylpalladium complexes is responsible for the very rapid merging of the signals due to the *syn*- and *anti*-protons at the terminal carbon atom of the allyl group[148,149,201–203]. The exchange of the *syn*- and *anti*-protons is apparently due to the monodentate coordination of the diene. This is indicated by the satisfactory agreement between the reactivities of many dienes in promoting the *syn*–*anti*-proton exchange[148] and in their reactions with 6-acetoxynorbornenylpalladium(III) hexafluoroacetylacetonate[128]: butadiene $\simeq$ ***cis***-penta-1,3-diene $\simeq$ *trans*-penta-1,3-diene > isoprene > 2,3-dimethylbutadiene; under these conditions, asymmetric dienes are coordinated via the less substituted double bond.

The modern treatment of the nature of the bond in the π-complexes formed by the interaction of the metal with unsaturated compounds, devised by Dewar[204] and Chatt and Duncanson[205] in terms of the molecular orbital theory, has been discussed in many detailed reviews and monographs[206–213]. Here one need only emphasise that dative binding plays a special role in reactions of transition metals. According to the familiar classification of Langford and Gray[214] of ligand substitution reactions involving transition metal complexes, substances capable of dative interaction as a rule react via a bimolecular (associative) mechanism. The interaction between the antibonding orbital of the olefin (diene) and *d* electrons takes place over distances longer than the donor–acceptor bond. This should promote a decrease of the overall activation energy for the formation of the metal–substrate π-complex[212].

It follows from the foregoing that the capacity of the ligand for dative binding can give it an appreciable advantage in coordination to the metal even in comparison with substances having a greater electron-donating capacity and in the case of diolefins can be responsible also for the preferential coordination of the double bond with the lower electron density.

The role of the dative interaction in the formation of the π-complex of a diene and a transition metal can be demonstrated most strikingly in relation to the addition of dienes to bis-(π-allylnickel halides)[131]. The study of the reactions of butadiene with $(C_4H_7NiI)_2$ in a medium containing Lewis bases showed that they can be clearly divided into two groups in terms of their effect on the addition reaction. The first group comprises σ-donors (water, ethers, and tertiary amines), which do not influence the rate and mode of reaction regardless of their σ-donor capacity. The second group includes substances (trialkyl- and triaryl-phosphines or the corresponding phosphites and pyridine), which exhibit a π-acceptor capacity in addition to the σ-donor capacity. Depending on their π-acceptor capacity, the latter substances decrease the yield of adducts or, in the limiting case, fully suppress the addition reaction.

On the basis of these facts, the unique ability of bis-(π-crotylnickel iodide) to initiate the polymerisation of diolefins in an aqueous emulsion[215] can be explained not only by the hydrolytic stability of the nickel–carbon bond, but also by the fact that in the transition state of the reaction the dative binding of the transition metal to tne substrate plays a significant role. In view of the d^8 character of the nickel atom in bis-(π-crotylnickel iodide), the considerable strength of the Ni–I bond, the large *trans*-effect of the iodide anion, and the presence of a diolefin molecule in the coordination sphere of the metal, presumably the insertion process proceeds via an associative mechanism with a pentacoordinate transition state formed with participation of the p_z orbital of nickel[131].

The next stage in the process involving the insertion of the diene in the metal–ligand bond is intramolecular transformation of the π-complex, in the course of which the active ligand (hydrogen, alkyl, allyl, or an acido-group) is bound to one of the carbon atoms of the diene system and a new metal–carbon bond is formed.

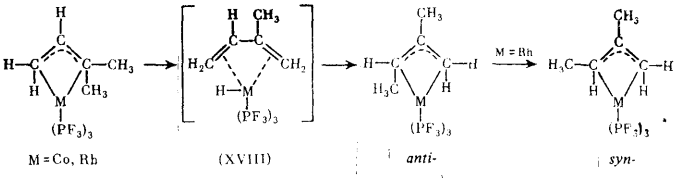
It follows from the data presented in Sections II–V that the order in which the diolefin combines with various reagents is determined by the sum of many factors. In contrast to the familiar characteristics, established for the addition of "classical" electrophiles and nucleophiles to diolefins[216–218], which is likely to have an ionic mechanism, the order of addition of transition metal derivatives

is independent of the direction of electron shifts induced in the molecules of these hydrocarbons under the influence of the electron-donating or electron-accepting substituents. The nature of the transition metal, its valence state, the number and nature of the ligands combined with the latter, the polarisation of the substrate molecule in the π-complex, and steric effects play the main role in the reactions which we have been considering. At the present level of our knowledge it is impossible to take into account all these factors in each specific case. However, there is one general very important characteristic of the reactions involving the insertion of diolefins in a transition metal–ligand bond: the addition reaction leads to the formation of only the *anti*-isomers of the π-allyl adducts; the *syn*-complexes are a result of the *anti*-*syn* isomerisation. This situation is illustrated by the examples in Table 9 and also by data obtained in the study of the mechanism of the hydrosilylation of 1,3-dienes under the influence of palladium, nickel, cobalt, and rhodium complexes [219-223].

Table 9. The configurations of the π-allyl ligand in the initial and final products of the addition of 1,3-diene to transition metal–ligand bonds.

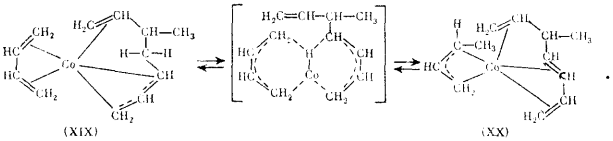
1,3-Diene	Initial transition metal compound	Configuration of π-allyl ligand		Refs.
		in initial compounds	in final products	
		π-Crotyl		
Butadiene	$HCo(CO)_4$	*anti*- and *syn*-	*syn*-(heating	11-13
Butadiene	$HCo(PF_3)[P(C_6H_5)_3]_3$	*anti*-	*syn*-(heating, addition of electron donors)	16
Butadiene	$CoCl_2 + Zn + P(C_6H_5)_3 + C_2H_5OH$	*anti*-	*syn*-	42,43
Butadiene	$HNi[P(OCH_3)_3]_4HSO_4$	*anti*-(88%) and *syn*-(12%)	*syn*-(95%) and *anti*-(5%) (70°C; 1.4 h)	18
Butadiene	$HFe(CO)_4SiCl_3$	*anti*-	*syn*-(heating)	9
Butadiene	$HPt(ClO_4)[P(C_6H_5)_3]_2$	*anti*-	*syn*-(heating)	34
Butadiene	$HPt(acetone)[P(C_6H_5)_3]_2 \cdot PF_6$	*anti*-	*syn*-(heating)	33,34
		1,3-Dimethyl-π-allyl		
Penta-1,3-diene	$HNi[P(OCH_3)_3]_4HSO_4$	*anti, syn*-(100%)	*syn, syn*-(80%) and *anti, syn*-(20%) (50°C; 0.4 h)	18
Penta-1,3-diene	$HCo(CO)_4$	*anti, syn*- and *syn, syn*-	*syn, syn*-	13
		1,2-Dimethyl-π-allyl		
Isoprene	$HNi[P(OCH_3)_3]_4HSO_4$	*anti*-(62%) and *syn*-(18%)	*syn*-(59%) and *anti*-(24%) (75°C; 0.9 h)	18
		1,2-Disubstituted π-allyl ligands		
Isoprene, 2-ethyl-2-isopropylbutadienes	$(C_4H_7NiI)_2$	*anti*-	*syn*- and *anti*- (heating)	14,16 155-160
2-t-Butylbutadiene	$(C_4H_7NiI)_2$	*anti*-	*anti*-	141,156 158-160

The formation of only the *anti*-isomers of the π-allyl adducts in the first stages of the insertion process suggests that in the transition state of the reaction there is always a *cis*-orientation of the diolefin molecule, which determines the stereoselectivity of the process. The relation between the *cis*-oriented 1,3-diene and the *cnti*-structure of the π-allyl ligand have been established experimentally. Consider, for example, the available data [26,88,89] for the skeletal isomerisation of the 1,1-dimethyl-π-allyl ligand to the 1,2-dimethyl-π-allyl ligand in the tris(trifluorophosphine) complexes of cobalt and rhodium. The proximity of the hydrogen atoms of the *anti*-methyl group in the 1,1-dimethyl-π-allyl complex to the metal permits the transfer of one of them to the metal with formation of the *cis*-dienemetal hydride complex (XVIII):



The migration of this hydrogen atom to the other end of the *cis*-oriented diene determines the ***anti***-structure of the 1,2-dimethyl-π-allyl complex.

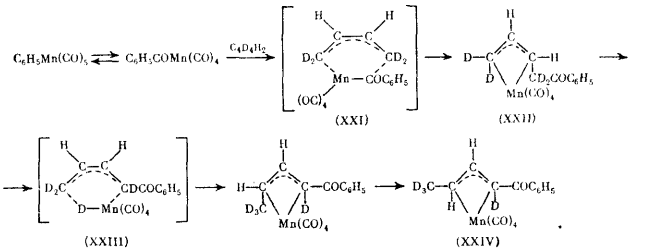
The ease of migration of hydrogen from the *anti*-methyl and *anti*-methylene groups is responsible for the existence of the complex having the general formula $CoC_{12}H_{19}$ in the form of two isomers, (XIX) and (XX), in equilibrium [39,40]. In this equilibrium the transition state is apparently a metallobicyclic complex:



It is easy to account similarly for the structure of the adduct of $C_6H_5Mn(CO)_5$ and butadiene [121] (Scheme 3).

Only the *cis*-orientation of the 1,3-diene in the transition stage (XXI) can lead to the complex (XXII) with deuterium atoms in the *anti*-substituent of the π-allyl ligand. The migration of the deuterium atom nearest to the metal atom via the transition state (XXIII) results in the skeletal isomerisation of the π-allyl ligand. The last reaction stage is the ***anti–syn*** isomerisation with formation of the observed product (XXIV).

Scheme 3

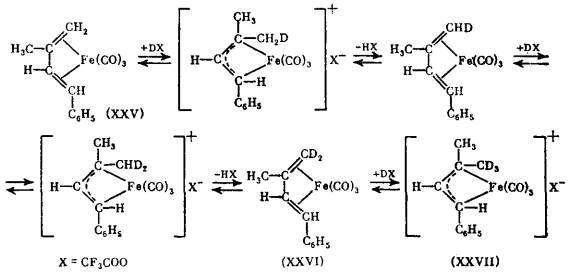


A clear demonstration of the genetic relation between the *cis*-structure of the coordinated diene and the *anti*-configuration of the substituent in the π-allyl complex formed is provided by data for the protonation of the diene complexes of iron [224-235], iridium [236], molybdenum [237,238], and cobalt [239]. For example, the cisoid form of the diene in the butadiene- and pentadiene-iron tricarbonyls is responsible for the selective formation of the *anti*-π-crotyl and ***anti,syn***-1,3-dimethyl-π-allyl complexes [224,225].

The experimental data for the protonation of butadiene-iron tricarbonyl at low temperatures showed that, regardless of the nature of the protonating agent, the proton adds

exclusively to the *anti*-methyl group of the π-crotyliron complex[226]. Treatment of 3-methyl-1-phenylbutadiene-iron tricarbonyl (XXV) with deuterium chloride yielded a π-allyl complex containing deuterium only in the *anti*-methyl group[227]. In solution in CF_3COOD compound (XXV) undergoes a number of successive transformations leading to the diene complex (XXVI) and the π-allyl complex (XXVII) containing the perdeuteromethylene and *anti*-perdeuteromethyl groups:

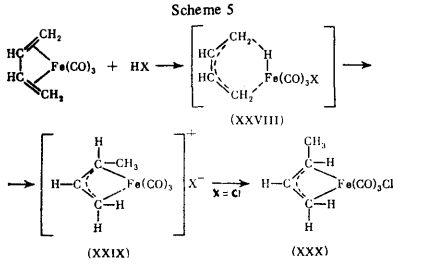
Scheme 4



The protonation and deprotonation reactions presented in Scheme 4 proceed via the intermediate hydridodieneiron complexes, whose existence has been demonstrated by a number of data[226,228-231].

The mechanism of the formation of π-allyl adducts, for example, from butadieneiron tricarbonyl and proton-containing acids, can be represented as follows:

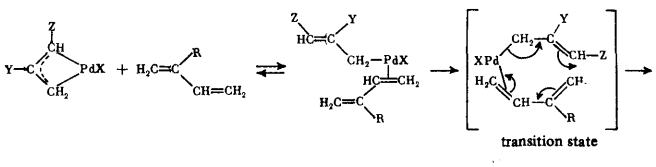
Scheme 5

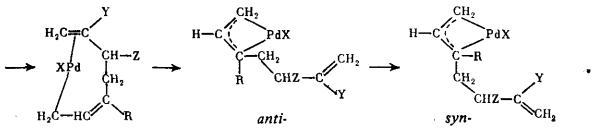


The first stage of the reaction is the oxidative addition of H–X to the initial zerovalent iron complex ($Fe^0 \rightarrow Fe^{2+}$). The *cis*-structure of the diene in the transition state, which precedes the insertion of the diene in the Fe–H bond in (XXVIII), is responsible for the exclusive formation of the *anti*-π-crotyl complex (XXIX) regardless of the nature of the anion of the Brønsted acid. However, if X = Cl, the latter enters the inner coordination sphere of the iron atom and promotes the rapid *anti*–*syn*-isomerisation of the π-crotyl ligand, giving rise to the observed *syn*-complex (XXX).[232,233] The metallocyclic transition state, analogous to compound (XXVIII), is apparently also responsible for the preferential formation of *cis*-σ-crotylmanganese pentacarbonyl when butadiene reacts with $HMn(CO)_5$.[4]

According to ideas put forward by Hughes and Powell[149], the products of the insertion of dienes in the allyl–palladium bond are formed via a metallocyclic transition state with a *cis*-oriented 1,3-diene. The new carbon–carbon bond then arises outside the coordination sphere of the palladium atom:

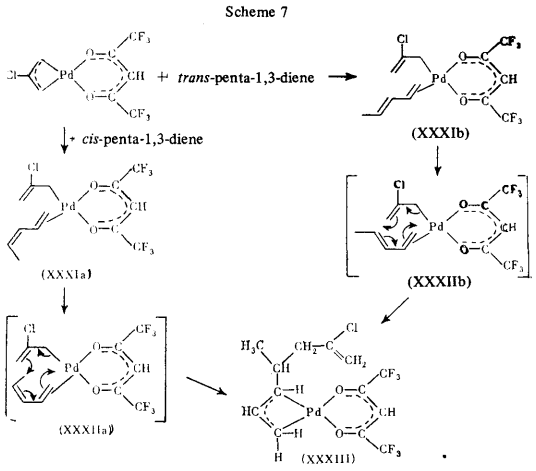
Scheme 6





The proposed mechanism agrees with the order in which π-allyl complexes of palladium add to conjugated dienes and also with the relative reactivity of the latter. For example, the structures of the intermediate π-complexes (XXXIa) and (XXXIb) (Scheme 7), formed on coordination of *cis*- and *trans*-penta-1,3-dienes, explain satisfactorily why the two dienes induce the *syn*–*anti* proton exchange in 2-chloro-π-allylpalladium hexafluoroacetylacetonate at virtually equal rates.

Scheme 7



In the transition state generated in the formation of the insertion product (XXXIII) the position of the methyl substituent in the *cis*-pentadiene (XXXIIa) is sterically less favourable than in the *trans*-pentadiene (XXXIIb). This is responsible for the much slower insertion of *cis*-penta-1,3-diene compared with the *trans*-isomer. This stereochemical requirement of a *cis*-planar structure of the diene before the insertion reaction resembles the behaviour of 1,3-dienes in Diels–Alder reactions[240-242].

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Thus, summarising the foregoing survey, one must conclude that the formation of *anti*-structures of the π-allyl products of the addition of 1,3-dienes to transition metal compounds is a kinetically controlled process. The subsequent reactions of the *anti*-complexes are determined by thermodynamic and steric factors. The knowledge of the exact chemical compositions of both the initial and final products of the reactions of 1,3-dienes with transition metal compounds is extremely important, since these complexes, involved in the addition reactions of subsequent 1,3-diene molecules, determine the microstructure of the monomeric units of the oligomeric or polymeric molecules formed.

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