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π-ALLYL COMPLEXES OF THE TRANSITION METALS

M. I. Lobach, B. D. Babitskii, and V. A. Kormer

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I. INTRODUCTION

In the chemistry of organometallic compounds there is now great interest in the π-allyl complexes of transition metals. On the theoretical side this interest is explained by the unusual bond of the allyl ligand with the metal, which is an inherent feature of the bonds of both alkene and aromatic complexes (ferrocene, dibenzenechromium).

The results obtained in recent years show the considerable part played by π-allyl complexes as intermediates in various reactions of organic synthesis: they are extremely effective catalysts for stereospecific polymerisation and oligomerisation (both linear and cyclic) of alkenes and dienes.

In these complexes the bond between the transition metal and the allyl ligand, analogous to the π-cyclopentadienyl and arene complexes, is multicentric: all three carbon atoms of the allyl group take part in the formation of the bond with the metal owing to the more or less complete delocalisation of the double bond.

According to Fritz [1], the ligand in the π-allyl complexes can be a π-allyl anion, radical, or cation. According to the molecular orbital theory, with the [approx.] sp^2-hybridised carbon atoms of the allyl group there are one bonding, one non-bonding, and one antibonding orbitals [1,2]. Of the three electrons of the allyl radical, two are in a bonding orbital and one in an antibonding orbital. In the allyl anion, there is a pair of electrons in [each of] these orbitals, whereas in the cation the two electrons are located in the bonding orbital. Complex formation proceeds by the transfer of these π-electrons to a vacant orbital of the metal†.

Because atoms of metals which form π-allyl complexes have lone pairs of *d*-electrons the possibility arises for formation of dative bonds by the interaction of these electrons with the antibonding orbitals of the π-allyl anions. Quantum-mechanical calculations show that the participation of the π-allyl ligand in a dative bond is less significant, unlike an alkenic ligand [3]. This, in particular, can explain the low stability of the so-called "pure" allyl compounds of the transition metals, that is, those in which there are no other stabilising ligands. In the presence of ligands such as CO, Cl, or C_5H_5 the stability of the complexes increases, this being explained by the lower energetic level of the antibonding orbitals of these ligands (in comparison with π-allyl) which also capture the *d*-electrons of the metal, forming a dative bond.

The first π-allyl complex was apparently made in 1952 by Prichard [4] in the reaction between a hydrocarbonyl of cobalt [hydrogen tetracarbonylcobaltate(−1)] and butadiene. The author erroneously ascribed to this compound the structure of a 1:1 addition compound $C_4H_7Co(CO)_4$. Later, Jonassen and coworkers [5] found that the reaction of hydrogen tetracarbonylcobaltate(−1) with butadiene is accompanied by the release of one molecule of carbon monoxide and suggested that in the product $C_4H_7Co(CO)_3$ the bond of the 1-methylallyl ligand with the metal is effected by one π- and one σ-bond [6]. Such a conception of the nature of the bonding of the allyl residue to the transition metal was viewed with suspicion after both Syrkin and coworkers [7] and Smidt and Hafner [8] obtained chloro-(π-allyl)palladium(II) $(C_3H_5PdCl)_2$. Soon after Heck and Breslow [9] used nuclear magnetic resonance to show the π-allyl structure of the compound $C_3H_5Co(CO)_3$.

π-Allyl complexes have now been obtained for all the transition metals of Groups IV–VIII except Hf, Re, Tc, and Os.

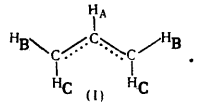
II. INVESTIGATION OF STRUCTURE

1. NUCLEAR MAGNETIC RESONANCE SPECTRA

The proton magnetic resonance method enabled slight differences in the structure of the allyl compounds of the transition metals to be observed. On the basis of their NMR spectra they can be classified into four types.

a. π-Allyl Compounds

The NMR spectra of the π-allyl complexes of cobalt [9,10], manganese [10], palladium [11,12], nickel [12], and some other metals are characterised by the presence of three types of signal with ratio of intensities 1:2:2 (Fig. 1*a*). The interpretation of the NMR spectra also leads to a structure for the complexes in which, owing to the delocalisation of the π-electrons, hybridisation of the allyl carbon atoms (which are in the same plane) occurs. The hydrogen atoms H_A, H_B, and H_C in (I) are evidently coplanar with the carbon atoms:



(I)

The different chemical shifts for the H_B and H_C hydrogens suggests that they are at different distances from the metal, with the H_C protons, which are closer to the metal atom, showing a shift at higher field intensities, owing to the greater screening by the metal atom. The proton at the central carbon atom, H_A, is further from the metal atom than the H_B and H_C protons and is therefore characterised by the least chemical shift. A similar conclusion can be drawn from a comparison of the spin–spin coupling constants J_{AC} and J_{AB}, the first of which is always the greater. The interaction between the protons H_B and H_C is almost zero, a possible explanation for this, according to Gutowsky and coworkers' results [13], being that the angle $H_C\!-\!C\!-\!H_B$ is close to 125°C. The introduction of a polar substituent (for example, a chlorine atom) at the central atom of the allyl group leads to the observation of some interaction between the protons H_B and H_C (J_{BC} = 2 Hz) [14]. On replacing the H_A hydrogen by alkyl groups simple spectra are also obtained: the signal with chemical shift 4.5–4.9, which belongs to the H_A proton, disappears, and a peak with chemical shift τ = 7.7–7.9, corresponding to the allyl group protons attached to the central carbon atom of the π-allyl group, is observed [15].

The spectra of π-allyl complexes substituted at a terminal carbon atom of the allyl group are more complex,

† However, the problem of how many electrons (2, 3, or 4) leave the π-allyl ligand to form the bond with the transition metal is not so important, since this, in turn, is compensated by the degree of oxidation of the central atom.

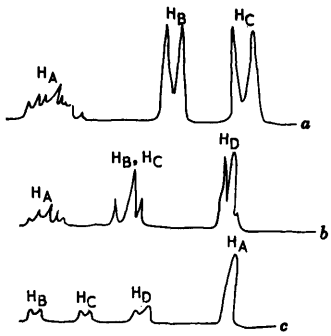
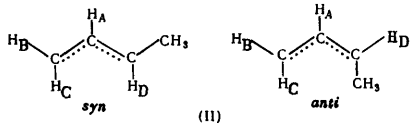


Fig. 1. NMR spectra of allyl compounds: *a*) π-allyl; *b*) σ-allyl; *c*) πσ-allyl.

the bands showing splitting due to the terminal alkyl group. For simplicity, we will discuss only 1-methyl-π-allyl (π-crotyl‡) complexes. The replacement of the H_B or H_C hydrogens of the π-allyl group leads to two isomeric complexes depending on the position of the methyl group in relation to the H_A hydrogen at the central atom of the π-allyl group—*syn*-(II) and *anti*-(II) respectively.



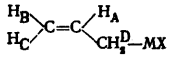
(II)

The spectra of $[(C_4H_7)Co(CO)_3]$ [10,16] and $(C_4H_7NiCl)_2$ [12] show five types of split peaks with the intensity ratio 1:1:1:3:1. The example of 1-methyl-π-allylcobalt-tricarbonyl showed that the spin–spin coupling constant J_{AD} is 10.5 Hz for the *syn*-isomer and 6.8 Hz for the *anti*-isomer [16]. Here the presence of the π-allyl structure is also confirmed by the equality of J_{AC} and J_{AB} for the *syn*-isomer and the similar values of J_{AB} and J_{AD} for the *anti*-isomer.

The possibility of *syn–anti*-isomerism is excluded for complexes with cyclic π-allyl ligands and therefore the NMR spectra of such compounds mainly contain three types of bands. Here it must be pointed out that the chemical shift for the H_A and H_B protons of (II) is quite close to the shift for the same protons of the unsubstituted π-allyl group of (I) [17]. The resonance lines of the methylene protons of a cyclic ligand appear at higher field strengths (τ = 8.5–9).

b. σ-Allyl Compounds

The σ-allyl compounds (III) are characteristic mainly of the non-transition elements. Of the transition metals, only Mn [10], Fe [18], W [19], and Mo [20] are known to form such compounds. In the NMR spectra of the compounds of this group four signals with the intensity ratio 1:1:1:2 are usually observed (Fig. 1*b*),



(III)

‡ sic (Ed. of Translation).

that is, the protons H_B and H_C are non-equivalent owing to the impossibility of rotation about the C=C bond. The signal from the H_A proton is split into a complex multiplet by the H_D and H_B nuclei, so that J_{CA} is considerably less than J_{AB}, as is usually observed for *cis–trans* hydrogen atoms in alkenes [21]. The signals from the H_B and H_C protons are split into a doublet by the H_A nucleus, but since these protons belong to the AC system both doublets overlap and three lines are usually obtained. Finally, the signal from the H_D protons is split into a doublet by the H_A nucleus.

c. "Dynamic" Allyl Compounds

The NMR spectra of compounds of this type show two signals with a 4:1 intensity ratio, that is, the CH_2 group protons have become equivalent. For the allyl compounds of non-transition metals (for example, magnesium [22]) this is explained by a rapid rearrangement of the type:

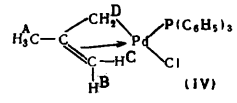
$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}MX \rightleftarrows XM-\overset{1}{CH_2}-\overset{2}{CH}=\overset{3}{CH_2}.$$

An analogous NMR spectrum was obtained at elevated temperatures for addition compounds of π-allyl- (or π-methyl-allyl-)palladium chloride with triphenylphosphine [23-26], dimethyl sulphoxide [25-27], and triphenylarsine [26]; of π-allylnickel chloride with triphenylphosphine [23]; of π-allylnickel bromide and cyanide with triethylphosphine [28]; and also for allyl compounds of thorium and zirconium [23,27,29]; and for complexes $C_3H_4RRh(X_2)[P(C_6H_5)_3]_2$ and $C_3H_5Pt(X).[P(C_5H_5)_3]_2$, [30] where R = H, CH_3; X = Cl, Br.

The equivalence of the CH_2 groups in the complexes mentioned above can be explained as follows: as a result of the deficit in *d*-electrons necessary for the formation of dative bonds between the metal and the π-allyl ligand it becomes possible for the latter to rotate around the axis passing through the metal atom and the centre of the CCC plane. According to the results of Wilke and coworkers [23] the energy barrier of this rotation is 10–15 kcal.

d. πσ-Allyl Compounds

These intermediate structures were observed for the 1:1 addition compound of π-methylallylpalladium chloride with triphenylphosphine [24-25]. In the NMR spectrum of this compound (IV) there are four signals with intensity ratio 1:1:2:3 (Fig. 1*c*):



(IV)

The signals from the protons H^B, H^C, and H^D are split into doublets by the interaction with the phosphorus atom.

2. INFRARED AND ULTRAVIOLET SPECTRA

Fritz [1] made the first detailed study of the infrared spectra of a series of π-allyl complexes of palladium and nickel.

Weak bands at 3079, 3040, 3010, and 2907 cm^{-1} were assigned to stretching vibrations of the CH_2 (ν_{CH_2}) and CH (ν_{CH}) bonds. The stretching vibrations at lower wave

numbers are due to the C–H_C bonds (I) situated close to the metal atoms. For $(C_3H_5NiCl)_2$ and $(C_3H_5PdBr)_2$ these absorption bands were observed at lower frequencies (2865 and 2849 cm^{-1} respectively)[12].

The interpretation of bands belonging to the vibrations of the carbon skeleton of the π-allyl group is of the greatest value in determining the structure of the complexes. Lanpher[31] showed that the allyl anions have an absorption band in the 1500–1560 cm^{-1} region: in the π-allyl complexes of the transition metals coordination leads to a displacement of the C–C asymmetric stretching vibrations (ω_{CC}) into the 1450–1470 cm^{-1} region[1,12,32]. The bands at 1021 and 511 cm^{-1} were attributed to the symmetric stretching vibrations of the C–C bonds (ω_{CC}) and the deformation vibrations of the C–C–C carbon skeleton (Δ_{CCC}) of the allyl group respectively. The bands at 1450–1470, 1021, and 511 cm^{-1} are characteristic of π-allyl systems. For the π-crotyl and π-methylallyl complexes of palladium and nickel Δ_{CCC} appears in the 520–567 cm^{-1} region[1,12,33] and for the complexes with cyclic ligands[1] it is at ~ 585 cm^{-1}.

The absorption bands at 1381, 1226 and 1191 cm^{-1} are attributed to the in-plane bending [scissoring] vibrations of the CH_2 (δ_{CH_2}) and CH (δ_{CH}) bonds and those at 981, 965, 940, 911, and 763 cm^{-1} to the out-of-plane bending [wagging] vibrations of the CH_2 (γ_{CH_2}) and CH (γ_{CH}) bonds.

Lupin and coworkers[34] dealt with the interpretation of the vibrational frequencies of the Pd–Cl bond in bridging allyl complexes.

The comparative instability of π-allyl complexes towards ultraviolet radiation greatly limits the possibility of studying them by this method. The limited information on the ultraviolet spectra of certain π-allyl complexes, mainly those of nickel and palladium[35–37], has not yet been satisfactorily explained.

3. X-RAY STRUCTURAL INVESTIGATIONS

X-Ray structural investigations of π-allylpalladium chloride, carried out by several investigators[38–43] have confirmed the structure proposed on the basis of the NMR and infrared spectra, in which the double bond of the allyl group is completely delocalised and the group is bonded with the metal directly by a π-bond analogous to the bond between the cyclopentadienyl ring and a metal atom.

It is expedient to give only the results of the analysis of three-dimensional projections of the $(C_3H_5PdCl)_2$ molecule[39–41] since they are much more accurate than the results of Rowe[43] and Porai-Koshits[38], who studied two-dimensional projections of crystals of the complex. Fig. 2 shows the intramolecular distances and angles for bis-(π-allylpalladium chloride). It was shown that, in contrast to other results[38,43], the plane of the three carbon atoms of the allyl groups is not perpendicular to the plane of the bridging system, $(PdCl)_2$: the angle between these planes is 108°C, and the central carbon atom of an allyl group is 0.05 Å above and the terminal carbon atoms are 0.04 and 0.09 Å below the plane of the palladium atoms [sic: presumably palladium and chlorine atoms is meant]. The large angle between the C–C–C carbon atoms of the allyl group (128.6°C ± 3.3°C) agrees well with the fact that in $(C_3H_5PdCl)_2$ it behaves as a bidentate ligand.

An X-ray structural analysis made by Smith[42] at −140°C confirmed in the main Oberhansli and Dahl's results[39–41]. However, according to Smith's results the three carbon atoms

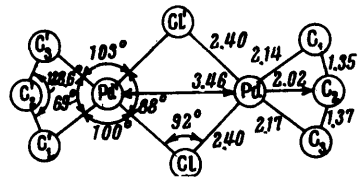


Fig.2. Intramolecular distances and angles in $(C_3H_5PdCl)_2$.

of the π-allyl group are at an equal distance from the palladium atom. The low-temperature investigation also established that all five hydrogen atoms lie in the same plane as the carbon atoms.

These have also been X-ray diffraction studies of bis-(π-methylallyl)nickel[44], cyclo-octenylnickel acetylacetonate[45], π-allylpalladium acetylacetonate[46], cyclo-octa-2,4-dienylpalladium acetylacetonate[47,48], the addition product of π-methylallylpalladium chloride and triphenylphosphine (VI)[49], π-allyl-π-cyclopentadienylpalladium[50], and π-allylirontricarbonyl iodide[51].

4. MEASUREMENT OF DIPOLE MOMENTS

The dipole moments found for π-allyl-π-cyclopentadienylnickel (0.78 D)[12,52] or π-cyclopentadienyl-π-cyclopentenylnickel (1.16 D)[53] agree well with the sandwich structure proposed for them. The appreciable dipole moment observed for dicarbonyl-π-cyclopentadienyl-π-cyclopentenylchromium (3.49 D)[54,55] indicates the asymmetric structure of the complex with the carbonyl groups in the *cis*-position.

The appearance of appreciable dipole moments in the π-allylhalogeno-complexes of nickel (1.3–1.6 D) and palladium (2.1–2.2 D) which are symmetrical in the crystalline state[7,8,12,52,56,57] suggests that evidently the centrosymmetrical configuration of these complexes undergoes considerable deformation in solution. Syrkin and coworkers[7] attributed the dipole moment of $(C_3H_5PdCl)_2$ in benzene to partial dissociation into the monomer, whereas Fischer and Bürger[12,52,57] suggested that the appearance of a dipole moment in these dimeric complexes can be explained by the angular displacement of the bridging halogen atoms. Moreover, during the dissolution of these compounds reorientation of the two allyl ligands from the *trans*-to the *cis*-position is possible (Fig. 3), which also can significantly affect the value of the dipole moment.

The first, and still the only, example of mirror [optical] isomerism in a transition metal π-allyl complex was described by Corradini and coworkers[58].

III. PREPARATION AND PROPERTIES

Owing to the great variety of both π-allyl complexes themselves and of methods for preparing them, it is desirable to examine the latter for each metal separately.

1. COMPLEXES OF TITANIUM, ZIRCONIUM, THORIUM, VANADIUM, NIOBIUM, AND TANTALUM

π-Allylbis-(π-cyclopentadienyl)titanium can be obtained by the reaction of bis-(π-cyclopentadienyl)titanium halides

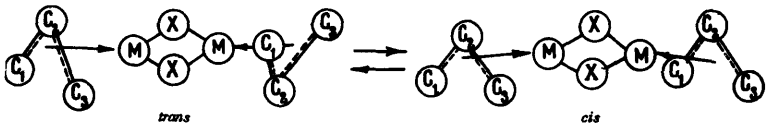


Fig.3. *cis–trans* Isomerism of halogeno-(π-allyl) complexes. M = Ni or Pd; X = Cl, Br, or I.

with allylmagnesium chloride in tetrahydrofuran solution[59,60]. The substance isolated by recrystallisation from *n*-pentane at –80°C consists of purple crystals, m.p. 118°C (decomp.). This complex and its pentane solutions are stable for a few months at room temperature in the absence of oxygen but in air rapid oxidation occurs. Reaction with octanol is accompanied by the liberation of propene in 80% yield: in methylene or allyl chlorides, $(C_5H_5)TiCl_2$ is formed. The compound is paramagnetic. The π-allyl structure has been advanced solely on the basis of infrared spectra. 1-Methyl- and 1,3-dimethyl-π-allyl-bis-(π-cyclopentadienyl)titanium have been prepared by the reaction of $(C_5H_5)_2TiCl_2$ with isopropylmagnesium bromide in the presence of buta-1,3-diene and penta-1,3-diene respectively[61].

The reaction of allylmagnesium chlorides with titanium, zirconium, thorium, vanadium, niobium, and tantalum salts [halides (Ed. of Translation)] gave the corresponding "pure" allyl compounds[23,29].

2. CHROMIUM COMPLEXES

Kurras and Klimsch[62] and Oberkirch[63] obtained tris-(π-allyl)chromium by the reaction of anhydrous $CrCl_3$ with allylmagnesium halides in ether at a temperature not exceeding –18°C. It forms red-black plates, which melt with decomposition at 77–79°C. According to cryoscopic measurements, the compound is monomeric. Solid tris-(π-allyl)chromium is extremely unstable and decomposes at –16°C, but the compound can be stored as a solid and in solutions for some time at –80°C. Bis-(π-allyl)chromium(III) was observed in the decomposition products: it is a dimer with a metal–metal bond[64]. The interaction of $(C_3H_5)_3Cr$ with hydrogen halides leads to the formation of bis-(π-allyl)chromium halides[63,65]. The latter can also be obtained as a result of the action of halogens on $(C_3H_5)_3Cr$, the course of the reaction depending considerably on the polarity of the solvent[63]. For example, $(C_3H_5)_3Cr$ and iodine in ether give bis-(π-allyl)chromium iodide, but when the reaction takes place in toluene the reaction leads only to chromium(II) halides.

When a mixture of $[(C_5H_5)Cr(CO)_3]_2$ and butadiene is irradiated with ultraviolet rays for 6 h in the presence of small amounts of mercury metal dicarbonyl-1-methyl-π-allyl-π-cyclopentadienyl is formed[66,67]. In this complex the 1-methyl-π-allyl ligand is in the *syn*-form but the CO groups are in the *cis*-position[35].

A compound similar in structure with a π-cyclopentadienyl ligand is obtained in low yield by the reaction of bis-(π-cyclopentadienyl)chromium, carbon monoxide, and hydrogen at 65–68°C.[54,55] The complex is stable in air and readily dissolves in polar organic solvents. Its NMR spectrum has four signals with intensity ratio 5 : 1 : 2 : 4, which agrees with the π-allyl structure of the complex. The presence in the infrared spectrum of two close absorption bands at 1894 and 1818 cm^{-1} shows the *cis*-position of the CO groups.

3. COMPLEXES OF MOLYBDENUM AND TUNGSTEN

When σ-allyl complexes of molybdenum and tungsten, which are obtained in high yields by the reaction of the sodium salt $Na^+[M(CO)_3(C_5H_5)]^-$ with an excess of allyl chloride, are subjected to ultraviolet irradiation in a vacuum, π-allyl complexes of these metals are formed[19,20]:

$$(\pi\text{-}C_5H_5)\,M\,(\sigma\text{-}C_3H_5)\,(CO)_3 \xrightarrow{uv} (\pi\text{-}C_5H_5)\,M\,(\pi\text{-}C_3H_5)\,(CO)_2 + CO.$$

Dicarbonyl-π-allyl-π-cyclopentadienylmolybdenum (or tungsten) differs from the initial complexes with π-allyl ligands in having considerably greater thermal stability and also great resistance to oxidation by oxygen.

According to King's results[68], in the complex $[(\pi\text{-}C_5H_5).(C_7H_7)Mo(CO)_2]$, obtained from $[(C_7H_7)Mo(CO)_2]I$ and cyclopentadienylsodium, the bonding of the molybdenum with the cycloheptatrienyl ligand has a π-allyl nature. The author came to this conclusion as a result of a comparison of the NMR spectra of this compound and of $[\pi\text{-}C_5H_5)(\sigma\text{-}C_5H_5)Fe(CO)_2]$[69].

King also succeeded in obtaining the complex $[(\pi\text{-}C_5H_5).(C_9H_7)Mo(CO)_2]$ from tricarbonylindenylmolybdenum and allyl chloride[70].

Murdoch[71] obtained new π-allyl complexes of molybdenum and tungsten, not containing π-cyclopentadienyl groups, in good yield from the tetraethylammonium salts of the halogenopentacarbonyl complexes of these metals and the allyl halides:

$$2\,[(C_2H_5)_4N]^+[MX(CO)_5]^- + 3\,R{-}C_3H_4Y \rightarrow [(C_2H_5)_4N]^+[M_2Y_3(R{-}C_3H_4)_3(CO)_4]^- + 6\,CO + R{-}C_3H_4X + [(C_2H_5)_4N]^+X^-,$$

where X = Cl, Br, or I; Y = Cl or Br; R = H or CH_3; and M = Mo or W.

These complexes are yellow crystalline substances, readily soluble in polar solvents. In air, the tungsten complexes are always less stable than the molybdenum.

The complex anions have a dimeric structure with halogen bridges between the metal atoms. Reaction of the molybdenum complexes with pyridine, 2,2′-bipyridyl, and ethylenediamine leads to the formation of monomeric complexes, for example, $R{-}C_3H_4Mo(CO)_2(C_5H_5N)_2Y$.[72] The latter work also describes the replacement of the halogen bridges Y by the groups OCH_3, OC_2H_5, SC_6H_5, and OH.

There are indications of the possibility of obtaining dimeric bis-(π-allyl)molybdenum and tetrakis-(π-allyl)-molybdenum and tungsten by the reaction of allylmagnesium chloride with molybdenum pentachloride and tungsten pentabromide[63,73,74].

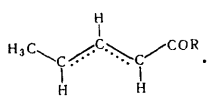
4. MANGANESE COMPLEXES

Two main methods for obtaining π-allyl complexes of manganese are known: (a) from the alkali salts of pentacarbonylmanganese and allyl halides[10,75,76]; (b) by the addition of $HMn(CO)_5$ to dienes[10].

In both instances complexes of the general formula allyl–$Mn(CO)_5$ are formed in the first stage of the reaction, these complexes containing σ-allyl ligands. On heating these compounds one molecule of carbon monoxide is lost and tetracarbonyl-π-allylmanganese complexes are formed. The infrared spectra show that the π-allyl complexes differ from the σ-allyl complexes in the presence of an absorption band at 1505 cm^{-1} and the absence of an intense absorption band at 1620 cm^{-1}, which is ascribed to the stretching vibrations of the non-coordinated double bond[10].

The above methods were used to prepare manganese π-allyltetracarbonyl complexes with the following ligands: allyl, 1-methylallyl, 2-methylallyl, 1-chloroallyl, and 1,1-dimethylallyl[10].

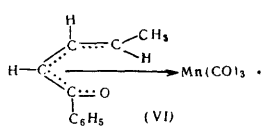
Recently Bannister and coworkers[77,78] reported another way of making π-allyl complexes of manganese. They found that phenyl-or methyl-pentacarbonylmanganese reacts readily with butadiene, forming a 1 : 1 addition product with the ligand of structure (V; R = CH_3, C_6H_5):



(V)

The mechanism of these processes was studied by Green and Hancock[79].

An interesting reaction took place on heating the complex with R = phenyl to the melting point (~ 108°C). Slow release of a molecule of carbon monoxide gave a new complex (VI) [from the allyl $Mn(CO)_4$ species (Ed. of Translation)] in which, according to the authors[80]§ the ligand was a five-electron system analogous to the three-electron system described below for tricarbonyl-π-oxapropenylcobalt.



(VI)

5. IRON COMPLEXES

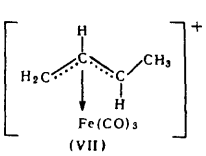
π-Allyl complexes or iron can be obtained in various ways, of which the two most general are: the action of strong acids on the π-(1,3)-dienecarbonyl complexes of iron, and the reaction of allyl halides with iron carbonyls—$Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$.

a. Action of Strong Acids on π-(1,3)-Dienecarbonyl Complexes of Iron

Impastato and Ihrman[81] found that tricarbonylbutadieneiron reacts at room temperature with anhydrous hydrogen chloride to give the 1 : 1 addition product of tricarbonylbutadieneiron and HCl in up to 45% yield. An investigation of the infrared spectra made by the authors showed that this compound is tricarbonyl-(1-methyl-π-allyl)iron chloride. The compound was also obtained by the reaction of tetracarbonylbutadieneiron with hydrogen chloride[82]. In the first stage of this reaction an intermediate cationic carbonyl complex $[Fe(CO)_4(C_4H_7)]^+ Cl^-$ is formed, which, on losing CO, is readily converted into tricarbonyl-(1-methyl-π-allyl)iron. The opinion in the literature as to the geometric configuration of this complex is divided. Impastato[81] and Heck and Boss[83] ascribe to the π-crotyl ligand the *anti*-configuration, whereas Murdoch and Weiss[82] consider the *syn*-form is correct.

When a benzene solution of the complex is boiled or the crystalline product is heated above its melting point (58–60°C), it decomposes to give $Fe(CO)_3(C_4H_6)$ and $FeCl_2$, with the simultaneous liberation of carbon monoxide and a mixture of butenes. The poor solubility of the complexes in water and their good solubility in organic solvents indicates the covalent nature of the bonding of the halogen with the metal.

The tricarbonyl-π-allyliron halides can be converted into salts containing the corresponding cations on treatment with $AgClO_4$ or $AgBF_4$,[84] for example, (VII)

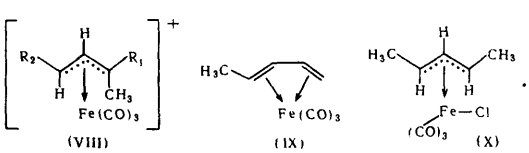


(VII)

The formation of cations proceeds without change in the configuration of the allyl ligand. The tricarbonyl-π-allyliron cationic complexes can also be obtained by treating tricarbonyldieneiron complexes in nitromethane solution with such acids as $HClO_4$, $HSbCl_6$, etc.[84,85]

Note that in the protonation of tricarbonylbutadieneiron, for example, with HBF_4, the tricarbonyl-(1-methyl-π-allyl)iron cation (VIII; $R_1 = R_2 = H$), having the opposite geometrical configuration to that of cation (VII), is formed.

The same behaviour is observed in the preparation of π-allyl complexes from tricarbonyl penta-1,3-dieneiron (IX).



(VIII) (IX) (X)

Study of the NMR spectrum of the chloride (X), produced when (IX) is treated with hydrogen chloride, showed that there is only one type of proton in the methyl groups. The salt obtained from (X) by reaction with $AgClO_4$, had an analogous NMR spectrum. On the other hand, in the complex made by reaction of (IX) with perchloric acid the protons of the methyl groups gave two doublets (7.86 and 8.35 τ)[85]. This feature suggests that here a complex of another configuration (VIII; $R_1 = H$, $R_2 = CH_3$) is formed

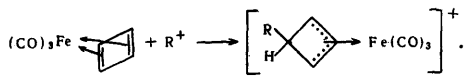
The fluoroborates of the tricarbonyl-(1,1-dimethyl-π-allyl)iron cation (VIII; $R_1 = CH_3$, $R_2 = H$) and the tricarbonyl-(1-methyl-3-phenyl-π-allyl)iron cation (VIII; $R_1 = H$, $R_2 = C_6H_5$) were obtained in a similar fashion from tricarbonyl-(2-methylbutadiene)iron and tricarbonyl-(1-phenylbutadiene)iron respectively.

Treatment of a salt of tricarbonyl-(1-methyl-π-allyl)-iron with water gives significant amounts of butan-2-one,

§ This reference appears to be entirely in error; the work referred to is to be found in Ref. 77 (Ed. of Translation).

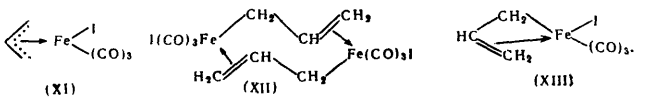
whereas pentan-2-one was obtained from the tricarbonyl-(1,3-dimethyl-π-allyl)iron salt.

A cationic complex analogous to (VII) but with a π-cyclobutenyl group was recently isolated by Fitzpatrik and coworkers[86] by the reaction of tricarbonylcyclobutadieneiron with electrophilic reagents:



b. Reaction of Allyl Halides with Iron Carbonyls.

$Fe(CO)_5$. When pentacarbonyliron is heated with allyl iodide the reaction leads to the formation of tricarbonyl-π-allyliron iodide[87], but the analogous reactions with allyl chloride and bromide could not be affected[12,87]. Later, Heck and Boss[83] found a convenient method of obtaining tricarbonyl-π-allyliron complexes, by ultraviolet irradiation of pentane solutions of the allyl halide and $Fe(CO)_5$. The iodo-complexes can also be obtained by the exchange reaction of the corresponding chloro-complex with sodium iodide or lithium iodide in acetone solution[82,83]. In turn, the bromo- and chloro-complexes were obtained by exchange reaction from the iodo-complex and the corresponding tetra-alkylammonium salts in chloroform[88]. Plowman and Stone[87] suggested that the iodo-complex in solution consists of a mixture of monomer and dimer, and on the basis of spectra they gave the monomer formula (XI) and the dimer formula (XII) with bridging allyl groups.



(XI) (XII) (XIII)

However, Nesmeyanov and coworkers[88] consider that the differences observable in the proton magnetic resonance spectra of $Fe(CO)_3(C_3H_5)I$ and the usual π-allyl complexes can be explained by some distortion of delocalisation and approach to structure (XIII), but not by the presence of dimers.

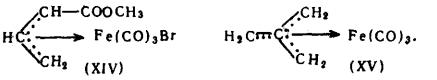
All the tricarbonyl-π-allyliron complexes react readily with triphenylphosphine, with replacement of one molecule of carbon monoxide by $(C_6H_5)_3P$,[83,88] but the product from π-$C_3H_5Fe(CO)_3Cl$ is extremely unstable, unlike its bromo- and iodo-analogues. According to Murdoch and Luncen[89] the loss of the halogen from the tricarbonylallyliron iodide in the presence of such anionic complexes as $[Mn(CO)_5]^-$ and $[(C_5H_5)Fe(CO)_2]^-$, and also its electrolytic reduction, takes place with the formation of the dimer of tricarbonylallyliron, which is readily split at the Fe–Fe bond to give a paramagnetic species $(C_3H_5)Fe(CO)_3$. Nesmeyanov and coworkers[88] detached the iodine from $[(C_3H_5)FeI(CO)_3]$ by treating it, in an inert atmosphere, with silver nitrate in nitromethane solution with the minimal quantity of methanol: this gave tricarbonylallyliron nitrate in 50% yield.

$Fe_2(CO)_9$. Allyl and 1-methylallyl halides react with $Fe_2(CO)_9$ at moderate temperatures, according to the equation[90]:

$$H_2C{=}CH{-}CH_2X + Fe_2(CO)_9 \rightarrow \pi\text{-}C_3H_5{-}Fe(CO)_3X + Fe(CO)_5 + CO.$$

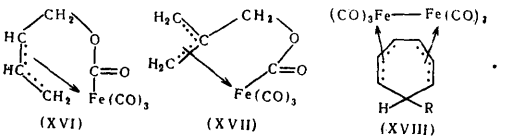
Similarly, methyl γ-bromocrotonate gave bromotricarbonyl-(1-methoxycarbonyl-π-allyl)iron (XIV), and 1,3- and 2,3-dibromoprop-1-ene gave the two isomeric bromotricarbonyl-(1-bromo-π-allyl)iron and bromotricarbonyl-(2-bromo-π-allyl)iron.

Reaction of 3-chloro-(2-chloromethyl)propene with $Fe_2(CO)_9$ for 12 h at room temperature leads to tricarbonyl-(trimethylenemethane)iron (XV)[91]. Protonation of the complex with strong acids, for example, 96% H_2SO_4, gives the tricarbonyl-π-methylallyliron cation, from which onfurther treatment with HCl the covalent chlorotricarbonyl-(π-methylallyl)iron was obtained.



(XIV) (XV)

A new type of compound was discovered by Murdoch[92], who observed that the product of the reaction of 4-chlorobut-2-en-1-ol and nonacarbonyldi-iron contained neither alcoholic nor chloro-groups. The same product, but in greater yield, was obtained from but-2-ene-1,4-diol and $Fe_2(CO)_9$. On the basis of chemical, analytical, and spectroscopic studies it was given the structure (XVI):

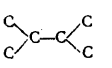


(XVI) (XVII) (XVIII)

The complex (XVII), isomeric to (XVI), was obtained from $Fe_2(CO)_9$ and 2-hydroxymethylprop-1-en-3-ol. Similar reactions of 2,3-dimethylbut-2-en-1,4-diol and hex-3-en-2,4-diol with $Fe_2(CO)_9$ led to the corresponding dimethyl derivative of complex (XVI). The reaction of (XVI) with triphenylphosphine gives a complex in which one CO group is replaced by a $(C_6H_5)_3P$ group.

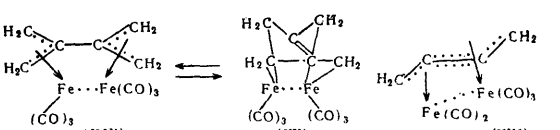
In reactions of $Fe_2(CO)_9$ with cycloheptatriene, 7-methoxycyclohepta-1,3,5-triene, cyclo-octa-1,3,5-triene[93], and cyclo-octatetraene[93–95], Pettit and coworkers always obtained orange-red crystalline complexes in which the $Fe_2(CO)_9$ grouping was attached to the corresponding cyclic diene. Investigation of the NMR and nuclear γ resonance [Mössbauer] spectra showed the equivalence of the two $Fe(CO)_3$ groups and it was therefore assumed that these compounds were new bis-(π-allylenironcarbonyl) complexes. Formula (XVIII) illustrates the structure of cyclopentatriene–$Fe_2(CO)_6$ (R = H) and its methoxy-derivative (R = OCH_3).

$Fe_3(CO)_{12}$. By the reaction of allene with $Fe_3(CO)_{12}$, Nakamura and coworkers[96] obtained a compound of composition $[(C_3H_4)Fe(CO)_3]_2$. From chemical investigations and studies of the infrared and NMR spectra it was found[97] that this compound has the skeleton



and is a second example of a bi-π-allylene compound.

Investigation of the NMR spectra of hexacarbonyl-(2,2′-bi-π-allylene)di-iron (XIX) showed[97] that the complex is in tautomeric equilibrium with a new complex of non-allyl type (XX); the equilibrium is established rather rapidly even at −10°C in carbon tetrachloride solution:



(XIX) (XX) (XXI)

The reaction of 1,4-dibromobut-2-yne, and also of 1,4-dichlorobut-2-yne or 1,4-diacetoxybut-2-yne, with $Fe_3(CO)_{12}$ in the presence of zinc dust at 60°C gave a red crystalline substance, $Fe_2(CO)_5(C_4H_4)$ [96,98]. The most probable structure for this compound is (XXI) with two π-allyl groupings arranged at an angle to one another.

c. Special Methods of Making π-Allyl Complexes of Iron

The σ-allyliron complexes π-$C_5H_5Fe(CO)_2$-σ-C_3H_5 and π-$C_5H_5Fe(CO)_2$-σ-C_4H_7, like the analogous molybdenum compounds, liberate one molecule of carbon monoxide under the action of ultraviolet radiation and are converted into the corresponding π-allyl complexes in high yields [18].

π-Allyl complexes of iron were recently obtained [99,100] with, in addition to carbonyl groups attached to the metal, one nitrosyl group. The carbonylnitrosylallyl complexes of iron are readily obtained from the corresponding sodium salts:

$$Na[Fe(CO)_3NO] + C_3H_5X \rightarrow NaX + \pi\text{-}C_3H_5Fe(CO)_2NO + CO.$$

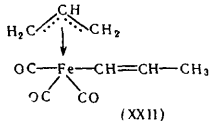
Complexes of this type can be obtained by the addition of $HFe(CO)_3(NO)$ to a conjugated diene, for example:

$$HFe(CO)_3NO + C_4H_6 \rightarrow \pi\text{-}C_4H_7Fe(CO)_2NO + CO.$$

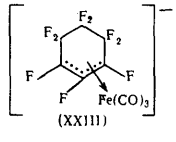
A method based on the reaction of halogenotricarbonyl-π-allyliron complexes or their phosphinic complexes with nitrogen(II) oxide has been proposed. A triphenylphosphine complex with a nitrosyl group can be obtained directly from $(C_4H_7)Fe(CO)_2(NO)$:

$$\pi\text{-}C_4H_7Fe(CO)_2NO + P(C_6H_5)_3 \rightarrow \pi\text{-}C_4H_7Fe(CO)(NO)[P(C_6H_5)_3] + CO.$$

Tris-(π-allyl)iron was obtained in 10–35% yield by the reaction of allylmagnesium chloride with iron(III) chloride or acetylacetonate at −80°C. [73,74,101] Reaction of trisallyliron with carbon monoxide at +10°C gives a compound which has been given the structure (XXII) on the basis of its infrared spectrum [23,101]:



(XXII)



(XXIII)

It is also reported [102] that tricarbonyl(perfluorocyclohexadiene)iron treated with caesium fluoride gives a caesium salt with a (π-perfluorocyclohexenyl)tricarbonylferrate anion (XXIII).

6. COBALT COMPLEXES

There are two main methods for preparing π-allyl complexes of cobalt.

a. Addition of Hydrocobalttetracarbonyl to Diene Hydrocarbons

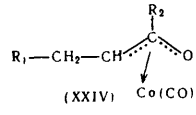
(1-Methyl-π-allyl)cobalttricarbonyl $Co(CO)_3(C_4H_7)$, obtained by Prichard [4] by the reaction of hydrogen tetracarbonylcobaltate(−1) with butadiene in isopropyl alcohol was, as mentioned above, the first π-allyl compound. $KCo(CO)_4$ [5] and $Co_2(CO)_8$ [10] can be used instead of $HCo(CO)_4$ if glacial acetic acid is used as the reaction medium. Aldridge and coworkers [6] showed that $Co(CO)_3(C_4H_7)$ is formed as a mixture of *syn* and *anti* forms in the ratio 6 : 4. The intermediate product in these reactions is the complex $Co(CO)_4(C_4H_7)$, which readily loses a molecule of carbon monoxide and is converted into tricarbonyl-1-methyl-π-allylcobalt [10].

The reactions of $HCo(CO)_4$ with 2-methylbuta-1,3-diene, penta-1,3-diene, and 2,3-dimethylbutadiene [32] proceed similarly. The reaction of penta-1,4-diene is accompanied by rearrangement of the alkadiene and leads to the formation of *syn* and *anti* isomeric forms of (1-ethyl-π-allyl)cobalttricarbonyl and of the 1,3-dimethyl complex. The yield of the latter does not exceed 10–15%. [103]

When the reaction is carried out under a pressure of carbon monoxide, some oxidation products, such as hex-5-enal and 2-methylcyclopentanone, [104,105] are formed as well as the (1-ethyl-π-allyl)cobalttricarbonyl. The yield of the complex decreases as the pressure is raised.

Addition of butadiene to the $[CoH(CN)_5]^{3-}$ ion gives the tetracyano-1-methyl-π-allylcobalt anion $[Co(CN)_4.(C_4H_7)]^{2-}$. [106,107] This process, as with hydrogen tetracarbonylcobaltate(−1), proceeds through the formation of the σ-allyl complex $[Co(CN)_5(C_4H_7)]^{3-}$.

When unsaturated aldehydes and ketones react with hydrogen tetracarbonylcobaltate(-1) under hydroformylation conditions the products are, according to the mechanism suggested by Goetz and Orchin [80], the so-called π-oxapropenyl complexes of type (XXIV). In this way the complex (XXIV; $R_1 = CH_3$, $R_2 = H$) was obtained from but-2-enal and the more stable complex (XXIV; $R_1 = H$, $R_2 = CH_3$) from butenone.

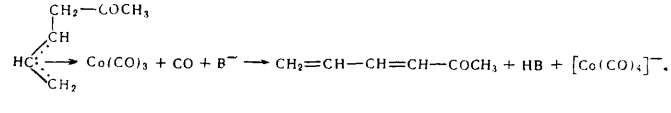


(XXIV)

Heck [108,109] found a way of obtaining substituted π-allyl complexes with an acyl group in the side-chain. These products are formed in the reaction of butadiene, $NaCo(CO)_4$, and alkyl or acyl halides in ethereal solution. The rate of the process depends on the reactivity of the halide. Tetracarbonylacylcobalt and tetracarbonylalkylcobalt complexes are formed in the first stage of the reaction, and then, by reaction with butadiene, are converted into active tricarbonylacylcobalt complexes.

1-Substituted tricarbonyl-π-allylcobalt complexes, obtained in the reaction of dienes with tetracarbonylalkylcobalt or tetracarbonylacylcobalt complexes, exist in *syn* and *anti* forms. For example, the complex from tetracarbonylmethylcobalt and *cis*-penta-1,3-diene is found in the *syn*, and that from 2,3-dimethylbutadiene, in the *anti* configuration. π-Allyl complexes have also been obtained by reactions with 2-methylbutadiene, 4-methylpenta-1,3-diene, and *trans*-1-methoxybutadiene in methyl sorbate [108].

The structure of the complexes formed was studied using their reactions with bases (dicyclohexylethylamine, sodium methoxide, or potassium t-butoxide) in the presence of carbon monoxide [110]. The bases evidently detach a proton from the α-methylene group (in relation to the carbonyl), which leads to the liberation of a tricarbonylcobalt group; this adds CO and forms a stable tetracarbonylcobaltate anion, for example:



On reaction with $CH_3Co(CO)_4$ and a base, *cis*-penta-1,3-diene gives

$$CH_3—CO—C(CH_3)=CH—CH=CH_2,$$

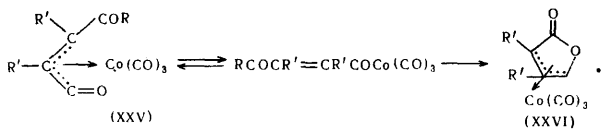
but *trans*-penta-1,3-diene gives:

$$CH_3—CO—CH=CH—CH=CH—CH_3.$$

When disubstituted acetylene is used instead of a diene in the reaction with a carbonylacylcobalt complex, then from the intermediate complex

$$C—R—CO—CR'=CR'—COCo(CO)_3,$$

which is essentially mainly in the form of a π-acrylic complex (XXV), a 2,3-dialkyl-π-(2,4-penteno-4-lactonyl)cobalttricarbonyl complex (XXVI) is obtained [111]:



(XXV) (XXVI)

As Heck has shown [112], the addition of acyl or alkyl tetracarbonylcobaltates(-1) to $\alpha\beta$-unsaturated aldehydes and ketones leads to tricarbonyl-(1-acyloxy-π-allyl)cobalt complexes, the triphenylphosphine derivatives of which have been characterised.

The carbonyl-π-allyl complexes of cobalt are usually characterised as their triphenylphosphine derivatives, which are more stable. The reaction of $Co(CO)_3(C_3H_5)$ with $(C_6H_5)_3P$ is accompanied by the formation of yellow crystalline dicarbonyl-π-allyltriphenylphosphinecobalt and the liberation of carbon monoxide. [113-115] Kinetic investigations showed that the rate of this reaction is independent of the phosphine concentration when the latter exceeds 0.06 M. [114] The replacement of the hydrogen atom at the central carbon atom of the π-allyl group by electron-donating or electron-accepting groups increases the reaction rate. On the other hand, replacement of a hydrogen atom at the first or third carbon atoms of the π-allyl group by an electron-accepting substituent decreases the reaction rate by a factor of almost 30. [112]

Tetracarbonyl-σ-allylcobalt reacts differently with triphenylphosphine [113-115]. Liberation of carbon monoxide is not observed but an acyl complex is formed:

$$CH_2=CH—CH_2COCo(CO)_3P(C_6H_5)_3$$

tricarbonyl(but-3-enoyl)(triphenylphosphine)cobalt, which can also be obtained by the reaction of allyl bromide with $NaCo(CO)_4$ and CO in the presence of triphenylphosphine.

In the reaction with triphenylphosphine as unusual type of metal–organic bond is clearly evident in the tricarbonyl-π-allylcobalt complexes, since compounds with a σ-bond (tetracarbonylalkylcobalt complexes) give acylcobalt derivatives with $(C_6H_5)_3P$ [115] but the cyclo-octatetraene ligand is displaced from a π-complex, tricarbonylcyclo-octatetraenecobalt [116].

The reaction of π-allylcobalttricarbonyl complexes with trimethylolpropan phosphite [? trimethylene propenyl phosphite (Ed. of Translation)] has been shown by Heck [117] to proceed by replacement of two molecules of carbon monoxide:

$$C_3H_5Co(CO)_3 + 2\,PO_3C_6H_{11} \rightarrow C_3H_5Co(CO)(PO_3C_6H_{11})_2 + 2\,CO.$$

Bis(trimethylolpropan phosphite) derivatives were also obtained from 2-chloro-π-allyl-, 1-acetyl-π-allyl, and 1-benzoylmethyl-3-methoxy-π-allyl-tricarbonylcobalt complexes.

All these compounds are crystalline, from yellow to orange in colour, and fairly stable in air.

b. Reaction of the $[Co(CO)_4]^-$ Anion with Allyl Halides

This method was used to make tricarbonyl-π-allylcobalt [9,10,113,114], and the 1-methyl- [9,10,113], 1- and 2-chloro- [10], 2-methyl-, 2-bromo-, 2-phenyl-, and 1-methoxycarbonyl- [114] π-allyltricarbonylcobalt complexes from allyl and 1-methylallyl halides, 2,3- and 1,3-dichloropropene, 2-phenylallyl bromide, and methyl 3-bromocrotonate respectively. The reaction was carried out with a slight excess of $KCo(CO)_4$ or $NaCo(CO)_4$.

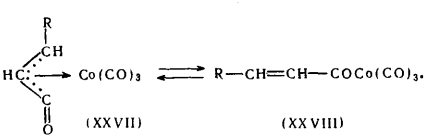
When there is an excess of the allyl halide, for example, C_3H_5Br, the reaction proceeds in another direction:

$$2\,C_3H_5Co(CO)_3 + 4\,C_3H_5Br \rightarrow 3\,C_6H_{10} + 2\,CoBr_2.$$

Tricarbonyl-π-allylcobalt complexes are also readily obtained by decomposition of acyl tetracarbonylcobaltates formed in the reaction of $NaCo(CO)_4$ with allyl halides in the presence of carbon monoxide [9,113,118]:

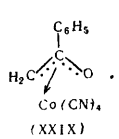
$$NaCo(CO)_4 + CH_2=CH—CH_2Cl + CO \xrightarrow{-NaCl} CH_2=CH—CH_2COCo(CO)_4 \xrightarrow{-2Co} \rightarrow C_3H_5Co(CO)_3.$$

When vinylacetyl chloride is used instead of allyl halides the reaction proceeds in the absence of carbon monoxide [9,113]. The reaction of $NaCo(CO)_4$ with acrylyl, crotonyl, or sorbyl chloride in the presence of carbon monoxide leads to the formation of an equilibrium mixture of π-acrylyl complexes (XXVII) and acyl complexes (XXVIII) [113,119,120]. On adding triphenylphosphine a complex of (XXVIII) with one molecule of $(C_6H_5)_3P$ was isolated:



(XXVII) (XXVIII)

π-Allyl anions with cyano-groups, already mentioned above, can also be obtained by the reaction of allyl halides with the pentacyanocobaltate(II) anion $[Co(CN)_5]^{3-}$. [106,107] The reaction of pentacyanocobaltate(II) with phenacyl bromide led to a complex which was given a structure of the π-oxapropenyl type (XXIX).

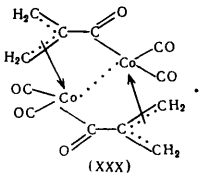


(XXIX)

In addition to these two general methods for the prepartion of π-allyl complexes of cobalt, some other synthetic routes must be noted.

Carbonyl-π-allyl-π-cyclopentadienylcobalt bromide was made by the reaction of allyl bromide with $Co(CO)_2(C_5H_5)$ [121]. Heck [122] showed that in this reaction not only $[Co(CO)(C_3H_5).(C_5H_5)]Br$ but also a little π-allyl-π-cyclopentadienylcobalt bromide is formed. With allyl iodide the main product was also an ionic complex, but more of the covalent $CoI(\pi\text{-}C_3H_5)(C_5H_5)$ was present (10%). With allyl chloride only carbonyl-π-allyl-π-cyclopentadienylcobalt chloride is formed. The treatment of a benzene solution of octacarbonylcobalt with allene at 40°C leads to a carbonyl-π-allylacylcobalt complex (XXX) [123], the structure of which

was established on the basis of NMR and infrared spectra, and by bromination.

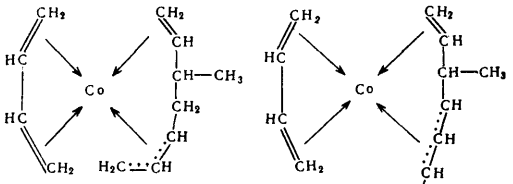


(XXX)

Tris-(π-allyl)cobalt $(C_3H_5)_3Co$ was obtained by the reaction of an ethereal solution of allylmagnesium chloride and cobalt acetylacetonate at −80°C (yield 45–50%)[73,74]. With cobalt chloride the yield did not exceed 20%. The compound is thermally unstable and decomposes rapidly, even at 0°C.

There are indications that the reaction of $(C_3H_5)_3Co$ with hydrogen halides leads to the formation of bis-(π-allyl)-cobalt halides[65]. The product of the reaction of $(C_3H_5)_3Co$ with CO at −35°C is π-allylcobalttricarbonyl[23].

By the reaction of an ethanol solution of $CoCl_2$ with sodium tetrahydroborate in the presence of butadiene Natta and coworkers[124] obtained a complex of composition $CoC_{12}H_{19}$, to which they ascribed one of the following structures:



(XXXI) (XXXII)

The compound melts at ~ 37°C, dissolves in hydrocarbons with the formation of red solutions, and is insoluble in water. On reaction with carbon monoxide two tricarbonyl-π-allyl complexes were isolated: $(C_4H_7)Co(CO)_3$ and $(C_8H_{13})Co(CO)_3$. The latter, in turn, was made from $Co_2(CO)_8$ and 3-methyl-hepta-1,4,6-triene in acetic acid solution.

7. NICKEL COMPLEXES

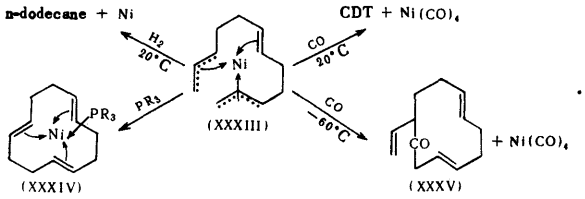
The following types of π-allyl complexes of nickel are known: bis-(π-allyl), bis-(π-allylnickel halides), π-allyl-π-cyclopentadienyl, and also complexes with cyclic π-allyl ligands.

a. Bis-(π-Allyl) Complexes

The simplest complex of this class, bis-(π-allyl)nickel, $(C_3H_5)_2Ni$, was first obtained by Wilke[23,29,125-128] by the reaction of an ethereal solution of allylmagnesium chloride with anhydrous nickel bromide at −10°C. 1-Methylallyl, 2-methylallyl, and phenylallyl complexes were obtained in a similar manner[73,74,129,130]. $(C_3H_5)_2Ni$ is readily soluble in hydrocarbons and stable in relation to water. It ignites in air. On reduction with hydrogen it liberates propane and metallic nickel is left. The reaction of $(C_3H_5)_2Ni$ with compounds which exhibit electron-donating properties is accompanied by the formation of biallyl. In addition to biallyl, in the presence of carbon monoxide or triphenylphosphine, nickelcarbonyl and $[(C_6H_5)_3P]_4Ni$ is formed[125,126,128].

Under certain conditions and at reagent ratios of 1 : 1 for bis-(1-methyl-π-allyl)nickel and bis-(2-methyl-π-allyl)-nickel their addition product with triphenylphosphine of composition $Ni(\pi\text{-}C_4H_7)(\sigma\text{-}C_4H_7).[P(C_2H_5)_3]$ was isolated[23,129].

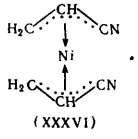
Wilke and coworkers[128,131] obtained compounds of general formula $C_{12}H_{18}Ni$ as an intermediate product in the preparation of cyclododecatriene (CDT) from butadiene. On the basis of the infrared spectra this complex was assigned structure (XXXIII) in which three molecules of butadiene form a chain of 12 carbon atoms with a *trans* double bond and two allyl groupings:



(XXXIV) (XXXIII) (XXXV)

Reaction of (XXXIII) with electron donors (carbon monoxide, phosphine, butadiene) leads to ring closure, and when phosphine is used detachment of the cyclododecatriene does not take place (XXXIV). With carbon monoxide at −60°C the reaction is quite different, tetracarbonylnickel and vinylcycloundecadiene (XXXV) being formed. When hydrogen reacts with (XXXIII) n-dodecane is formed[125,128,131].

According to Schrauzer[132], complexes of nickel with acrylonitrile (XXXVI), acrolein, cinnamonitrile, and fumaronitrile, which are obtained by the reaction of tetracarbonylnickel with corresponding unsaturated compounds, can be classified as π-allyl complexes:



(XXXVI)

b. Bis-(π-Allylnickel Halides)

Bis-(π-allylnickel halides) are obtained by the reaction of tetracarbonylnickel with allyl halides[12,52,57]:

$$2\,Ni(CO_4) + 2\,RX \rightarrow [RNiX]_2 + 8\,CO.$$

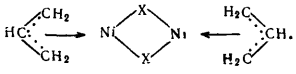
Benzene is the most suitable solvent for this reaction[12].

The reaction of tetracarbonylnickel with allyl halides in an alcoholic medium leads to the dimerisation of the allyl residues[133]. Thus, hexa-1,5-diene is obtained from allyl halides and octa-2,6-diene (7.8%) and 3-methylhepta-1,5-diene (22%) from a mixture of crotyl chloride and 3-chloro-but-1-ene.

Both in the dimerisation and in the formation of π-allyl complexes, the reaction evidently proceeds through the formation of an intermediate compound, $R-[(C_3H_4)NiX(CO)]$[35,134].

Bis-(π-allylnickel halides) can also be obtained by the reaction of allyl halides with other complexes of nickel(0), such as bis(cyclo-octadiene)nickel(0), cyclododecatriene-nickel[135] or by reaction of bis-(π-allyl) complexes of nickel with hydrogen halides in ethereal solution at −80°C[65,129].

According to Fischer and Bürger [12,52,57] bis-(π-allylnickel halides) have structure (XXXVII) with halogeno-bridges.



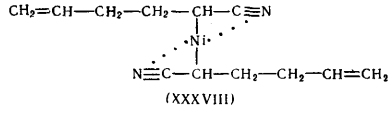
(XXXVII)

They are readily soluble in organic solvents to give dark red solutions. In water saturated with nitrogen bis-(π-allylnickel halides) form orange-red solutions which are stable for a short time but which decompose on long standing, with the formation of metallic nickel.

Chiusoli and Merzoni [136] found that during the carbonylation of methanol solutions of $(C_3H_5NiBr)_2$ methyl vinylacetate is formed. A mixture of acetylene and carbon monoxide acts on $(NiXC_3H_5)_2$ to give, in addition to tetracarbonylnickel, derivatives of hexa-2,5-dienoic acid, depending upon the nature of the solvent; for example, in ether at ~ 0°C the following reaction takes place [137]:

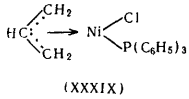
$$(C_3H_5NiBr)_2 + 10\,CO + 2\,C_2H_2 \rightarrow 2\,CH_3{=}CH{-}CH_2{-}CH{=}CH{-}COBr + 2\,Ni(CO)_4.$$

The reaction of bis-(π-allylnickel bromide) with methyl acrylate in benzene solution at room temperature leads to the formation of methyl hexa-2,5-dienoate and methyl hex-5-enoate [138,139]. Acrylonitrile reacts with $(C_3H_5NiBr)_2$ with the separation of a complex which has been given the structure (XXXVIII):



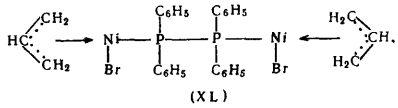
(XXXVIII)

The reaction of bis-(π-allylnickel halides) with triphenylphosphine leads to the breaking of the halogeno-bridges [23,29,140]. The complexes thus formed (XXXIX):



(XXXIX)

were also obtained by the reaction of allyl chloride with $Ni(CO)_3[P(C_6H_5)_3]$ [141]. The reaction of tetraphenyldiphosphinedinickelhexacarbonyl [μ-(tetraphenyldiphosphenylene)bis(tricarbonylnickel)(Ed. of Translation)] with allyl bromide leads to the π-allyl complex (XL) with a diphosphinic bridge [142]:



(XL)

Bogdanović and coworkers [140] obtained π-allylmethylnickel by the reaction of $(C_3H_5NiBr)_2$ with methylmagnesium chloride in ether (-78°C). This product is extremely unstable and even at -60°C it changes into bis-(π-allyl) nickel. π-Allylmethylnickel-triphenylphosphine was made in a similar fashion from complex (XXXIX).

Wilke and coworkers [28] obtained bis-(π-allylnickel cyanide) in methanol starting from $(C_3H_5)_2Ni$ and HCN or $(C_3H_5NiBr)_2$ and KCN.

c. π-Allyl-π-Cyclopentadienyl Complexes of Nickel

π-Allyl-, and also 1-methyl-π-allyl-π-cyclopentadienyl complexes of nickel are obtained from the corresponding bis-(π-allylnickel halides) and cyclopentadienylsodium [12,52]:

$$(C_3H_5NiBr)_2 + 2\,NaC_5H_5 \rightarrow 2\,C_3H_5NiC_5H_5 + 2\,NaBr.$$

In addition, the same products are obtained by the reaction of bis-(π-cyclopentadienylnickel) with the corresponding allylmagnesium halides [10,143], for example:

$$C_3H_5MgCl + (\pi\text{-}C_5H_5)_2\,Ni \rightarrow C_5H_5MgCl + C_3H_5NiC_5H_5.$$

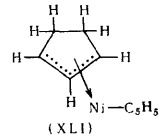
1-methyl-π-allyl-π-cyclopentadienylnickel was also obtained by the reaction of $(C_5H_5)_2Ni$ with butadiene and consisted of a mixture of *syn*- and *anti*-isomers [144]. The reaction of 1-methylallyl chloride with the potassium salt of π-cyclopentadienylnickelcarbonyl leads to the formation of the same complex [144]:

$$C_4H_7Cl + K[C_5H_5NiCO] \rightarrow C_4H_7NiC_5H_5 + CO + KCl.$$

All the π-allyl-π-cyclopentadienyl complexes of nickel are readily soluble in most organic solvents. These compounds rapidly decompose in air. Cryoscopic measurements in benzene have shown that the complexes have a monomeric structure.

d. Complexes with Cyclic π-Allyl Ligands

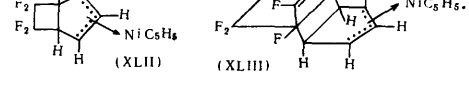
A π-allyl complex of nickel with a cyclic ligand was first obtained by Fischer and Werner [53,145] by the reaction of tetracarbonyl nickel with cyclopentadiene in n-hexane solution. However, it was incorrectly given the structure of bis(cyclopentadiene)nickel, $(C_5H_6)_2Ni$. [53] It was later found, from infrared and NMR spectra, that this compound is a π-cyclopentadienyl-π-cyclopentenyl complex (XLI) [1,17,146-150].



(XLI)

Dubeck and Filbey [149] prepared it by reduction of $(C_5H_5)_2Ni$ with sodium amalgam in methanol solution, and also by the reaction of cyclopentenylmagnesium bromide, C_5H_5Na, and anhydrous $NiBr_2$ at -10°C.

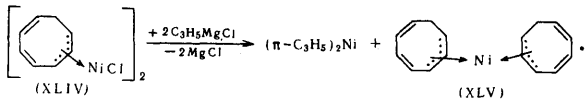
Reaction of bis-(π-cyclopentadienyl)nickel with tetrafluoroethylene gave a π-allyl complex of structure (XLII), which was proposed on the basis of an examination of the ^1H- and ^{19}F-NMR spectra [151]. Complexes analogous to (XLII) were also obtained by the reaction of $(C_5H_5)_2Ni$ with chlorotrifluoroethylene and hexafluorobut-2-yne [149,151]. The product of the reaction of $(C_5H_5)_2Ni$ with octafluorocyclohexa-1,3-diene was represented as the π-allyl complex (XLIII) on the basis of spectroscopic data [152]:



(XLII) (XLIII)

Nickel compounds with cyclobutenyl [39,40,153-157] and cyclopropenyl [158,159] ligands must also be classified as complexes of the π-allyl type. A series of cyclic π-allyl nickel complexes has been isolated in Wilke's laboratory [23,129]—bis-(π-cyclohexenyl)nickel, bis-(π-cycloheptenyl)nickel, bis-(π-cyclo-octenyl)nickel, and also the corresponding π-enylnickel chlorides formed from them on treatment with HCl. The reaction of cyclo-octatetraenylnickel with HCl

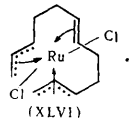
at −80°C in toluene gave red crystals of bis-(π-cyclo-octatrienylnickel chloride) (XLIV)[23], which when treated with allylmagnesium chloride yielded bis-(π-cyclo-octatrienyl)nickel (XLV) and bis-(π-allyl)nickel, instead of the expected π-allyl-π-cyclo-octatrienylnickel:



(XLIV) (XLV)

8. COMPLEXES OF RUTHENIUM, RHODIUM, AND IRIDIUM

Two π-allyl complexes of ruthenium are known at present. Complex (XLVI) was obtained by the reaction of ruthenium(III) chloride and butadiene in 2-methoxyethanol solution at 100°C.[160,161] It is a monomer in benzene. Complexes of rhodium and iridium with butadiene were obtained in the same way.



(XLVI)

The reaction of $RuCl_3$ in alcoholic solution with 2-methylbuta-1,3-diene leads to the formation of the dimeric dichloro-(2,7-dimethylocta-2,6-dien-1,8-ylene)ruthenium, to which Porri and coworkers[162] ascribed a π-allyl structure.

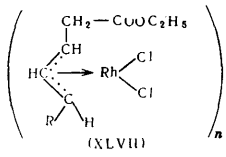
The diamagnetic cyclododeca-1,5-dienylrhodium dichloride, the first π-allyl complex of rhodium(III), was obtained by Paiaro and coworkers[163,164] from $RhCl_3.3H_2O$ and cyclododeca-*trans*-1,*trans*-5,*trans*-9-triene in boiling ethanol. The polymeric nature of the substance is shown by its insolubility in the usual organic solvents, and its ability to dissolve in dilute ammonia and to react with Lewis bases (CO, amines, alkenes) with the formation of monomeric complexes $C_{12}H_{19}RhCl_2B$, where B is the base.

Dimeric bis-(π-allyl)rhodium chloride was prepared by Shaw and coworkers[165] by the reaction of $[RhCl(CO)_2]_2$ with allyl chloride in methanol containing a little water. The reaction of the complex with pyridine, thallium(I) acetylacetonate, and cyclopentadienylthallium led to the corresponding monomeric compound. Treatment of $[(\pi\text{-}C_3H_5)_2RhCl]_2$ with allylmagnesium chloride gives trisallylrhodium[166], which was also obtained by the reaction of anhydrous $RhCl_3$ with C_3H_5MgCl at 0°C.[167] The same work[167] also gave information on the temperature dependence of the NMR spectra of $(C_3H_5)_3Rh$.

The reaction of rhodium trichloride with butadiene in ethanol leads to the complex[166]:

$$[(C_4H_7)RhCl_2(C_4H_6)Cl_2Rh(C_4H_7)].$$

$RhCl_3.3H_2O$ also reacts with diene acids (sorbic, vinylacrylic) to form the complexes (XLVII; R = H, CH_3)[168]:



(XLVII)

Corresponding monomeric complexes were obtained from (XLVII) with 2,2-bipyridyl, ethylenediamine, or carbon monoxide.

π-Allyl-π-cyclo-octa-1,5-dienerhodium was made by the reaction of $[C_8H_{12}RhI]_2$ with an excess of allylmagnesium bromide at 0°C.[169]

Wilkinson and coworkers[170] recently reported the preparation of the complexes

$$R—C_3H_4RhCl_2[PC_6H_5)_3],$$

the NMR spectra of which were studied by Volger and Vrieze[30].

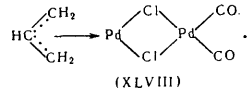
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9. PALLADIUM COMPLEXES

A. Preparation

a. Reactions with allyl halides. Yellow bis-(π-allylpalladium bromide) is obtained when palladium sponge is heated with allyl bromide[12,56]. However, in experiments with allyl chloride and iodide, and also with crotyl bromide, π-allyl palladium compounds were not obtained.

The reaction of a solution of allyl chloride in 50% acetic acid with palladium chloride at 30°C leads to the formation of bis-(π-allylpalladium chloride)[171,172]. At room temperature methylallyl chloride gives a red complex sparingly soluble in organic solvents, $(C_4H_8PdCl_2)_2$. When this is boiled in water it decomposes to metallic palladium and bis-(π-methylallylpalladium dichloride). Dent and coworkers[33] found that these complexes can be obtained almost quantitatively by the action of carbon monoxide on a mixture of Na_2PdCl_4 and allyl chlorides in methanol at atmospheric pressure and room temperature. In the presence of palladium and calcium chlorides in addition to π-allylchloride complexes of palladium a compound insoluble in the usual organic solvents could be isolated, to which the authors ascribed the structure (XLVIII) on the basis of the infrared spectra.



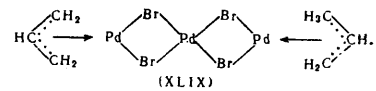
(XLVIII)

Subsequently Shaw and coworkers[173] showed that in the absence of CO and H_2O allylpalladium chloride cannot be prepared by Dent's method.

b. Reactions with allyl alcohol, alkenes and acetylenes. Bis-(π-allylpalladium chloride) was first obtained independently by Syrkin and coworkers[7] and by Smidt and Hafner[8,174] by the reaction of palladium chloride with allyl chloride in acid medium at room temperature.

Dimeric $(C_3H_5PdCl)_2$ is a yellow crystalline substance readily soluble in polar solvents and also in dilute aqueous acids and alkalis. The report by Syrkin and coworkers[7] on the preparation of a second dark green form of $(C_3H_5PdCl)_2$ at temperatures below 10°C was not confirmed in work by other investigators[175].

When allyl alcohol reacts with $PdBr_2$ in hydrobromic acid solution under the same conditions, bis-(π-allylpalladium bromide) is formed[176]. On increasing the $PdBr_2$ concentration a complex of composition $C_6H_{10}Pd_3Br_4$ is also formed, for which structure (XLIX) has been proposed:



(XLIX)

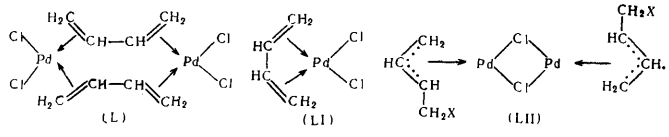
The reaction of alkenes with various palladium compounds (for example, $PdCl_2$, Na_2PdCl_4, and $[PdCl_2(C_6H_5CN)_2]$) is a most general and convenient method for obtaining π-allyl complexes of palladium.

For most alkenes the reaction with palladium chloride passes through the stage of formation of π-complexes of the type $[(alkene)PdCl_2]_2$, which lose HCl at a higher temperature, being changed into π-allyl complexes. Raising the reaction temperature to 50–100°C allows the π-allyl complexes to be obtained directly.

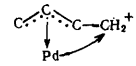
The Table gives the complexes prepared from the corresponding alkenes.

In the reaction of propene with an acetic acid solution of $PdCl_2$ saturated with sodium acetate a yellow complex of composition $C_6H_{11}PdCl$ is formed [180]. Study of the chemical properties and infrared and NMR spectra of the product showed that it is bis-(3-*syn*-ethyl-1-*syn*-methyl-π-allylpalladium chloride) [181]. The same complex is produced in the reaction of hex-1-ene with $PdCl_2$.

Some π-allyl complexes can be obtained by treatment of bis(benzonitrile)palladium chloride with dienes. The product of the reaction with butadiene was earlier given the structures (L, LI) [182-184]. However, Shaw [185] showed that butadienepalladium chloride is a π-allyl complex with halogen bridges (LII; X = Cl). Recently Donati and Conti [186] obtained the π-complex $(C_4H_6PdCl_2)_2$ by the reaction of butadiene with $(n\text{-}C_5H_{10}PdCl_2)_2$ at −40°C. At temperatures above −20°C the complex is converted into a π-allyl complex (LII; X = Cl).



Treatment of (LII) with methanol converts it into the less stable methoxy-derivative (LII; X = OMe). The methoxy- and also the ethoxy-π-crotylpalladium complexes are best obtained by passing butadiene into an alcoholic suspension of $Na_2[PdCl_4]$. Hence it is possible to obtain complexes from a large number of 1,3-dienes, such as 2-methylbutadiene, 4-methylpentadiene, 2,3-dimethylbutadiene, 2,4-dimethylpenta-1,3-diene, 1,1,4,4-tetramethylbutadiene, sorbic acid, and methyl sorbate [36,185,187]. It was also found [36] that methoxy-π-allyl palladium chloride treated with an ethanol solution of hydrogen chloride readily forms the corresponding ethoxy-derivative. The authors suggest the intermediate formation of a carbonium ion of type

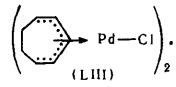


the considerably stability of which was explained (by analogy with the stability of α-ferrocenylcarbonium ions) by the participation of the palladium atom in the stabilisation of the neighbouring cationic centre.

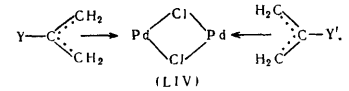
Cycloalkenes also react with palladium salts: cyclohexene [172,188], cycloheptene [188], cyclododecene [189], and their methyl derivatives, and also methylcyclo-octene [189]. The yields of the complexes increase with the number of carbon atoms in the ring, and here π-alkene complexes are formed initially, which are converted into π-allyl complexes with various degrees of ease. It has been noted [188], however, that cyclopentene gives a stable alkene complex which is not converted into a π-allyl compound. π-Allyl complexes are formed much more readily in the reaction of palladium salts with cyclic 1,3-dienes [190-192].

Robinson and Shaw [37] obtained dimeric methoxy-π-cyclohexenylpalladium chloride from cyclohexa-1,3-diene at room temperature. The stability of the product was much less than that of the corresponding acyclic complex [36].

A complex of composition $(C_7H_9PdCl)_2$ was obtained from cyclohepta-1,3-diene, and on the basis of the infrared spectra Robinson and Shaw [37] gave it the formula (LIII), where the palladium atom is associated with five atoms of the cycloheptadienyl ligand, as occurs in the π-cyclopentadienyl complexes.



π-Allyl complexes have also been obtained by passing allene or methyl-, dimethyl-, or tetramethyl-allenes through a methanol suspension of $Na_2[PdCl_4]$ [14,187]. The π-allyl complexes isolated had substituents at the central carbon atom of the π-allyl group $\left(\text{LIV; } Y = Y' = -C\begin{matrix}CH_2\\CH_2Cl\end{matrix}\right)$.



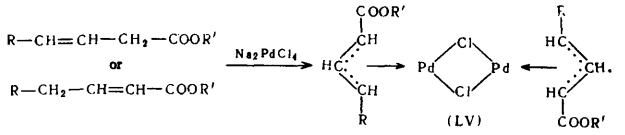
However, when allene is introduced into a methanol solution of dichlorobis(benzonitrile)palladium(II), then in addition to the above product about the same amount of the methoxy-derivative $\left(\text{LIV; } Y = Y' = -C\begin{matrix}CH_2\\CH_2OCH_3\end{matrix}\right)$ [193] is formed; the 2-methoxy-derivative is not formed. The reaction of $[PdCl_2(C_6H_5CN)_2]$ with allenes can also be effected in benzene or benzonitrile solutions [194]. The nature of the products formed depends on the method of preparation. When allene is introduced into a benzene solution of dichlorobis-(benzonitrile)palladium(II) the product is bis-(2-chloro-π-allylpalladium chloride) (LIV; Y = Y′ = Cl). In benzonitrile solution this complex with two 1-(chloromethyl)vinyl substituents at the central carbon atom in the π-allyl group is

TABLE. Bis[dichloro(π-allyl)palladium(II)] complexes

Initial alkene	Organic residue of the π-allyl complex	Reference
2-Methylpropene	2-methyl-π-allyl	172,177
2-Methylbut-1-ene 2-Methylbut-2-ene	1,2-dimethyl-π-allyl	177,178
2-Methylpent-1-ene 2-Methylpent-2-ene	1-ethyl-2-methyl-π-allyl	177,178
3-Methylpent-2-ene	1,2,3-trimethyl-π-allyl	177
2,3-Dimethylbut-1-ene 2,3-Dimethylbut-2-ene	1,1,2-trimethyl-π-allyl	177,178
2-Methylhex-2-ene	2-methyl-1-propyl-π-allyl	177
3-Ethylpent-2-ene	2-ethyl-1,3-dimethyl-π-allyl	177
2,4-Dimethylpent-2-ene	1-isopropyl-2-methyl-π-allyl	177
2,5-Dimethylhex-2-ene	1-isobutyl-2-methyl-π-allyl	177
2,4,4-Trimethylpent-1-ene (di-isobutene)	2-neopentyl-π-allyl	172,1
2,4,4-Trimethylpent-2-ene (di-isobutene)	1-t-butyl-2-methyl-π-allyl	177
Tri-isobutene (mixture of isomers)	mixture of isomers of composition $(C_{12}H_{21}PdCl)_2$	172
α-Methylstyrene	2-phenyl-π-allyl	172,179
β-Methylstyrene	1-phenyl-π-allyl	172
$\alpha\beta$-Dimethylstyrene	1-methyl-1-phenyl-π-allyl or 2-phenyl-1-methyl-π-allyl	172
Methylstilbene	1,2-diphenyl-π-allyl	172

obtained. On addition of solid $[PdCl_2(C_6H_5CN)_2]$ to a benzene solution of allene a mixed complex was obtained (LIV; Y = Cl, Y' = $-C\begin{matrix}CH_2\\CH_2Cl\end{matrix}$). The mechanism of the above reactions of allene hydrocarbons has been discussed by Heck[195] and Schultz[193].

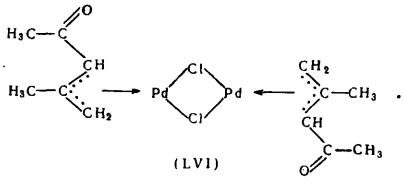
A π-allyl complex with an alkoxycarbonyl group at a terminal carbon of the allyl group was obtained in the reaction of $\alpha\beta$- or $\beta\gamma$-unsaturated carboxyl-containing esters with an alcoholic solution of $Na_2[PdCl_4]$[196]:



(LV)

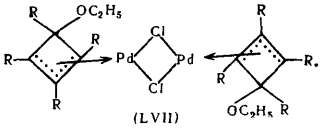
A compound of type (LV) can also be obtained by heating esters in the presence of palladium chloride or by adding the esters to a benzene solution of dichlorobis(benzonitrile)palladium(II).

A complex with a carbonyl group was first observed by Syrkin and coworkers[7] in the reaction of palladium chloride with mesityl oxide. Parshall and Wilkinson[197] showed that the complex has the structure (LVI) and is better obtained from $Na_2[PdCl_4]$:



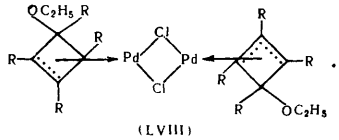
(LVI)

Mention must also be made of the complexes of palladium with four-membered cyclic π-allyl ligands. Such complexes can be obtained by the reaction of diphenylacetylene with alcoholic solutions of $PdCl_2$, $Na_2[PdCl_4]$, or $[PdCl_2(C_6H_5CN)_2]$[198-203], an orange-red complex of composition $C_{30}H_{25}OPdCl$ always being formed. Guy and Shaw[204] proposed for it a π-cyclobutenyl structure (LVII):



(LVII)

On treating the complex with hydrochloric acid a tetraphenylcyclobutadiene complex is obtained, $[(C_6H_5)_4C_4PdCl_2]$[199,200,202,204], from which treatment with ethanol gave an insoluble yellow substance of the same composition as complex (LVII) but with somewhat different chemical and physical properties. X-Ray diffraction examination, by Dahl and Oberhansli[39,40,205], confirmed the structure proposed by Guy and Shaw (LVII) and showed that both complexes are geometrical isomers (*exo*- and *endo*-), differing in the arrangement of the ethoxy-group in the cyclobutenyl ring. The complex obtained from tetraphenylcyclobutadiene palladium dichloride is the dimeric di-μ-chlorobis-(1-*exo*-ethoxy-1,2,3,4-tetraphenylcyclobutenylpalladium) (LVIII: R = C_6H_5).



(LVIII)

A substance with hydroxo groups was obtained on treating a dimethylformamide solution of $[(C_6H_5)_4C_4PdCl_2]$ with water[206].

In addition to diphenylacetylene, the compounds dichloro(diphenylacetylene) and methylphenylacetylene react with palladium compounds, for example, $[PdCl_2(C_6H_5CN)_2]$[204,207].

The preparation of π-cyclopentadienylethoxy-π-tetraphenylcyclobutenylpalladium[157,208] and of a complex with the triphenylcyclopropenyl ligand[209] has been reported.

c. Reaction with allyl Grignard compounds. On mixing a benzene solution of chlorobis(benzonitrile)palladium with 150% excess of an ethereal solution of allylmagnesium chloride, a bright yellow substance of composition $(C_6H_5CN)(C_3H_5)PdCl$ is formed. It is stable in air at room temperature but decomposes on heating to 115°C or over[210].

Bis-(π-allyl)palladium and bis-(π-methylallyl)palladium are obtained by the reaction of anhydrous palladium chloride with allyl- and methylallyl-magnesium chloride respectively in ethereal solution at −40°C.[73,74,129]

Bis-(π-allyl)palladium is a yellow crystalline substance, m.p. 31°C, readily soluble in organic solvents, and does not react with alcohol or water. When hydrogen chloride is passed into an ethereal solution of bis-(π-allyl)palladium (−80°C) π-allylpalladium chloride is formed quantitatively. The latter is also formed by reaction of bis-(π-allyl)palladium with palladium(II) chloride[129].

B. Chemical Properties

a. Reactions leading to breaking of the halogen bridges. On treatment with cyclopentadienylsodium, bis-(π-allylpalladium chloride) gave a diamagnetic substance $(C_5H_5)(C_3H_5)Pd$ which was stable in air for a long time at low temperature[10,211]. The chemical properties of the product were studied in detail by Nesmeyanov and coworkers[212]. Reactions of π-allyl-π-cyclopentadienylpalladium with many electrophilic and nucleophilic reagents in acid, neutral, or alkaline media led to rapid removal of the cyclopentadienyl ligand. In the presence of an alkali metal halide the main product of the reaction was the bis-(π-allylpalladium halide). NaC_5H_5 reacts in an analogous fashion with the dimeric alkoxy-π-allylpalladium chlorides[36,185] and with complexes with cyclic allyl ligands[37,146-148,150,157,190].

$[(C_3H_5)(C_5H_5)Pd]$, just like $[(C_5H_5)(C_6H_9)Pd]$, on reacting with isopropyl or cyclohexyl isocyanide forms $[Pd(^iPrNC)_2]$ and $[Pd(C_6H_{11}NC)_2]$ respectively[213]. The reaction of $[(C_5H_5)(C_6H_9)Pd]$ with $AsCl_3$ or $SbCl_3$ proceeds by the reaction:

$$2\,C_5H_5PdC_6H_9 + AsCl_3 \rightarrow (C_6H_9PdCl)_2 + 2\,C_5H_5AsCl_2$$

with the formation of bis-(π-cyclohexenylpalladium chloride)[213].

A characteristic reaction of the π-allyl complexes with chlorine bridges is the breaking of the bridge by amines[36,37,187], which results in the formation of complexes of general formula [(allyl)PdCl(amine)]. Usually these compounds lose the amine easily, giving the initial complexes. Cryoscopic measurements have shown the monomeric structure of the compounds with the amines.

The infrared spectra of the products of addition of pyridine to $[(C_3H_5)PdCl]_2$ and $[(C_6H_{11})PdCl]_2$ had bands at 517 and 520 cm^{-1} respectively, owing to the retention of the π-allyl grouping in them[181]. With increase in the basicity of the amine there is an increase in the tendency of the complexes to decompose with separation of metallic palladium.

Moiseev and coworkers[181] consider that this decomposition is the result of the alkylation of the amine by the allyl grouping connected to the palladium atom:

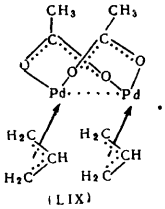
$$\pi\text{-}C_3H_5PdClNR_3 \rightarrow Pd + Cl^- + \overset{+}{N}R_3\text{—}C_3H_5.$$

However, it is possible that alkylation precedes the isomerisation of the complex, in which the π-allyl group is converted into a σ-bound ligand. A similar π–σ change of an allyl ligand is observed in the reaction of π-allyl complexes with triphenylphosphine[23-26] and dimethyl sulphoxide[25-27,175]. It was shown[24-26] that this change precedes the formation of an intermediate compound in which one π- and one σ-bond is present.

The Pd–Cl bond is covalent in all the monomeric complexes described in this section.

Compounds with an ionic Pd–Cl bond were obtained in using bidentate amines such as ethylenediamine and 2,2-bipyridyl (bipy)[214]. When bis-(π-allylpalladium chloride) or bis-(π-crotylpalladium chloride) reacts with these amines, taken in twofold molar excess, complexes are formed which are readily soluble in methanol and water. When the stoichiometric amount of 2,2′-bipyridyl is taken, a compound of the type $[(C_3H_5)Pdbipy]^+[(C_3H_5)PdCl_2]^-$ is obtained, in which a π-allyl ligand is present in both the cation and the anion. The preparation of other salts with the $[(C_3H_5)PdCl_2]^-$ anion has been described[215].

b. Replacement of the halogeno-bridges. Replacement of the chlorine bridges in π-allyl complexes of palladium by bromo- or thiocyanato-groups takes place readily on treatment with the corresponding alkali metal salt in a polar solvent (acetone, alcohol, etc.)[8,36,37,187,200]. Complexes with bridging carboxylato-groups (acetato-, propionato-, benzoato-, and trimethylacetato-) were made by treating acetone solutions of dichlorobis-(π-allylpalladium) complexes with the corresponding silver salt[46,187,216]. Cryoscopic and ebullioscopic measurements in benzene showed that all the complexes are dimers. They are somewhat less stable than the corresponding chloro-complexes. X-Ray diffraction examination of bis-(π-allylpalladium acetate) showed[46] that it has the structure (LIX) with a weak bond between the palladium atoms. Carboxylato-bridges are easily replaced by other groups. For example, on treating the acetato-complex with dry HCl, dichlorobis-(π-allylpalladium) was obtained, and treatment with trifluoroacetic acid gave the trifluoroacetato-complex $[(C_3H_5)(O_2CCF_3)Pd]_2$.



(LIX)

With acetylacetone and sodium carbonate, monomeric π-allylpalladium acetylacetonates are formed, which were obtained earlier on treating π-allylpalladium chlorides with thallium acetylacetonate[36,187] and also with sodium acetylacetonate. The π-allylpalladium acetylacetonates thus obtained have sharp melting points and can be used for the identification of the π-allyl complexes. Furthermore, it has been shown[217] that the hydrogen of the acetylacetonato-ligand is capable of being replaced by bromine under the action of *N*-bromosuccinimide. The action of other electrophilic and nucleophilic agents leads to loss of the acetylacetonato-ligand.

c. Reactions leading to breaking of the bond between the palladium and the allyl ligand. When heated to 145°C, $[(\pi\text{-}C_3H_5)PdCl]_2$ decomposes violently, the main products being allyl chloride and metallic palladium[8,172]. The decomposition of bis-(3-ethyl-1-methyl-π-allylpalladium chloride)[181]:

$$(C_6H_{11}PdCl)_2 \rightarrow 2\,C_6H_{11}Cl + 2\,Pd$$

and of some other complexes[172] took place in a similar fashion. However, when complexes with four or more carbon atoms in the allyl ligand are heated without solvent in a high vacuum, conjugated dienes are obtained[218].

As Christ and Hüttel showed[219], the reaction of π-allylpalladium chloride complexes with methanol solutions of potassium hydroxide leads to the formation of metallic palladium and an alkene with the same number of carbon atoms as in the π-allyl ligand. Reduction of the complexes $[(C_3H_5)PdCl]_2$ and $[(C_6H_{11})PdCl]_2$ with a methanol solution of sodium methoxide gave propene and hexene respectively[181].

Smutny[220] studied the decomposition products of methoxy-substituted π-allylpalladium chlorides on boiling in alcoholic medium with sodium acetate or hydrogen at room temperature.

During the bromination of $[(\pi\text{-}C_3H_5)PdCl]_2$ and other π-allyl palladium complexes there is stepwise absorption of two bromine molecules at each allyl–PdCl grouping[181,221]. In the first stage there is oxidation of the π-allylpalladium chloride with the formation of an acido-complex of the palladium and allyl bromide. In the second, slower stage, bromination of the C_3H_5Br takes place, which uses up another molecule of bromine.

Prolonged boiling of $[(\pi\text{-}C_3H_5)PdCl]_2$ with water in the presence of oxygen leads to the formation of propene and acrolein[172]. The oxidation of bis-(σ-methylallylpalladium chloride) goes only as far as α-methylacrolein[172,177]. A little isobutyraldehyde is apparently formed by the reaction

$$(C_4H_7PdCl)_2 + 2\,H_2O \rightarrow 2\,CH_3\text{—}CH(CH_3)\text{—}CHO + 2\,Pd + 2\,HCl.$$

π-Allyl complexes with substituted allyl ligands are oxidised in acid solutions in the presence of palladium(II) chloride, chromic acid, or manganese dioxide, to give the $\alpha\beta$-unsaturated carbonyl compounds[177]. The polarographic reduction of π-allylpalladium halides has also been studied[222].

The carbonylation of $[(\pi\text{-}C_3H_5)PdCl]_2$, just like that of the analogous nickel complex, leads to the formation of but-3-enoyl chloride as the main product, when the reaction takes place in benzene. In methanol solutions, there is direct conversion of the chloride into methyl vinylacetate[223]. Similarly, methyl 2-methylbut-1-enoate and methyl pent-2-enoate were obtained from the π-methylallyl and π-crotyl complexes[224].

The carbonylation of complex (LII) in benzene solution together with dichlorobutene gives 1-chloropent-2-enoyl chloride, from which in methanol and ethanol the corresponding esters of these acids are obtained[225,226].

On reaction with carbon monoxide in methanol, the π-allyl complex with a methoxycarbonyl group at a terminal carbon atom of the organic ligand (LV; $R' = CH_3$, $R = H$) gives dimethyl pent-2-endioate.

From all the above examples it is clear that the attack of carbon monoxide proceeds at the terminal, less substituted carbon atom of the π-allyl group of the complex. There is also a report of the carbonylation of π-allyl complexes (LIV)[227].

Two interesting reactions were described recently, which also involve breaking the bond between the palladium and the allyl ligand. The reaction of $[(C_3H_5)PdCl]_2$ with $Fe_2(CO)_9$ leads, as a result of the transfer of the allyl ligand from the palladium to the iron, ($\pi \rightarrow \pi$ transfer), to the formation of tricarbonyl-π-allyliron chloride[228]:

$$(C_3H_5PdCl)_2 + Fe_2(CO)_9 \rightarrow 2\,C_3H_5Fe(CO)_3Cl + 2\,Pd + 3\,CO.$$

Treatment of bis-(π-allylpalladium chloride) with metallic mercury gives the quantitative yield of allylmercury(II) chloride ($\pi \rightarrow \sigma$ transfer)[229]. This method was used by the authors for the synthesis of a series of substituted allylmercury halides. In this reaction, as in the reaction with carbon monoxide, the attack of the mercury atom takes place at the unsubstituted terminal carbon atom of the π-allyl group.

Tsuji and coworkers[230,231] showed that the reaction of π-allylpalladium chloride with nucleophilic reagents (ethyl malonate, ethyl acetate, etc.) also leads to the splitting of the π-allyl complex:

$$(C_3H_5PdCl)_2 + 2\,X\overline{C}H{-}COOC_2H_5 \rightarrow 2\,CH_2{=}CH{-}CH_2{-}CHX{-}COOC_2H_5 + Pd + PdCl_2$$

where $X = CO_2C_2H_5$ or $COCH_3$.

The decomposition of ethyl diazoacetate in the presence of the π-allylpalladium chloride dimer has been described by Armstrong[232].

10. PLATINUM COMPLEXES

There is little information about π-allyl complexes of platinum. Bis-(π-allyl)platinum was obtained by the reaction of platinum(II) chloride with allylmagnesium chloride in ether at 0°C.[73,74,129] It is a colourless crystalline compound, m.p. 41°C, with a very unpleasant odour. Treatment of $[(C_3H_5)_2Pt]$ in pentane with hydrogen chloride at −80°C leads to the formation of $[(C_3H_5)PtCl]_2$, the structure of which has been shown by its reaction with NaC_5H_5.[129] This gives the complex $[(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)Pt]$ prepared earlier[148] by the reaction of propeneplatinum chloride with a mixture of allylmagnesium chloride and cyclopentadienylsodium. The compound is lemon-yellow and stable in air.

Another π-allyl complex of platinum was described[30] recently. $[(C_3H_5)PtCl\{P(C_6H_5)_3\}_2]$, obtained as follows:

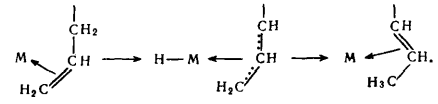
$$[(C_6H_5)_3P]_4Pt + C_3H_5Cl \rightarrow C_3H_5Pt[P(C_6H_5)_3]_2Cl + 2\,(C_6H_5)_3P.$$

IV. π-ALLYL COMPLEXES IN ORGANIC SYNTHESES

In this section we will discuss the participation of π-allyl complexes of the transition metals as intermediates in the isomerisation, oxidation, hydrogenation, carbonylation, and polymerisation reactions of unsaturated compounds.

1. ISOMERISATION OF ALKENES

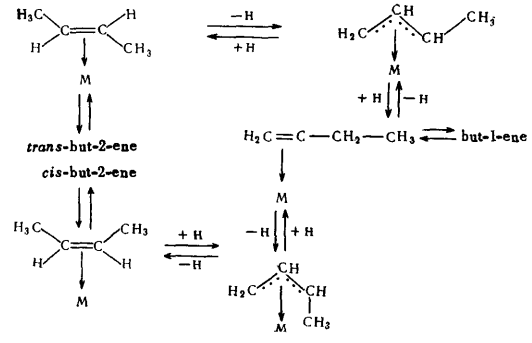
When treated with iron carbonyls[233,234], or with hydrogen carbonylferrate[235,236] or carbonylcobaltate[237], alk-1-enes isomerise into alkenes with non-terminal double bonds. A possible mechanism was proposed for these reactions, isomerisation with participation of the intermediate π-allyl metal hydride complexes[233,234,238,239]:



A similar scheme was proposed for the isomerisation of octenes[240] and of cyclo-octa-1,3-diene by iridium, palladium, and platinum compounds[241-244] and also of allyl alcohol to propionaldehyde by $Fe(CO)_5$.[85]

The isomerisation of alkenes by palladium salts evidently takes place analogously, with the formation of intermediate π-allyl complexes[245-247].

From the standpoint of the π-allyl mechanism Rooney and Webb[248] have explained the *cis–trans*-isomerisation of the monoalkenes. The general picture of the isomerisation of alkenes with the participation of π-allyl intermediate complexes can be represented as follows, for the example of the butenes:



The geometrical configuration of the alkene formed is determined by the structure of the intermediate π-allyl complex. The *syn*-isomer leads to *trans*-but-2-ene, and the *anti*-isomer gives *cis*-but-2-ene.

It is necessary to note that Davies[249], Harrod and Chalk[250], and Cramer and Lindsey[251] criticise the generality of the above scheme. For example, Cramer and Lindsey consider that the formation of π-allyl structures should lead sometimes even to inhibition of the isomerisation.

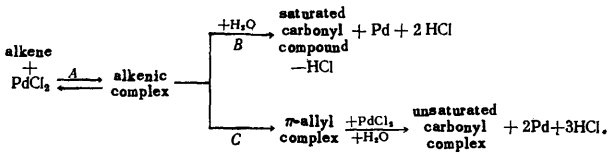
Asinger and coworkers[252] have proposed a method by which it is possible in some instances to confirm the π-allyl mechanism of the isomerisation of alkenes. When the isomerisation is carried out in a mixture with an alkene labelled with tritium, they think that the transfer of tritium will indicate the intermolecular hydride mechanism, but the absence of transfer, the intramolecular π-allyl mechanism.

2. OXIDATION OF ALKENES

In studying the catalytic conversion of alkenes into compounds of the platinum group metals, Smidt and coworkers[253] showed that methylglyoxal is formed from allyl halides.

Hüttel and coworkers [172] obtained the same product in the oxidation of bis-(π-allylpalladium chloride). In support of the π-allyl mechanism there is the identity of the products obtained in oxidising most alkenes and the corresponding π-allyl complexes listed in the Table (p. 488).

Hüttel and Christ [177] proposed the following general scheme for these reactions:



Depending on whether saturated or unsaturated carbonyl compounds are formed this scheme gives an answer about the nature of the intermediate complexes. The course of the reaction in direction *B* or *C* is determined mainly by the nature of the initial alkene, and primarily by its degree of branching. For example, linear aliphatic alk-1-enes give only saturated ketones [253] but branched alkenes listed in the Table give unsaturated carbonyl compounds [177].

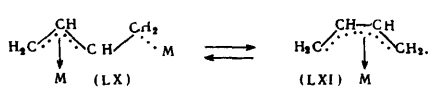
In the oxidation of the higher alk-1-enes by palladium chloride in anhydrous acetic acid containing sodium or potassium acetate, in the first stage π-allyl complexes are formed, which, as Vargaftik and coworkers have shown [254], are in equilibrium with the σ-allyl complex, the reaction of which with acetate ion give substituted allyl acetates:

$$R{-}CH{=}CH{-}CH_2PdCl + CH_3COO^- \rightarrow R{-}CH{=}CH{-}CH_2OCOCH_3 + Pd + Cl^-.$$

3. HYDROGENATION OF ALKENE DERIVATIVES

Kwiatek and coworkers who used the pentacyanocobaltate anion in aqueous solution to hydrogenate a series of organic compounds [255], later showed [107] that the intermediate products in these syntheses were cyano(allyl)cobalt complexes: whether they were π- or σ-complexes was mainly determined by the cyano : cobalt ratio. When butadiene was hydrogenated with a catalyst of low CN : Co ratio, *trans*-but-2-ene was mainly formed, but at high ratios but-1-ene was obtained. The authors explain these results by the formation of an intermediate cyano(methylallyl)cobaltate, in which at high CN : Co ratio the allyl ligand is connected to the cobalt atom by a σ-bond, and at low ratios by a π-allyl bond. The corresponding butene was obtained from these complexes on their reaction with the hydride $[CoH(CN)_5]^{3-}$.

The hydrogenation of buta-1,3-diene by transition metal compounds can, in the general example, pass through intermediate complexes of two types [248]:



On addition of hydrogen to these, the *syn*- and *anti*-forms of methyl-π-allyl complexes will be formed, which, in accordance with the above scheme, for the isomerisation of alkenes will give all three isomeric butenes.

4. CARBONYLATION OF ALLYL HALIDES

The carbonylation of allyl halides in the presence of nickel carbonyl was first described by Chiusoli [256-258]. On carrying out the reaction in water or alcoholic medium the corresponding acids or their esters were isolated:

$$R{-}CH{=}CH{-}CH_2Cl + CO + R'OH \xrightarrow{Ni(CO)_4} R{-}CH{=}CH{-}CH_2{-}COOR' + HCl.$$

The main product obtained from allyl chloride was vinylacetic acid, that from crotyl chloride, pent-3-enoic acid, etc.

In later work, Chiusoli and coworkers [259-262] showed the possibility of π-allyl complexes, $(\pi\text{-}C_3H_5)NiX(CO)$ where X = halogen, participating in these reactions as intermediates.

The carbonylation of allyl halides in the presence of acetylene is a reaction important for the synthesis of organic substances [127,258-267]. Here the π-allyl complexes formed as a result of the reaction of $Ni(CO)_4$ with the allyl halides then react with carbon monoxide in the presence of acetylene, with a molecule of acetylene being introduced between the allyl residue and the carbon monoxide. Hexa-2,5-dienoyl chloride is isolated under carbon monoxide pressure. In aqueous medium, in addition to hexa-2,5-dienoic acid a little phenol was obtained which shows that cyclisation takes place [263].

When the carbonylation of allyl halides is carried out in the presence of substituted acetylenes in water–acetone solution, cyclisation predominated with the formation of carboxyl derivatives of cyclopentenone and cyclohexenone [268,269].

Some of their derivatives behave similarly to the allyl halides in the carbonylation. Thus 1-chloro-4-cyanobut-2-ene gives 5-cyanopent-3-enoic acid, from which caprolactam can be obtained by hydrogenation, or caprylic acid in the presence of acetylene [258]. In the presence of acetylene 1,8-dichloro-octa-2,6-diene gave tetradeca-2,5,9,12-tetraen-1,14-dioic acid.

Prop-2-ynyl chloride also undergoes carbonylation in the presence of $Ni(CO)_4$ and water [270]. The main products are buta-2,3-dienoic and itaconic acids.

The identity of the products obtained from allyl chloride or allyl alcohol [271] and from bis-(π-allylpalladium chloride) [223] also supports the π-allyl mechanism of the carbonylation of allyl compounds with palladium catalysts ($PdCl_2$) at elevated temperatures. At room temperature allyl chloride gives 3,4-dichlorobut-3-enoyl chloride, and not but-3-enoyl chloride.

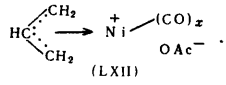
It has been shown that [272,273] that bis-(π-allylpalladium chloride) is an active catalyst for the carbonylation of allyl halides, giving alkenoyl chlorides as the main products, in high yields.

Of the other catalysts for the carbonylation of allyl derivatives, mention may be made of rhodium compounds [271] and platinum compounds [274].

5. SOME OTHER REACTIONS IN WHICH π-ALLYL INTERMEDIATE COMPLEXES PARTICIPATE

$\alpha\beta$-Unsaturated aldehydes and ketones are obtained in the hydroformylation of conjugated and non-conjugated

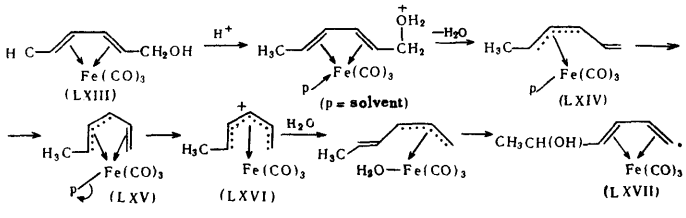
alkadienes in the presence of hydrogen tetracarbonylcobaltate(-1). Under the conditions of the reaction these aldehydes and ketones are easily reduced by the hydrogen tetracarbonylcobaltate(-1) through an intermediate π-oxapropenyl complex of type (XXIV) to saturated aldehydes and ketones[80]. The same complex evidently participates in the reaction for the formation of 1,2-dibenzoyloxystilbene from benzoyl chloride or bromide and tetracarbonylnickel in tetrahydrofuran or hexane solution[275]. As Bauld has shown[276], the reaction of allyl acetate with $Ni(CO)_4$ proceeds through the stage of complex (LXII), the structure of which is analogous to that of complex (XXXIX), and leads to biallyl:



(LXII)

Bicinnamyl is obtained in the same way from cinnamyl acetate.

Mahler and coworkers[277,278] showed that some of the reactions of tricarbonyldieniron complexes can be satisfactorily explained by starting from the formation of π-allyl complexes. For example, the action of strong acids on tricarbonyl(hexa-*trans*-2,*trans*-4-dien-1-ol)iron (LXIII) gives the intermediate π-allyl complexes (LXIV, LXV) and then tricarbonyl-*syn*-1-methylpentadienyliron cation (LXVI)[274], which on hydrolysis is converted into tricarbonyl(hexa-*trans*-3,5-dien-2-ol)iron (LXVII)[275]:

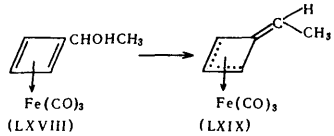


(LXIII) (LXIV) (p = solvent) (LXV) (LXVI) (LXVII)

Pettit and coworkers[279] proposed a π-allyl structure (LXIX) for the intermediate product formed on treating complex (LXVIII) with hydrochloric acid followed by solvolysis in methanol.

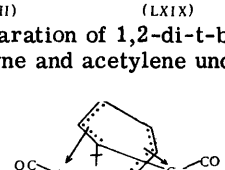
$Co_2(CO)_4[C_2H{-}C(CH_3)_3]_2(C_2H_2)$ (LXX).

Mills and Robinson[280] used X-ray structural analysis and NMR spectroscopy to show the π-allyl nature of the intermediate product:



(LXVIII) (LXIX)

obtained in the preparation of 1,2-di-t-butylbenzene from 3,3-dimethylbut-1-yne and acetylene under the influence of cobalt carbonyl:



(LXX)

6. POLYMERISATION AND OLIGOMERISATION OF ALKENES AND ALKADIENES

Catalysts based on π-allyl complexes of nickel have been studied in most detail.

Wilke found that bis-(π-allyl)nickel brings about the cyclic trimerisation of butadiene into cyclododeca-1,5,9-triene[23,125,127]. Bis-(π-methylallyl)nickel and bis-(π-crotyl)nickel behave in the same manner[129,281].

π-Allylnickel halides initiate the stereospecific polymerisation of butadiene[130,282-285]. The microstructure of the polymer formed is determined by the nature of the halogen in the π-allyl complex: compounds which contain chlorine lead to *cis*-1,4-polymers, whereas iodine complexes are capable of forming polybuta-1,4-dienes. It has been shown radiochemically that the π-allylnickel ligands of the initial complexes entered into the composition of the polymer[286].

The products of the reaction of π-allylnickel halides with Lewis acids (halides of B, Al, Ti, Sn, V, Mo, and W) exhibit high activity in the polymerisation of butadiene[130,282,283,285,287]. In this, irrespective of the halogen in the π-allyl complex or in the Lewis acid, polybutadienes with a high proportion of *cis*-1,4-links are formed[283].

Active catalysts for the polymerisation of butadiene are also formed in the reaction of bis-(π-crotyl)nickel with the halides of various metals[130,281,282,287]. The proportion of links of different configurations in the polymers obtained under the influence of these systems is determined by the nature of the halogen in the metal halide[281,282].

The products of the reaction of π-cyclopentadienyl(π-cyclopentyl)nickel with Lewis acids act similarly[288,289].

Propene and ethylene are dimerised extremely rapidly in the presence of catalytic systems consisting of bis-(π-allyl)nickel or bis-(π-allylnickel halides), aluminium halides or alkylaluminium halides, and trialkylphosphines[23,29,290,291]. It has been shown[23,29] that the basicity of trialkylphosphines affects the structure of the dimers formed.

Bis-(π-allylnickel bromide) polymerises cyclobutene with opening of the double bond: a polycyclobutylenamer is formed[284]. There is also a report of the polymerisation of acetylene in the presence of bis-(π-allylnickel bromide)[138,139]. Crystalline 1,2-polyallene was obtained in the presence of $Ni(\pi\text{-}C_3H_5)_2$, $[NiBr(\pi\text{-}C_3H_5)]_2$, and $[Ni(\pi\text{-}CH_2CHCN)_2]$[292].

Bis-(π-allyl)cobalt iodide polymerises butadiene to *cis*-1,4-polymer[23,29,128,290].

The π-allyl cobalt complex of composition $CoC_{12}H_{19}$ described by Natta and coworkers[124] is a catalyst for the linear dimerisation of butadiene and 3-methylhepta-1,4,6-triene. The same dimer is also formed by the action of tris-(π-allyl)cobalt[23,29,290,293].

1,2-Polybutadiene is formed in the presence of tris-(π-allyl)chromium[23,29,63,128,281,290]. The products of the reaction of $(\pi\text{-}C_3H_5)Cr$ with $NiCl_2$ or TiI_4 bring about the formation of *cis*-polybuta-1,4-diene, but with $NiBr_2$ the *trans*-1,4-polymer is obtained[281].

Bis-(π-allyl)chromium iodide, like bis-(π-allyl)nickel, catalytically trimerises butadiene into cyclododeca-1,5,9-triene[23,29,63,128]. In the presence of $(\pi\text{-}C_3H_5)_2CrCl$ butadiene is converted into a polymer[63]. Furthermore, it must be mentioned that at room temperature and moderate pressure (15 atm) $(\pi\text{-}C_3H_5)_3Cr$ polymerises ethylene into linear high-molecular-weight polyethylene, analogous to the polyethylene obtained with Ziegler catalysts[63].

Bis-(π-allyl)palladium converts butadiene solely into linear oligomers, whereas its addition products with electron donors gives cyclic dimers[23,129].

Tris-(π-allyl)iron gives a mixture of cyclic and aliphatic oligomers, and also polymerises but-2-yne into hexamethylbenzene[101].

An examination of the mechanism of the polymerisation of diene hydrocarbons with participation of π-allyl complexes allowed ideas of primary importance to be formulated about the formation of the links of a polymeric chain as a function of the direction of attack of the active centre of the monomer molecule[283,294-296]. The polymerisation of butadiene in an aqueous medium under the influence of the rhodium compounds has been examined from the aspect of a π-allyl mechanism[297-299].

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Several new papers on the subject of the present review have appeared whilst the latter was being written.

The reaction of π-allylpalladium chlorides with electron donors has been investigated by NMR and infrared spectra[300-302]. Hegarty and Kitching[303] have interpreted the ultraviolet spectra of π-allyl complexes of palladium in various solvents. Several papers[304-307] have described the preparation of π-allyl complexes of palladium. Moiseev and coworkers[308] investigated the thermal decomposition of six π-allyl complexes of palladium.

Wilkinson and coworkers[309] prepared new allyl complexes of rhodium. The results of an X-ray diffraction study of bis-(π-allyl)rhodium chloride have been reported[310].

Nesmeyanov and coworkers[311] studied the decomposition products of carbonyl-π-allyl complexes of iron. King[312,313] has studied the π-allyl complexes of molybdenum and iron.

The participation of π-allyl complexes of the transition metals as intermediate products in isomerisations has been discussed[314-317]. A patent[318] deals with the polymerisation and copolymerisation of alkenes under the influence of the π-allyl complexes of Cr, Mo, W, and Zr.

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DEHYDROGENATION OF ALKANES AND ALKENES AT LOW PRESSURES

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I. INTRODUCTION

The catalytic dehydrogenation to alkenes and alkadienes of alkanes containing 2 to 5 carbon atoms is a promising method for the preparation of unsaturated hydrocarbons. In recent years there has been greatly increased interest in the preparation of alkenes and alkadienes by the catalytic dehydrogenation of low-molecular-weight alkanes at low pressures of the starting materials, because thermodynamic calculations have shown that under these conditions considerable yields of useful products should be obtained. Notwithstanding a certain complexity in the technological design of dehydrogenation processes at low hydrocarbon pressures (that is, under vacuum or with the use of solvents), the application of such processes results in substantial economic gains. It is for this reason that, in the United States and Western Europe, the production of bivinyl by Houdry's method has been developed as the most economic method of dehydrogenation[2]; in this method n-butane is dehydrogenated under vacuum in a single stage[1]. In the USSR the problem of using this method is under consideration[3,4].

A large amount of experimental information on the catalytic dehydrogenation of hydrocarbons at low pressures is now available, and this merits a special review; in our opinion such a review provides an essential supplement to modern informative reviews[5-7] on the dehydrogenation of hydrocarbons. The present review considers problems of the thermodynamics of the dehydrogenation of C_2–C_6 hydrocarbons at low pressures, as well as catalysts and the operating conditions for industrial applications of the process.

II. THERMODYNAMIC CALCULATIONS OF HYDROCARBON DEHYDROGENATIONS

Thermodynamic calculations permit us to select the optimal conditions for carrying out a reaction. Using such calculations, we can calculate whether a given reaction could proceed in such a way as to give a useful product in sufficiently high yield to warrant its practical application, and also the most favourable temperatures and pressures for carrying out the reaction. An increase in the temperature of a process and reduction in pressure result in an increase in the degree of equilibrium dehydrogenation, and therefore favour an increased yield of alkenes or alkadienes[5,8].

Using experimental data on the dehydrogenation of alkanes in the presence of chromium catalysts, Frey and Huppke[9] determined the equilibrium constants for the dehydrogenation of n-butane to each of the isomeric butenes, and of propane to propene, and ethane to ethylene. Using the data of these workers, Zharkova[10] determined the dependence of $\lg k_{equil}$ on temperature. Dement'eva and coworkers[11,12] calculated the dependence of the degree of dehydrogenation of n-butane, isobutane, and propane on