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π-Allyl Cationic Complexes of Palladium(II) with Closoborate Anion

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The interaction of $[(h^3\text{-}C_3H_5)PdCl]_2$ *with silver salts of closoborate ions* $B_{10}Br_{10}^{2-}$ *and* $B_{12}Br_{12}^{2-}$ *in the presence of aceto- and benzonitrile was investigated. Stable complexes of formula* $[(h^3\text{-}C_3H_5)Pd(RCN)_2]_2\text{-}B_{10}Br_{10}$ *(R = Me, Ph) were obtained. Raman, IR, PMR and ESCA spectra were investigated. The electronic structure of these complexes and lability of allyl ligand are discussed.*

Introduction

The use of polyhedral borate anions as stabilizing counterions has made it possible to synthesize a number of new palladium(II) complexes [1], $\{[(C_6H_5)_3P]_4Pd_2Cl_2\}B_nX_n$ and $\{[(C_6H_5)_3P]_3PdCl\}_2B_nX_n$, were n = 10, 12; X = Cl, Br.

The anions may be introduced into synthesis in the form of dibasic acids, or their salts, normally of metals of group I of the periodic system. When reactions are conducted in organic solvents, use is often made of silver salts readily soluble in them, like silver salts of other slightly deformable anions [2, 3].

This paper summarizes the results of a study of the interaction of di-μ-chloro-di-π-allylpalladium $[(h^3\text{-}C_3H_5)PdCl]_2$ with $Ag_2B_{10}Br_{10}$ and $Ag_2B_{12}Br_{12}$ in the presence of nitriles, aimed at elucidating the possibility of inserting two monodentate donor ligands into the inner coordination sphere of complex containing a π-allyl ligand which can change the distribution of the electron density in the allyl–metal–donor ligand system and alter the strength of the metal–allyl bond.

The synthesis of such complexes may be interesting from the standpoint of various catalytic processes as well as using them as biologically active compounds [4].

Results and Discussion

The interaction of $[(h^3\text{-}C_3H_5)PdCl]_2$ (I) with $Ag_2B_{10}Br_{10}$ in the presence of nitriles permits two donor ligand molecules to be inserted into the inner coordination sphere, in accordance with the following equation:

$$[(h^3\text{-}C_3H_5)PdCl]_2 + Ag_2B_{10}Br_{10} \xrightarrow{R-CN} 2AgCl + [(h^3\text{-}C_3H_5)Pd(RCN)_2]_2\cdot B_{10}Br_{10}$$

where R = CH_3 or C_6H_5

In the case of R = CH_3 the interaction occurs in the presence of acetonitrile with subsequent recrystallization of the complex from the mixture of acetonitrile, methylene chloride and benzene, yielding yellow crystals (complex II).

X-ray analysis of monocrystal has established that complex II contains two $[(C_3H_5)Pd(CH_3CN)_2]^+$ cations, the anion $B_{10}Br_{10}^{2-}$ and a benzene molecule between two cations and anion, that is, a system is formed in the crystal similar to an ion pair separated by a solvent molecule [5].

The 'benzene-free' complex III may be produced by recrystallization of complex II from the mixture of the same solvents but in the presence of n-heptane and by heating up to 40 °C.

When acetonitrile is replaced by benzonitrile, complex $[(h^3\text{-}C_3H_5)Pd(PhCN)_2]_2B_{10}Br_{10}$ (IV) is obtained from the solution, which is much less stable than complex II, probably due to the less pronounced donor capacity of benzonitrile as compared to acetonitrile [6].

Complexes II–IV cannot be obtained through a reaction in which *trans*-$[(RCN)_2PdCl_2]$ (R = Me, Ph)

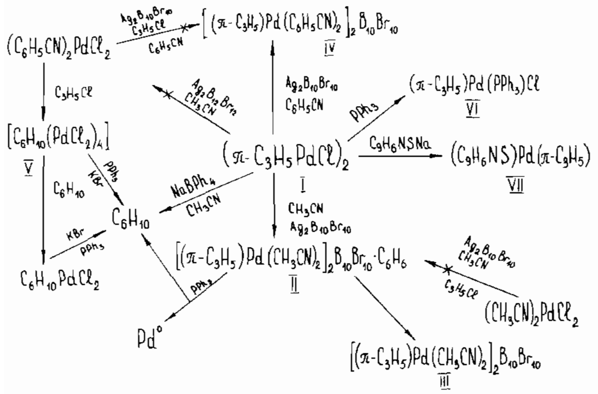

Fig. 1. Reaction sequence for π-allylpalladium chloride.

interacts with allyl chloride and $Ag_2B_{10}Br_{10}$ in the presence of the respective nitrile.

Attempts to insert nitrile ligands into the inner coordination sphere of palladium by breaking the bridging bonds in complex I plus direct interaction with nitriles do not produce any positive results. Replacement of anion $B_{10}Br_{10}^{2-}$ by other large anions such as $B_{12}Br_{12}^{2-}$ or BPh_4^- does not yield compounds of types II–IV either (Fig. 1). The introduction into the reaction system of tetraphenylborate anion already at room temperature yields metallic palladium and hexadiene-1,5. Anion $B_{12}Br_{12}^{2-}$ cannot be made to react at room temperature; heating leads to reduction of the reaction mixture.

Gaseous hexadiene-1,5 as a product of displacement of the allyl ligand followed by its subsequent dimerization is formed when complex II interacts with triphenylphosphine as well.

In the examined systems we did not observe any coordination of the forming hexadiene to the palladium atom, whereas a reaction between a benzene solution of $(PhCN)_2PdCl_2$ and allyl chloride has yielded the diolefin complex $[(C_6H_{10})(PdCl_2)_4]$ (V) [7].

The labilization of the allyl ligand in the complex II and its displacement by triphenylphosphine is a rather curious phenomenon in the chemistry of π-allyl compounds of palladium and must be due to the presence of nitrile ligands in the inner coordination sphere of palladium.

It is known that the insertion of a single donor ligand even as strong as triphenylphosphine leads to breakage of only chlorine bridges with formation of complex $[(h^3\text{-}C_3H_5{-}Pd(PPh_3)Cl]$ (VI) [8] but without changes in the nature of the allyl ligand [9]. The introduction of another PPh_3 molecule in the presence of an allyl ligand changes the bonding between allyl and the metal and may be carried out only if groups $C_6F_5^-$ and $C_6HCl_4^-$ are linked with palladium instead of the chlorine atom [10].

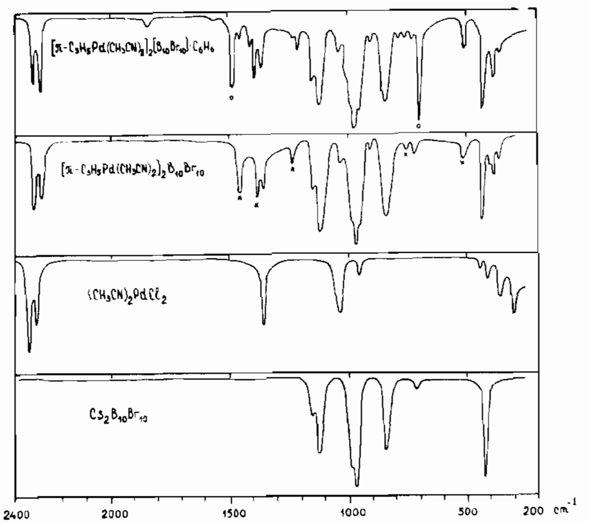

Fig. 2. Infrared spectra of acetonitrile complexes and related compounds: ○, benzene band; *, h^3-allyl group.

Substitution of a chelate ligand (complex VII) for the chlorine atoms even strengthens the bond between palladium and the π-allyl ligand which cannot be displaced even by a large excess of chelate 8-mercaptoquinoline [11].

The presence of π-allyl group along with two donor ligands (PPh_3) in the inner coordination sphere of palladium is believed by Kuran and Musco [12] to be a feature of intermediate $[(h^3\text{-}C_3H_5)Pd(PPh_3)_2]^+$ whose existence seems doubtful in the light of our results.

To gain an insight into the character of the palladium–allyl bond in the synthesized complexes and to determine the nature of the allyl ligand we resorted to vibrational and NMR ^1H spectroscopy.

Earlier we carefully studied the vibrational spectra of both π-allyl complexes of various transition metals [13, 14] and salts of polyhedral anions $B_nX_n^{2-}$ (n = 10, 12; X = H, Cl, Br) [15], which enabled us to confirm the presence in complex II of π-allyl group and anion $B_{10}Br_{10}^{2-}$ as well as to compare the spectral characteristics of these groups in complex II and allied compounds. The results are shown in Figs. 2 and 3.

The IR spectrum of complex II permits the anion $B_{10}Br_{10}^{2-}$ to be identified by intense IR bands at 430, 840, 1120, and 1150 cm^{-1}, whose frequencies exactly coincide with those of the corresponding bands in the IR spectrum of salt $Cs_2B_{10}Br_{10}$ (Fig. 2). The acetonitrile molecule σ-bonded to palladium via the nitrogen atom is characterized by strong IR bands at 2290 and 2320 cm^{-1}.

The benzene molecule in complex II manifests itself by the presence in the IR spectrum of a strong narrow band at 700 cm^{-1} (ρ_{CH}) and a band of mode-

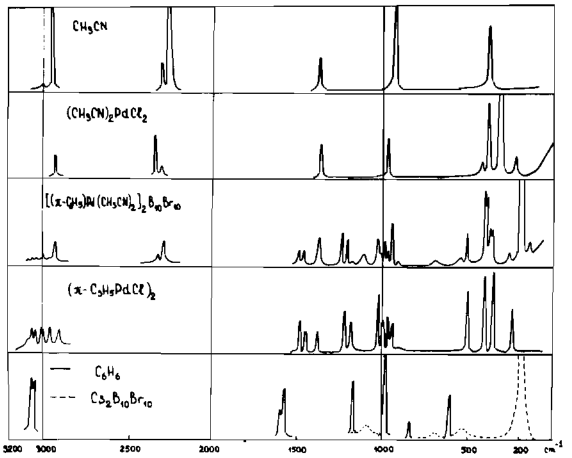

Fig. 3. Raman spectra of acetonitrile complexes and related compounds.

rate intensity at 1485 cm^{-1}. In the IR spectrum of the 'benzene-free' complex III these bands disappear. Note that ρ_{CH} frequency (700 cm^{-1}) in the spectrum of complex II does not coincide with that at 671 cm^{-1} in the IR spectrum of 'free' benzene, which is indicative of some changes in the benzene molecule under the effect of the crystalline field of the complex, although it is important to point out that the selection rules for the symmetry of the 'free' benzene ring (D_{6h}) are not violated.

The π-allyl ligand could be reliably identified only with the aid of the Raman spectra because the intensity of the allyl ligand bands in the IR spectrum is low (510, 752, 1230, 1380, and 1460 cm^{-1}). When complex II is placed in an argon laser beam it immediately decomposes yielding metallic palladium. Even the low-energy He–Ne laser beam decomposes complex II which accounts for the poor quality of the Raman spectra obtained. On the contrary, the Raman spectrum of complex III proved to be excellent (Fig. 3). No decomposition of complex III was observed in the low-energy argon laser beam. The weak Raman spectrum lines which could be produced for complex II coincide with those observed in the case of complex III.

The Raman spectrum of complex III clearly shows a set of lines representative of the π-allyl ligand bonded to palladium (513 cm^{-1}, four lines in the region of 950 to 1030 cm^{-1}, 1208, 1238, 1468 and 1495 cm^{-1}). The frequencies of these lines coincide within 10 cm^{-1} with those of the Raman spectrum of complex I (Fig. 3). Note the region of stretching vibration ν(Pd–C$_3$H$_5$) where the Raman spectrum of complex III exhibits two pairs of intense lines;: 370/372 and 396/407 cm^{-1} (*cf.* 376 and 405 cm^{-1} in the Raman spectrum of I).

Anion $B_{10}Br_{10}^{2-}$ manifests itself in the Raman spectrum of complex III by strong lines about 200 cm^{-1}, while the acetonitrile ligand is recognized by the same lines as in the IR spectrum – 2290 and 2320 cm^{-1}. The remaining acetonitrile lines overlap with the π-allyl group ones.

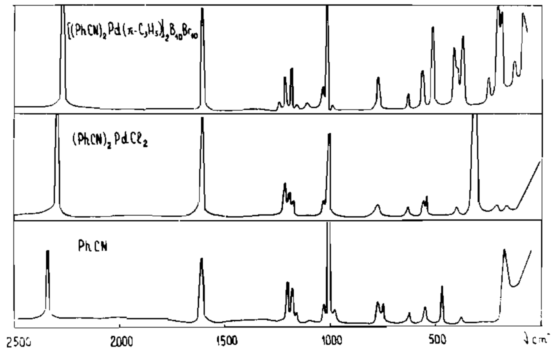

Fig. 4. Raman spectra of benzonitrile compounds.

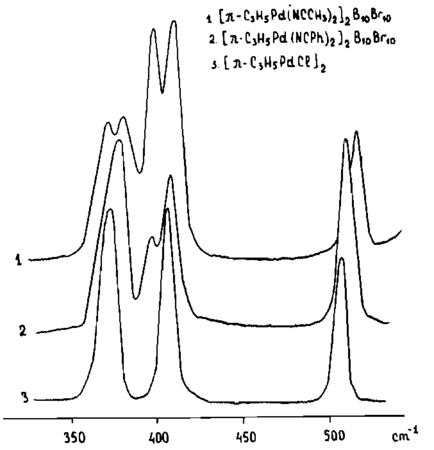

Fig. 5. Raman spectra of h^3-allyl complexes in the region of the ν(Pd–Allyl) and δ(C^{C}C) vibrations.

Despite the fact that complex IV is less stable than II and III its IR and Raman spectra could be obtained. It is difficult, though, to determine the frequencies of the allyl ligand of complex IV in the region beyond 550 cm^{-1} (Fig. 4) because the Raman lines of benzonitrile ligands bonded to palladium are very intense and mask those of the allyl group. However, the Raman spectrum of complex IV in the region of 350 to 520 cm^{-1} (Fig. 5) containing the lines corresponding to ν(Pd–allyl) and δ(C ^{C} C) – 510 cm^{-1} – vibrations is close to that of complex III, which suggests that the ligand environment about the palladium atom in the cations of complexes II and IV is identical.

Anion $B_{10}Br_{10}^{2-}$ in the IR and Raman spectra of IV is characterized by the same set of absorption bands as in the spectra of II and III.

Thus, the vibrational spectrum of the π-allyl ligand in the complexes II, III, and IV is identical with that

TABLE I. X-ray Photoelectron Spectra of Synthesized Complexes and Related Compounds.*

Compound	Pd $3d^{5/2}$	N 1s	Cl $2p^{3/2}$
$[(h^3\text{-}C_3H_5)Pd(PPh_3)Cl]$	337.9	–	198.0
$[(h^3\text{-}C_3H_5)PdCl]_2$	337.6	–	198.8
$[(h^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}\cdot C_6H_6$	338.1	400.5	–
$(CH_3CN)_2PdCl_2$	338.9	400.3	–
$[(h^3\text{-}C_3H_5)Pd(C_6H_5CN)_2]_2B_{10}Br_{10}$	338.1	400.0	–
$(C_6H_5CN)_2PdCl_2$	338.6	400.2	–
$C_6H_{10}PdCl_2$	338.8	–	–
$[(h^3\text{-}C_3H_5)Pd(C_9H_6NS)]$	337.6	400.1	–
$Pd(C_9H_6NS)_2$	337.9	400.1	–

*Binding energy in eV.

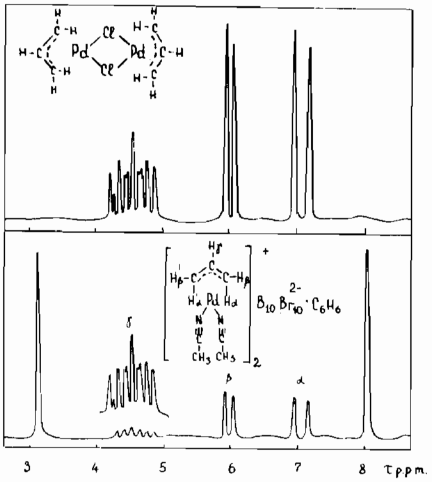

Fig. 6. ^{1}H n.m.r. spectra of indicated complexes in acetone-d_6 solution.

of complex I. Examination of the NMR ^{1}H spectrum of complex II also indicates that the spectrum of the allyl ligand in this complex remains the same as in complex I (Fig. 6).

However, the results of investigating the ESCA spectra (Table I) of the synthesized compounds clearly indicate that the electron density in the metal–allyl system redistributes when two donor ligands are introduced into the complex. For example, E Pd $_{3d}5/2$ for complexes II and IV is greater than for I by 0.5 eV, that is, when the acceptor ligands – chlorine atoms – are replaced by donor acetonitrile ones, the electron density at the palladium atom decreases rather than the other way round.

Earlier it was established on the basis of quantum-chemical calculations as well as ESCA and vibrational spectroscopy data [16], that in the metal–allyl bonding the σ-donation of electrons from the ligand to the metal plays a major role, while in the metal–olefin bond back donation of electrons from the metal to the ligand is predominant. The decrease in the electron density at the central atom in complexes II and IV with the vibrational frequencies of the π-allyl ligand remaining the same indicates, with due account for the results reported earlier [14, 16], that either the σ-donor properties of the π-allyl ligand become less pronounced or its π-acceptor properties become stronger, that is, back donation of the metal electrons to the nonbonding orbital of the allyl ligand takes place.

If back donation of electrons had occurred from the metal to the antibonding orbital of the ligand, a decrease in frequency $\nu(C\overset{C}{\cdots}C)$ and an increase in $\delta(C\overset{C}{\cdots}C)$ would have been observed, which does not take place.

Thus, the presence in the inner coordination sphere of the palladium atom of two donor ligands does not bring about any perceptible changes in the vibrational and PMR spectral characteristics of the π-allyl ligand. However the redistribution of the electron density in the metal–ligand system produces a tangible effect on the reactivity of complexes II to IV, as opposed to I.

Experimental

Complex I – $[(C_3H_5)PdCl]_2$ – was derived by interaction of palladium dichloride with allyl chloride in 50% acetic acid [17], while complex VII was obtained by an earlier described method [11].

The halogenated polyhedral borate anions were prepared by another known method [18], and their silver salts $Ag_2B_{10}Br_{10}$ and $Ag_2B_{12}Br_{12}$ were obtained by addition of silver nitrate to an aqueous solution of the respective cesium salt, acidified with HNO_3, and drying of the precipitate over P_2O_5 in vacuum.

The solvents were purified by standard procedures [19].

The IR spectra of solid samples in the form of nujol and fluorolube mulls, as well as KBr and CsI pellets were taken using a PE-457 spectrophotometer in the range 250–4000 cm^{-1}. The Raman spectra of polycrystalline samples were obtained using a MOLE microprobe laser spectrometer as well as a Ramanor HG-2S one with Ar$^+$ beam excitation at 5145 Å and a Coderg-PHO laser spectrometer with He–Ne beam excitation of 6328 Å.

The NMR ^{1}H spectra were taken in deuteroacetone solution on a Varian A 56/60 spectrometer at 60 MHz using TMS as the internal standard.

The X-ray photoelectron spectra were obtained on a Varian VIEE-15 spectrometer.

The X-ray powder patterns were obtained in a standard Debye camera (diameter 114.6 mm) with Fe-radiation.

The TLC were taken on precoated silica gel sheets (Silufol, Kavalier, ČSSR). The spots were detected using iodine vapors.

The gas chromatograms of the products of interaction of complex I and II with triphenylphosphine were taken on a Tsvet-4 chromatograph (3 m long column, sorbent PEGA, carrier gas helium, column temperature 80 °C) and, at the same time, on an LKhM-8DM chromatograph (5 m long column, sorbent 15% Apiezon-L on Chromosorb-W, carrier gas helium, column temperature 100 °C). The reaction product – hexadiene-1,5 – was identified by the retention time of the standard hexadiene-1,5 solution in ether. The liquid phase was separated prior to chromatography by recondensation into a cooled trap with the aid of a vacuum unit.

Synthesis of $[(h^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}$*, (III)*

A solution of $[(C_3H_5)PdCl]_2$ (0.11 g, 0.30 mmol) in 5–7 ml methylene chloride is added to a solution of $Ag_2B_{10}Br_{10}$ in 10 ml purified acetonitrile. After a few hours the silver chloride residue was filtered out and the clear pale yellow solution was evaporated in vacuum. Solid residue is dissolved in a minimum quantity of CH_2Cl_2, 10 ml chloroform and n-hexane as well as 3 ml of CH_3CN are added and the mixture is left to stand on 40 °C hot plate.

As the solvents evaporate well defined, clear crystals are formed at the bottom. Yield of the compound was 0.37 g (91% from theory). The X-ray powder pattern has confirmed the individuality of the obtained compound. The TLC did not reveal the presence of any compounds other than III. Calculated for $C_{14}H_{22}N_4Pd_2Br_{10}B_{10}$: C 12.31; N 4.10; Pd 15.57; Br 58.48. Found: C 12.48; N 3.98; Pd 16.10; Br 58.04.

Independently complex III may be obtained through heating of complex II at 90 °C for six hours with periodical evacuation.

Complex II is obtained by isothermal crystallization of clear solution after reaction of I and $Ag_2B_{10}Br_{10}$ in the presence of benzene [5]. Calculated for $C_{20}H_{28}N_4Pd_2Br_{10}B_{10}$: C 16.63; H 1.95; N 3.88. Found: C 16.55; H 1.94; N 4.09.

Complex II is readily soluble in acetone, acetonitrile, methylene–chloride, nitromethane, nitrobenzene. It is insoluble in chloroform, alcohols, aromatic and aliphatic hydrocarbons. It is stable in air for at least three months.

Synthesis of $[(C_3H_5)Pd(C_6H_5CN)_2]_2B_{10}Br_{10}$*, (IV)*

A solution of complex I (0.32 g, 0.27 mmol) in 5 ml of methylene chloride was added to a solution of $Ag_2B_{10}Br_{10}$ (0.1 g, 0.27 mmol) + 3% excess) in 3 ml of benzonitrile with continuous stirring. The silver chloride sediment was immediately filtered and 200 ml of chloroform were added to the filtrate. The mixture was stirred for 30 minutes and the solution turned yellow-green. A white flocculent sediment was dissolved in 350 ml of warm absolute ethanol, evaporated in vacuum to a volume 70 ml, then salted out with chloroform again. The resulting sediment was washed with ether and dried in vacuum. Calculated for $C_{34}H_{30}N_4Pd_2Br_{10}B_{10}$: C 25.29; H 1.87; N 3.46. Found: C 25.07; H 1.54; N 2.82.

The complex (white crystals) has a light odor of benzonitrile, is soluble in warm ethanol and insoluble in chloroform, methylene chloride, acetone, benzene.

Interaction of Complex II with Triphenylphosphine

Crystalline triphenylphosphine (0.16 g, 0.56 mmol) was added to a solution of complex II (0.22 g, 0.14 mmol) in 5 ml acetone with continuous stirring for 30 minutes. The color changed from yellow to red-orange, metallic palladium precipitated, and gaseous products were evolved, including hexadiene-1,5, which was identified by gas chromatography.

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