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CLOSOBORATE ANIONS AS A MEANS OF SYNTHESIZING NEW COORDINATION COMPOUNDS

I.A. ZAKHAROVA

Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Leninsky Prospekt 31, Moscow 117071 (U.S.S.R.)

CONTENTS

A. INTRODUCTION

In 1964, Muetterties and co-workers described the properties of, and methods for synthesizing various acids and salts containing the ions $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$ and their halogen derivatives [1,2]. Extensive studies since then have been made into salts of metals of Groups 1 and 3, containing these anions and compounds with various organic cations. It is notable that hydrogen-containing anions with 10 or even 12 boron atoms are characterized by high thermal stability and resistance to attack by acids, alkalis and various oxidizing agents, unlike other boron hydrides. In addition, the size of these anions and their solubility in a wide range of solvents provides possibilities for the synthesis of some new transition metal complexes. It should also be borne in mind that $B_{10}X_{10}^{2-}$ (X = H, Cl, Br) forms salts which are soluble in water and whose toxicity is extremely low. For example, the lethal dose determined for rats is 7.5 g kg^{-1} for $Na_2B_{10}H_{10}$ and more than 7.5 g kg^{-1} for $Na_2B_{12}H_{12}$.

B. NICKEL CLOSOBORATE COMPLEXES

Analysis of the literature indicates that interactions between Group 8 metal complexes and the closoborate anions are practically unknown. For

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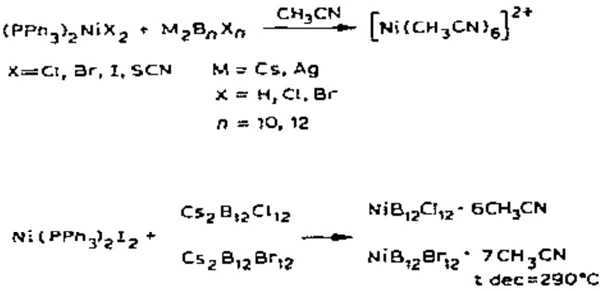


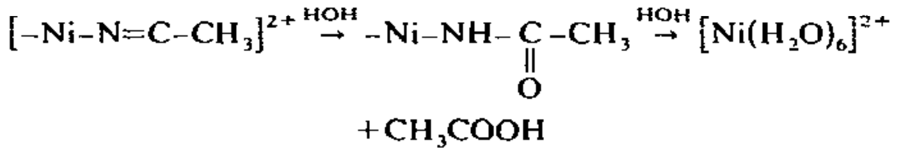
Fig. 1. Nickel(II) closoborates.

example, for nickel, only the compounds $[Ni(H_2O)_6]B_{12}Cl_{12} \cdot nH_2O$, $[Ni(H_2O)_6]\ B_{12}H_{12} \cdot nH_2O$ and $[Ni(NCl_3)_6]B_{12}H_{12} \cdot nH_2O$ have been isolated and their properties are virtually unknown [1,2].

I have therefore studied the interaction of $Ni(PPh_3)_2X_2$ with $M_2B_nX_n$ ($M = Cs$, Ag; $X = H$, Cl, Br; $n = 10$, 12) in acetonitrile solution (Fig. 1). The known acetonitrile complexes of nickel chloride contain two or four acetonitrile molecules in the inner coordination sphere and are characterized by low stability and pronounced hydrolyzability [3]. The use of the phosphine complex of nickel iodide as the initial reagent has allowed the isolation of the individual compounds $NiB_{12}Cl_{12} \cdot 6\,CH_3CN$ (**I**) and $NiB_{12}Br_{12} \cdot 7\ CH_3CN$ (**II**). For the case of $Ni(PPh_3)_2X_2$ ($X = Cl$, Br, SCN) it was not possible to separate the products of reaction [4].

The electronic spectra of solutions of compounds **I** and **II** are consistent with an octahedral structure of the inner coordination sphere of nickel in these complexes. The magnetic moments of 3.29 B.M. for **I** and 3.18 B.M. for **II**, the frequencies of the absorption bands in the IR spectra and the energy of the N 1*s* level (400.3 eV) of acetonitrile from ESCA data indicate the presence of a coordinate bond between nickel and the nitrogen atom of acetonitrile.

The complexes are not hydrolyzable in air and exhibit high thermal stability, the onset of thermal decomposition occuring at temperatures above 250°C. This process is accompanied by the loss of an entire acetonitrile molecule and the formation of a highly hygroscopic compound $NiB_{12}Cl_{12}$. The stability of complexes **I** and **II** is presumably due to the similarity in shape and size of the cation resulting from decomposition and the anions $B_{12}Cl_{12}^{2-}$ and $B_{12}Br_{12}^{2-}$. Nevertheless, in water vapor and at temperatures ranging from 110 to 115°C, hydrolysis of **I** and **II** does occur but only becomes noticeable after 20 to 25 h. The process then speeds up and the faster rate is maintained until acetic acid is formed via a nickel amide intermediate, according to eqn. (1).



$$[-\mathrm{Ni}-\mathrm{N}{=}\mathrm{C}-\mathrm{CH_3}]^{2+} \xrightarrow{\mathrm{HOH}} -\mathrm{Ni}-\mathrm{NH}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{CH_3} \xrightarrow{\mathrm{HOH}} [\mathrm{Ni(H_2O)_6}]^{2+} + \mathrm{CH_3COOH} \qquad (1)$$

The IR spectrum of the intermediate product corroborates the presence of coordinated amide; it exhibits absorption bands at 3200, 1680, 1630 and 1460 cm^{-1}.

Interestingly, neither $Cs_2B_{12}H_{12}$ nor $Cs_2B_{10}X_{10}$ (X = H, Cl, Br) react with $Ni(PPh_3)_2 \cdot I_2$ under similar conditions. On the other hand, reaction with $Ag_2B_{12}H_{12}$ as the initial reagent in dry acetonitrile and a flow of dry nitrogen, results in the precipitation of silver halide and the solution changing colour from red-brown to lilac-violet, the latter colour being typical of complexes **I** and **II**. By careful evaporation of the solution in a flow of dry nitrogen, the extremely hygroscopic complex, $NiB_{12}H_{12} \cdot 6CH_3CN$, was isolated.

The interaction of $Ni(PPh_3)_2 \cdot I_2$ with $AgB_{10}X_{10}$ (X = H, Cl, Br) also yields lilac-violet solutions which rapidly hydrolyze in air with a concomitant colour change to green, typical of the cations $[Ni(H_2O)_6]^{2+}$. According to the electronic spectra of the solutions obtained after removal of silver halide, the octahedral cation $[Ni(CH_3CN)_6]^{2+}$ is invariably present (Table 1).

Thus, the data obtained substantiate the stabilizing effect of a large spherical anion. Indeed, of the series of ions $B_{10}H_{10}^{2-}$, $B_{10}Cl_{10}^{2-}$, $B_{10}Br_{10}^{2-}$ and $B_{12}Br_{12}^{2-}$, only the latter two yield complexes which are stable in air, while the others yield the octahedral cations $[Ni(CH_3CN)_6]^{2+}$ in solution.

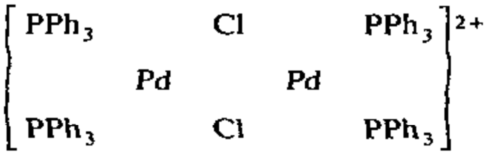
TABLE 1

Electronic spectral data [18]

System	Transitons		
	$^3A_{1g}-^3A_{2g}$	$^3A_{1g}-^3T_{1g}(F)$	$^3A_{1g}-^3T_{1g}(P)$
$NiB_{12}Cl_{12} \cdot 6CH_3CN$	11000	17500	28000
$NiB_{12}Br_{12} \cdot 7CH_3CN$	11000	17400	27300
$Ni^{2+}-CH_3CN-B_{12}H_{12}^{2-}$	10950	17800	27500
$Ni^{2+}-CH_3CN-B_{10}Cl_{10}^{2-}$	10400	16000	25800
$Ni^{2+}-CH_3CN-B_{10}Br_{10}^{2-}$	10500	15600	25400

C. PALLADIUM CLOSOBORATE COMPLEXES

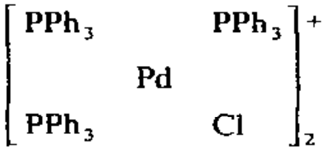
The platinum and palladium, complexes with two triphenylphosphine molecules, $M(PPh_3)_2Cl_2$ ($M = Pd, Pt$) have long been known. In 1971, Dixon and Hawke [5] used silver tetrafluoroborate in a reaction with $(PPh_3)_2PdCl_2$ to derive, with great difficulty, the cation **III**.



$$\left[\begin{array}{ccccc} PPh_3 & & Cl & & PPh_3 \\ & Pd & & Pd & \\ PPh_3 & & Cl & & PPh_3 \end{array}\right]^{2+}$$

III

The reaction proceeded in a dry inert atmosphere, the yield being 60% at most. We succeeded [6] in obtaining the same cation stabilized by closoborate anions in a single step by heating an aqueous solution of palladium chloride in $H_2B_nX_n$ ($n = 10, 12$; $X = Cl, Br$) with subsequent addition of triphenylphosphine. By changing the palladium to triphenylphosphine ratio in the reaction or by exposing **III** to triphenylphosphine, we derived a number of compounds containing a new cation (**IV**) in which three triphenylphosphine molecules are coordinated to palladium [6] (Fig. 2).



$$\left[\begin{array}{ccc} PPh_3 & & PPh_3 \\ & Pd & \\ PPh_3 & & Cl \end{array}\right]^{+}_{2}$$

IV

In the low-frequency region, the IR spectra of the complexes containing **III** are similar as are those of the complexes containing **IV**, but differences between the two series can be detected in both the number and position of the absorption bands. For example, in series **III**, the bands at 305–296 cm^{-1} (depending on the ion $B_nX_n^{2+}$), 275 and 218 cm^{-1} can be attributed to

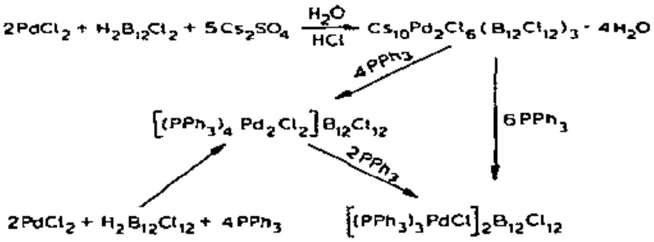


Fig. 2. Reaction sequence for reaction of triphenylphosphine palladium(II) complexes with closoborate anions.

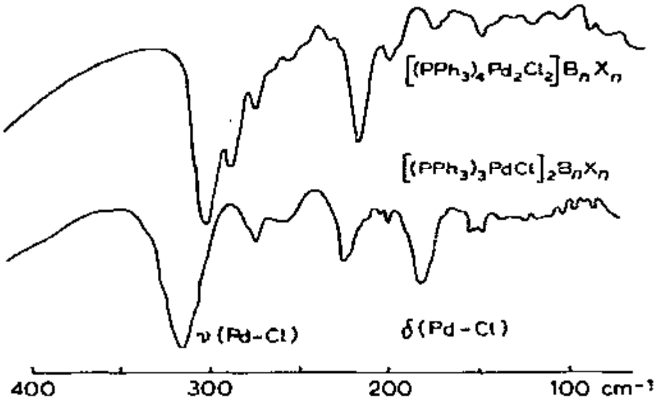


Fig. 3. Far-IR spectra of triphenylphosphine palladium(II) complexes with closoborate anions.

vibrations of the metal–chlorine bond, whereas in the IR spectra of series **IV** the absorption bands at 318–314 cm^{-1} correspond to the stretching vibrations [7] (Fig. 3).

Compounds of types **III** and **IV** are stable in air, the onset of thermal decomposition occurring at temperatures of 220 to 250°C. Molar conductivity studies confirm that complexes **III** are 1 : 1 electrolytes, while **IV** are 2 : 1 electrolytes. The position and shape of the IR bands corresponding to the borate anions in complexes **III** and **IV** do not undergo any significant changes relative to those of $Cs_2B_nX_n$ which confirms their inner-sphere position. This is also corroborated by ESCA data, since the energies of P $2p^{3/2}$, Pd $3d^{5/2}$, and B 1*s* almost coincide and lie within the limits known for complexes of palladium(II) and salts of borate ions with alkali metals *.

The results above clearly indicate that the use of polyhedral borate ions can, in some cases, stabilize the inner coordination sphere and, in other cases, the additional incorporation of, for example, triphenylphosphine into the inner coordination sphere, permits the direct synthesis of compounds with different properties to those already known. Complexes $[(PPh_3)_3PdCl]B_nX_n$, for example, catalyze hydrosilylation processes [20] in organic systems, on the one hand, and inhibit the activity of certain enzymes on the other, whereas the complex $(PPh_3)_2PdCl_2$ is inert in both cases [8].

However, the cation-stabilizing effect of closoborate anions may, in some cases, due to the introduction of additional ligands into the inner coordination sphere, lead to intraspheric electron-density redistribution in the central atom–ligand system and to labilization of the ligand. Evidence for this

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* A method for the synthesis of $[(PPh_3)_3PtCl]_2B_nX_n$ was published [19] during the preparation of this article.

phenomenon is found from a study of the interaction of π-allylpalladium chloride with $Ag_2B_{10}Br_{10}$ [9,10].

The reaction between $[(C_3H_5)PdCl]_2$ and $Ag_2B_{10}Br_{10}$ in the presence of nitriles makes it possible to incorporate two nitrogen-donor ligands into the inner coordination sphere in accordance with eqn. (2).

$$[(\eta^3\text{-}C_3H_5)PdCl]_2 + Ag_2B_{10}Br_{10} \xrightarrow{RCN} 2\,AgCl + [(\eta^3\text{-}C_3H_5)Pd(RCN)_2]_2B_{10}Br_{10} \qquad (2)$$

If $R = CH_3$, complexes **V**, $[(\eta^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10} \cdot C_6H_6$, and **VI**, $[(\eta^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}$ are formed, and if $R = C_6H_5$, complex **VII**, $[(\eta^3\text{-}C_3H_5)Pd(C_6H_5CN)_2]_2B_{10}Br_{10}$ results. The structure of these complexes was studied, using mainly **V** and **VI** as examples.

The molar conductivity of complex **V** and ESCA data show that it contains the cation $[(\eta^3\text{-}C_3H_5)Pd(CH_3CN)_2]^+$ and the anion $B_{10}Br_{10}^{2-}$. In the solid complex a benzene molecule is inserted between the cations and anions, i.e. in the crystal a system similar to the solvent-separated ionic pair is formed [9]. The benzene molecule can be removed by heating complex **V** at 90°C, as a result of which complex **VI** is formed, as verified by thermogravimetric data.

Benzene-free complex **VI** can also be obtained by recrystallization of complex **V** from a mixture of the same solvents but in the presence of heptane and by heating to 40–50°C.

Using benzonitrile yields the complex $[(\eta^3\text{-}C_3H_5)Pd(C_6H_5CN)_2]_2B_{10}Br_{10}$ (**VII**) from solution, which is much less stable than **VI**; this can be explained by a less pronounced donor capacity of benzonitrile than that of acetonitrile [11].

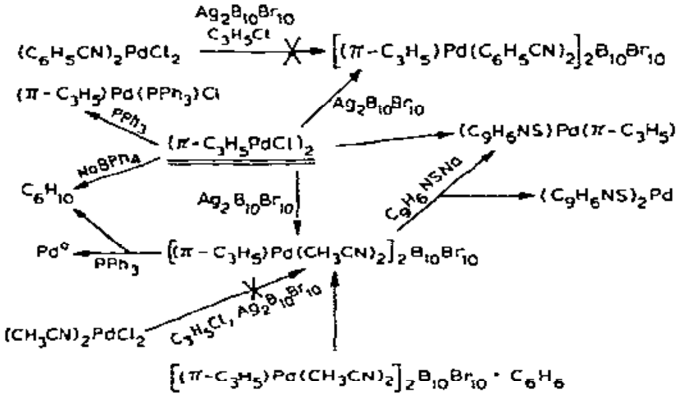

Fig. 4. Reaction sequence for η^3-allylpalladium chloride.

Attempts to synthesize complexes **V–VII** by reaction between *trans*-$(RCN)_2PdCl_2$ ($R = CH_3$, C_6H_5), allyl chloride and $Ag_2B_{10}Br_{10}$ in the presence of an appropriate nitrile were not successful (Fig. 4). Neither was it possible to introduce nitrile ligands into the inner coordination sphere of palladium by breaking the bridge bonds in the initial allyl compound through direct interaction with nitriles. Using other large anions, such as $B_{12}Br_{12}^{2-}$ or $B(C_6H_5)_4^-$, does not yield compounds of the types **V–VII** either. The tetraphenylborate anion leads to reduction of palladium(II) to palladium (0), as well as dimerization of the allyl radicals to hexa-1,5-diene.

Thus, for the first time in the chemistry of π-allyl compounds of palladium, two donor ligands have been introduced into the inner coordination sphere of palladium while retaining the allyl ligand.

It is known [12] that the effect of a strong donor ligand such as triphenylphosphine on $[(\eta^3\text{-}C_3H_5)PdCl]_2$ leads to the breaking of the chlorine bridges, yielding the complex $(\eta^3\text{-}C_3H_5)Pd(PPh_3)Cl$. The incorporation of a second triphenylphosphine molecule in the presence of an allyl ligand changes the bonding between the allyl ligand and the metal and can be accomplished only if $C_6F_5^-$ or $C_6HCl_4^-$ groups, instead of chlorine, are linked to palladium [13]. Substitution of both chlorine atoms by a chelate ligand, such as 8-mercaptoquinoline, strengthens the bond between palladium and the π-allyl group, which cannot then be displaced, even when this ligand is present in greater than ten-fold excess [14]. Hence, the allyl ligand remains unchanged in the inner coordination sphere [15].

It was of interest to determine whether saturation of the coordination sphere of palladium with nitrile ligands affects the properties of the complex as a whole or its reactivity determined by the strength of the metal–ligand bonds. For example, the effect of triphenylphosphine on complex **V** could lead to displacement of ligands from its inner coordination sphere. Through

TABLE 2

ESCA data (eV) for synthesized complexes and related compounds

Compound	Pd $3d^{5/2}$	$N\ 1_s$	Cl $2p^{3/2}$
$(\eta^3\text{-}C_3H_5)Pd(PPh_3)Cl$	337.9	–	198.0
$[(\eta^3\text{-}C_3H_5)PdCl]_2$	337.6	–	198.8
$[(\eta^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}\cdot C_6H_6$	338.1	400.5	–
$(CH_3CN)_2PdCl_2$	338.9	400.3	–
$[(\eta^3\text{-}C_3H_5)Pd(C_6H_5Cn)_2]_2\cdot B_{10}Br_{10}$	338.1	400.0	–
$(C_6H_5CN)_2PdCl_2$	338.6	400.2	–
$(\eta^3\text{-}C_3H_5)Pd(C_9H_6NS)$	337.6	400.1	–
$Pd(C_9H_6NS)_2$	337.9	400.1	–

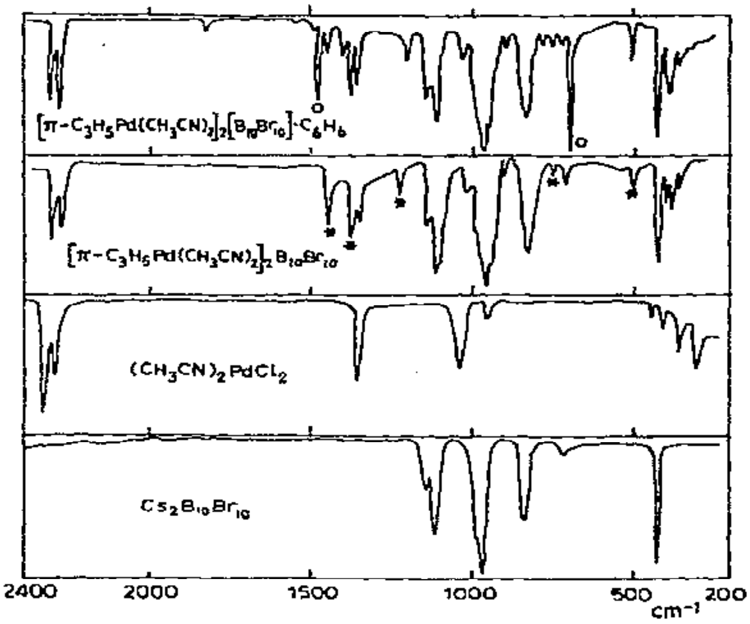

Fig. 5. IR spectra of acetonitrile complexes and related compounds.

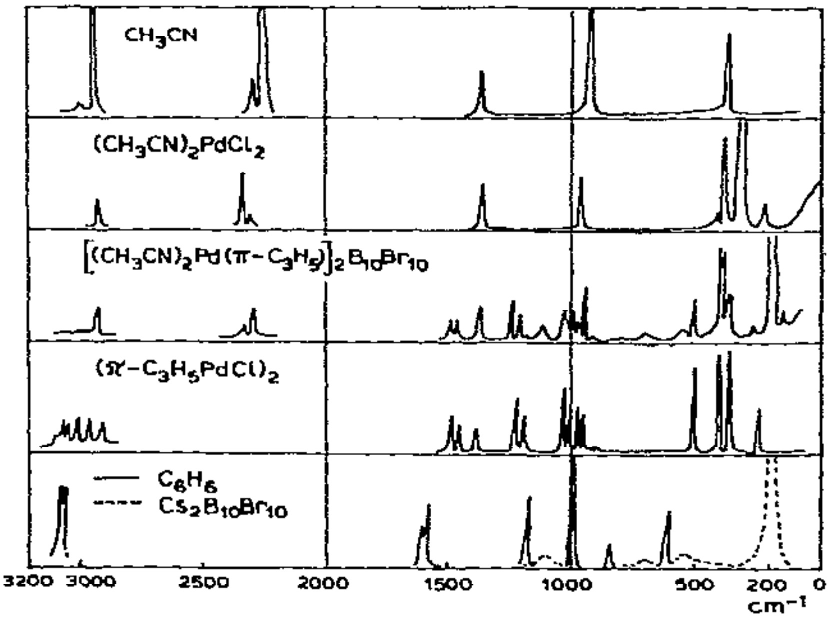

Fig. 6. Raman spectra of acetonitrile complexes and related compounds.

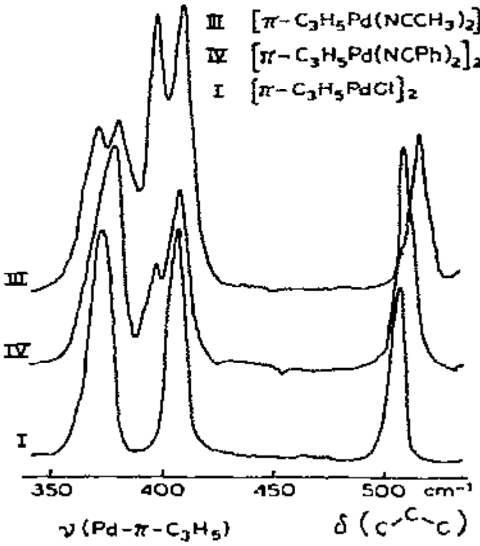

Fig. 7. Raman spectra of η^3-allyl complexes in the region of the ν(Pd–allyl) and δ(C$\overset{\frown}{=}$C$\overset{\frown}{=}$C) vibrations.

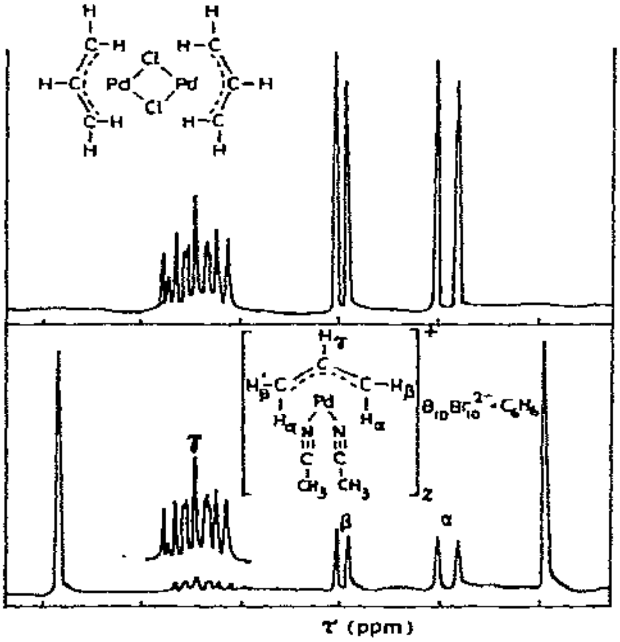

Fig. 8. ^{1}H NMR spectra of η^3-allyl complexes.

this reaction we obtained hexa-1,5-diene as the result of displacement of the allyl ligand and its subsequent dimerization. Thus, in the presence of two donor ligands, labilization of the allyl ligand occurs. The use of a chelate ligand such as 8-mercaptoquinoline has shown that the nitriles are substituted first, followed by the allyl ligand. Hence, it is desirable to know what causes such lability and how the electron-density distribution in the η^3-allylpalladium system changes in the presence of two donor ligands.

The ESCA data of the appropriate compounds clearly indicate the redistribution of the electron density in the metal–allyl system when two donor ligands are present. For example, the value of Pd $3d^{5/2}$ for **V** and **VI** is 0.5 eV higher than that for $[(\eta^3\text{-}C_3H_5)PdCl]_2$; i.e. when acceptor ligands, or chlorine atoms, are replaced by acetonitrile donor ligands, the electron density at the palladium atom decreases rather than increases (Table 2).

From Raman spectral identification of the π-allyl ligand (the set of lines representative of π-allyl ligands bonded to palladium appearing at 513, four lines in the range 950–1030, 1208, 1238, 1468 and 1495 cm^{-1}), the frequen-

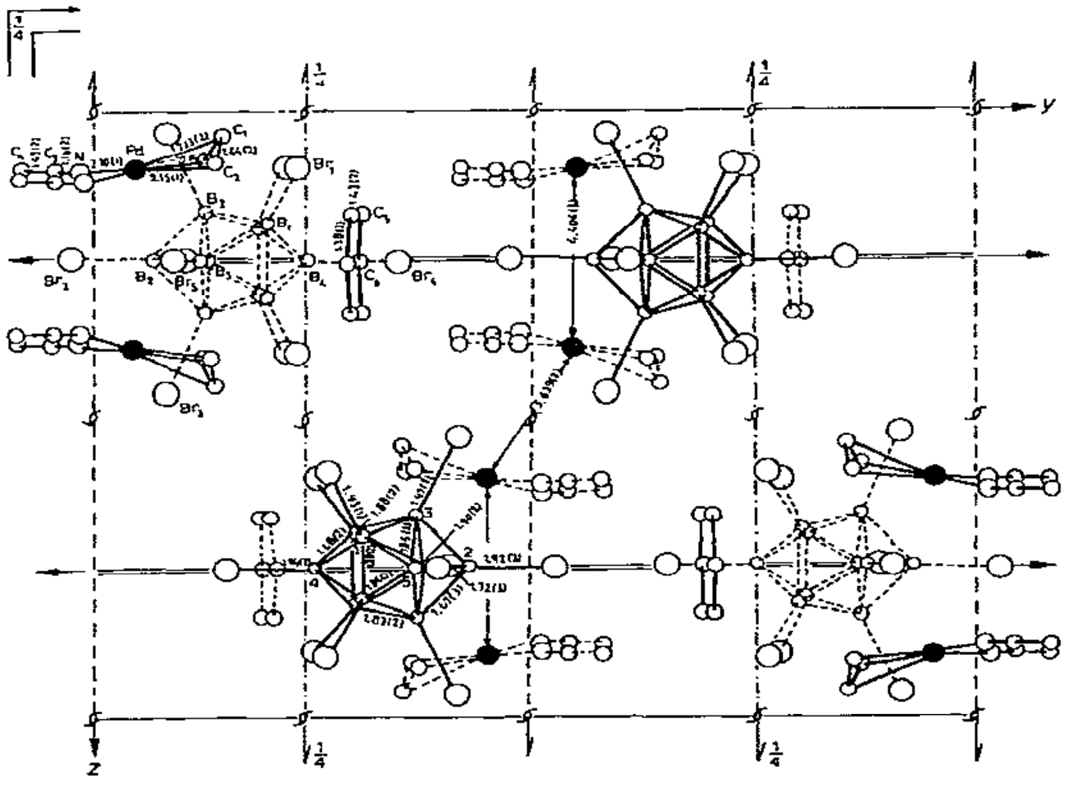

Fig. 9. Crystal structure of $[(\eta^3\text{-}C_3H_5)Pd(CH_3CN)_2]_2B_{10}Br_{10}\cdot C_6H_6$.

cies of which coincide within 10 cm^{-1} with those observed in the Raman spectrum of $[(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{PdCl}]_2$, one can infer that the vibrational spectrum of the π-allyl ligand in complexes **V**, **VI** and **VII** is identical with that in $[(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{PdCl}]_2$ (Figs. 5–7). Analysis of the ^{1}H NMR spectrum of **V** also indicates that the allyl ligand in this complex is unchanged (Fig. 8).

It was established earlier by quantum chemical calculations and ESCA measurements, that the major role in metal–allyl bonding is played by σ donation of electrons from the ligand to the metal [16,17]. It should be noted for comparison that in the metal–olefin bond the major contribution is from back-donation of the electron from the metal to the ligand. The decrease in electron density at the central atom in complexes **V** and **VII**, together with the invariant vibrational frequencies of the π-allyl ligand and taking into account the data of ref. 17, is indicative either of the σ-donor properties of the π-allyl ligand becoming less pronounced or of an increase in its π-acceptor properties. If the back-donation of electrons from the metal had been to the antibonding orbital of the ligand, the frequency $\nu(\mathrm{C}\overset{\mathrm{C}}{\underset{\mathrm{Pd}}{\cdots}}\mathrm{C})$ would have decreased and $\delta(\mathrm{C}\overset{\mathrm{C}}{\cdots}\mathrm{C})$ would have increased, but this was not observed (Fig. 7).

Thus, the presence of two donor ligands in the inner coordination sphere of palladium presents a situation where the transfer of electrons from the allyl ligand to the metal is strained and the Pd–allyl bond is weakened, which manifests itself in varying reactivity of the complex.

In order to determine whether these variations affect the structure of the ligand or the complex as a whole, an X-ray single-crystal investigation of $[(\eta^3\text{-}\mathrm{C_3H_5})\mathrm{Pd(CH_3CN)_2}]_2\mathrm{B_{10}Br_{10}}\cdot\mathrm{C_6H_6}$ was carried out. The results indicate that the Pd–C(allyl) distances are conventional, but that the carbon–carbon distance, 1.44(2) Å, is longer than usual (1.36–1.38 Å).

In conclusion, the above examples clearly indicate the scope of such ligands as closoborates in the synthesis of novel coordination compounds, the stabilization of intermediate products and in the investigation of reaction mechanisms.

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