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ON THE STRUCTURE OF Pd, Pt AND Rh COMPLEXES WITH 1,5-HEXADIENE

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Summary

A number of halogen complexes of Pd, Pt and Rh with 1,5-hexadiene have been synthesized; three of them, $C_6H_{10}PdBr_2$, $C_6H_{10}PtBr_2$ and $(C_6H_{10}RhCl)_2$, for the first time. An intermediate while preparing $C_6H_{10}PdCl_2$ was the polynuclear polymeric moiety $[C_6H_{10}(PdCl_2)_4]_n$. IR, Raman and ESCA spectroscopy show that the diallylic ligand in all the complexes has the *cis*-configuration and that the strength of the metal—diallyl bond increases in the series Pd < Pt < Rh.

Introduction

In spite of the fact that the first complexes of Pt and Pd with diallyl were synthesized about 20 years ago [1], their structure and properties have not yet been investigated in detail. This investigation deals with the question what happens to the olefinic ligand on coordination with a metal atom.

According to vibrational spectroscopic data [2], the "free" diallyl exists as an equilibrium mixture of *trans* and *gauche* conformers. If diallyl acts as a bidentate ligand, a certain tightening of double bonds will take place on coordination, which necessarily leads to a change of the molecular geometry. In fact, X-ray investigation of the complex $C_6H_{10}PdCl_2$ (Ia), obtained by one of us from the unusual reaction of allyl chloride with bis(benzonitrile)palladium chloride [3], revealed the *cis*-configuration of the ligand in this molecule, the central C_3—C_4 bond (Fig. 1) being 0.1 Å shorter than the normal single bond. The results of NMR study of Ia [3] and $C_6H_{10}PtCl_2$ [4], which show the equivalence of the two $=CH_2$ groups in these complexes, are in agreement with the X-ray data.

The compounds of analogous composition $C_6H_{10}PdCl_2$ (II), $C_6H_{10}PtCl_2$ (III) and $C_6H_{10}PtI_2$ (IV) were synthesized by Jensen [1] from diallyl. Hendra

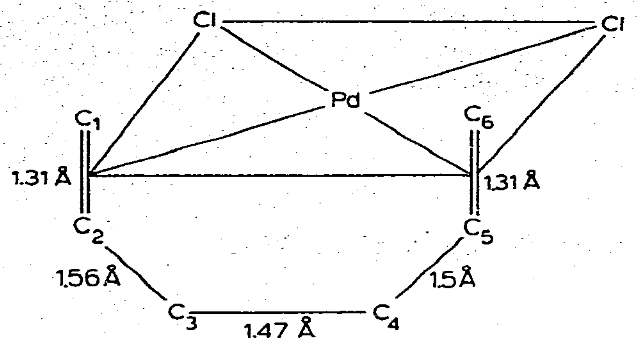


Fig. 1. The structure of $C_6H_{10}PdCl_2$ (Ia) from ref. 3.

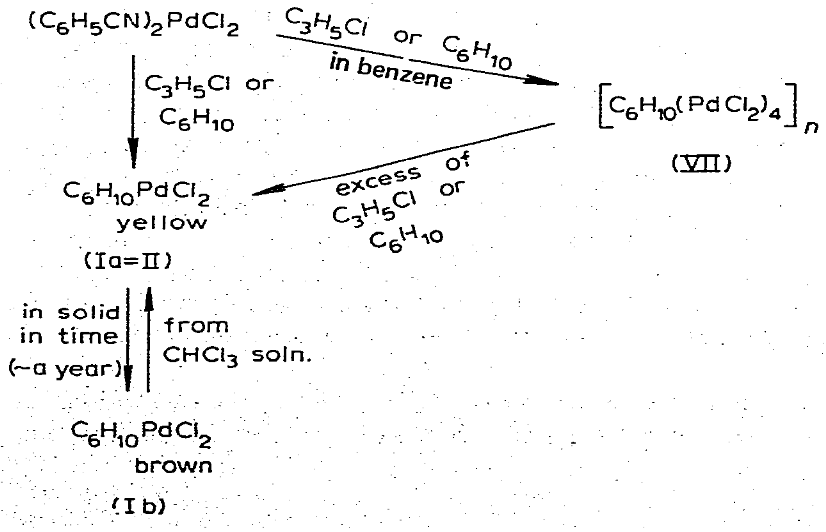
and Powell [5] have assigned the *gauche*-configuration to these complexes on the basis of the non-equivalence of $=CH_2$ groups in the PMR spectrum of IV, and Nakamoto [6] agreed with this point of view. In order to test this conclusion and to investigate in detail the structure and mutual influence of the ligand and the metal atom in diallylic complexes of Pd, Pt and Rh, we have undertaken the study of vibrational and ESCA spectra of I—IV, and also the spectra of the new compounds $C_6H_{10}PdBr_2$ (V), $C_6H_{10}PtBr_2$ (VI), $[C_6H_{10}(PdCl_2)_4]_n$ (VII), and $(C_6H_{10}RhCl)_2$ (VIII).

Results and discussion

As a starting point we considered the spectra of Ia in which the *cis*-configuration of the ligand had been reliably proved. Description of synthetic and spectral methods is given in the experimental section.

In the course of the synthesis of the complex II an intermediate $[C_6H_{10}(PdCl_2)_4]_n$ was isolated, which had been overlooked by the previous authors [1], and was found to be identical to the intermediate VII, obtained previously while preparing Ia [3]. The interaction of both these compounds with diallyl or allyl chloride was shown to give a monomeric diallylic complex Ia or II (Scheme 1), via the polymeric species which later was cleaved at the bridging Pd—Cl bonds.

SCHEME 1. SYNTHESIS OF THE Pd COMPLEXES



Under long-term storage in a sealed ampule at room temperature yellow Ia gradually turns into brown Ib without change in its composition or visible destruction of the monocrystal. We succeeded in obtaining only a few reflections on the roentgenogram of the monocrystal Ib, which rapidly decomposed. Attempts to recrystallize Ib from its chloroform solution lead only to Ia. Thermal decomposition of Ib (with diallyl separation as the first stage) was found to begin 20° higher than that of Ia.

The structure of the ligand in the complexes

The vibrational spectra of 1,5-hexadiene have been studied in detail [2, 9]. Comparison with the IR and Raman spectra of Ia shows the complication of the latter (Figs. 2, 3 and Table 1).

In the spectra of solid Ia the splitting of several bands is observed, which (at least for some of them: $\approx$ 1540, $\approx$ 1000 cm^{-1}) does not disappear in the solution spectra. The so-called "C=C stretching" vibration of diallyl is at 1642 cm^{-1} , but in the spectra of Ia there are no bands in this region. However, there is a doublet $\approx$ 1540/1530 cm^{-1} of medium strong intensity in the IR and Raman spectra. From the IR spectrum of Ia in $CDCl_3$ solution it is obvious that the splitting of this band cannot be explained by crystal effects. It is natural to assign these frequencies to symmetrical and asymmetrical modes [$\nu(C=C)_s$ and $\nu(C=C)_{as}$], in which the stretching vibration of coordinated double bonds takes a prominent part (the point group of the molecule Ia is C_s). The assignment of ν(C=C) vibration in the spectra of olefinic complexes of Pd and Pt has till recently been a point of dissent. Most investigators [10—13] were of the opinion that the lowering of ν(C=C) on coordination to a transition metal atom is about

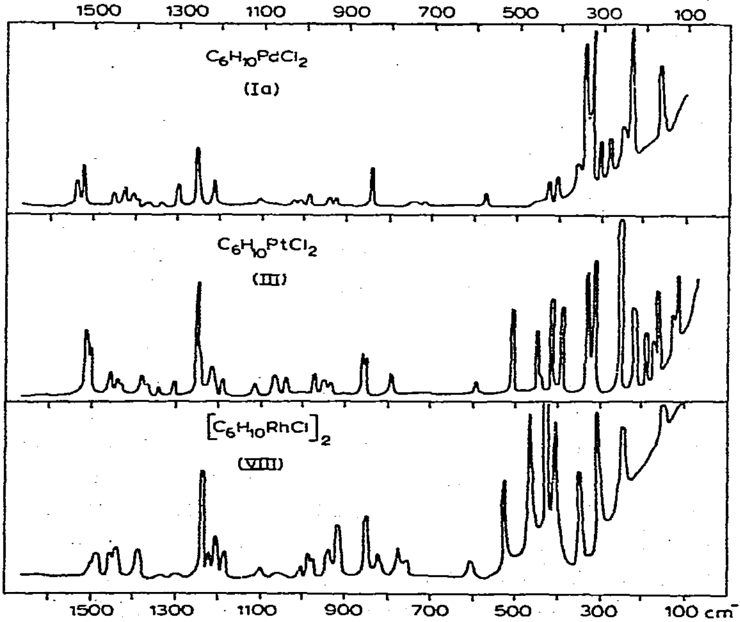


Fig. 2. The Raman spectra of the diallylic complexes of Pd, Pt and Rh.

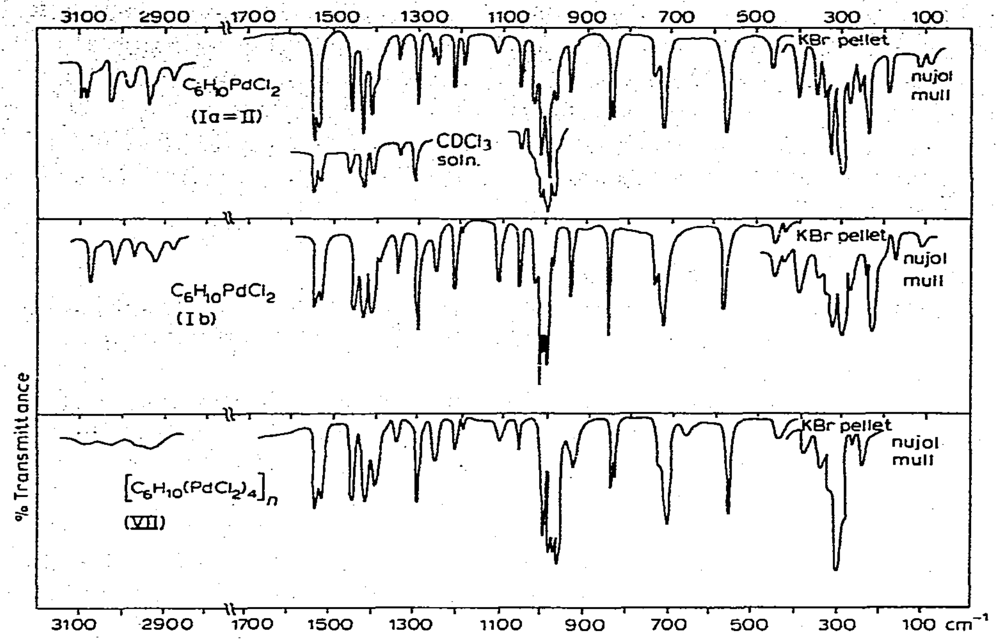


Fig. 3. The IR spectra of the diallylic complexes of Pd.

100—150 cm^{-1} and the corresponding band is situated near 1500 cm^{-1}. However, Babushkin et al. [14], assigned this band to a CH deformation, based on an examination of the previous data and on the results of a normal coordinate analysis for a fragment $(CH_2)_2Pt$; they were of the opinion that the olefinic complexes of Pt have a three-membered ring structure. Later Hiraishi [15] succeeded in recording the Raman spectrum of Zeise's salt and assigned the weak line ≈ 1500 cm^{-1} to CH deformation [β(=CH)], and the strong line ≈ 1240 cm^{-1} to ν(C=C). Hiraishi et al. took this to be true also for complexes of Pt with 2-butene [16]. However, in a recently published work [17] Powell, Scott and Sheppard have compared the IR and Raman spectra of Pd and Ag complexes with the same olefinic ligands and have shown that both vibrations (≈ 1500 cm^{-1} — "band (i)" and ≈ 1250 cm^{-1} — "band (ii)") have a complicated origin, C=C stretching and CH deformation being strongly coupled. If the ligand is a substituted ethylene, then band (i) is predominantly due to ν(C=C) and band (ii) to β(=CH).

The results presented here and our data for norbornadiene complexes [18] are in agreement with this point of view. In the Raman spectra obtained for all the diallylic complexes one can also see band (ii), an intense line at ≈ 1250 cm^{-1}.

In the low frequency region the spectrum of Ia is very rich. From a comparison with the spectrum of V it is obvious that the bands at 305 and 330 cm^{-1} are related to the Pd—Cl stretching vibrations [ν(Pd—Cl)]. The bands in the region of 340—500 cm^{-1}, which may correspond to Pd—C stretches, are less intense in Raman than ν(Pd—Cl); an analogous picture is observed in the Raman spectrum of Zeise's salt [15], in contrast to the case of π-allylpalladium halides [19, 20].

TABLE 1

VIBRATIONAL SPECTRA OF DIALLYLIC COMPLEXES Ia, Ib, V AND VII OF Pd

$C_6H_{10}PdCl_2$ (Ia = II)			$C_6H_{10}PdCl_2$ (Ib)	$C_6H_{10}PdBr_2$ (V)	$[C_6H_{10}(PdCl_2)_4]n$ (VII)
Raman solid	IR solid	IR $CDCl_3$ soln.	IR solid	IR solid	IR solid
	92 w				
	116 w		114 w		
167 m			177 w		
	194 m				196 w
236 s	239 s		238 s		
252 vw	253 m		248 w		240 m
284 w	281 m		286 m	280 } vs	281 w
				290	
305 w	304 vs		306 vs		305 (sh)
328 vs	332 s		331 s		320 vs
343 vs	342 (sh)		344 (sh)	350 vw	336 (sh)
361 vw	361 w		360 (sh)	362 vw	363 w
405 w	402 m		403 m	398 w	398 w
435 w			440 w	440 vw	
457 vw	466 w		466 m	470 w (br.)	461 vw
				540 w	
577 w	575 s		582 s	578 m	575 m
					674 m
				713 m	719 m
723 w	724 m		727 s	735 (sh)	
743 vw	745 w		742 (sh)		737 (sh)
843 (sh)	843 } m				841 } m
848 w	849		851 s	847 s	849
931 w					938 (sh)
942 w	947 m		945 m	944 m	945 w
	978 (sh)	985 s	984 (sh)	987 vs	980 s
994 w	996 vs	1000 vs	1001 vs	1002 s	990 (sh)
					999 (sh)
1015 w	1015 s	1012 s	1010 s	1010 vs	1014 s
			1019 vs	1020 (sh)	
1023 w	1028 (sh)	1020 (sh)	1028 (sh)		
	1063 m		1067 m	1064 w	1065 m
1110 w	1115 w		1114 m	1116 w	1115 w
	1194 w		1199 vw		1199 w
1213 w	1213 m		1218 m	1215 w	1219 m
1257 m	1258 w		1260 w	1259 w	1265 w
	1267 (sh)				
1301 w	1302 m	1310 m	1304 s	1306 m	1308 s
1345 w	1349 w	1353 w	1350 w		1355 w
1371 vw					
1394 vw	1397 (sh)		1396 vw	1400 (sh)	
1403 w	1410 m	1410 m	1408 m	1407 m	1408 m
1428 w	1433 m	1435 m	1431 m	1429 m	1427 m
1449 w	1460 m	1465 m	1455 m		1460 m
1526 m	1532 m	1533 m	1531 m	1533 m	1529 m
1541 m	1544 m	1550 m	1545 m	1546 m	1543 m

The IR spectrum of Ib in all its main features coincides with the spectrum of Ia. The only difference is in the relative intensities of the components of multiple bands. Thus we conclude, that the compound Ia, crystallizing from the solution, is a metastable crystal modification, which gradually turns into the thermodynamically stable form Ib. Our attempts to determine the effect of the phase transition by DTA were unsuccessful because of the slow rate of the process.

Unexpectedly, the spectrum of II was found to coincide completely with that of Ia, indicating the full identity of II and Ia. Therefore, the ligand in the compound $C_6H_{10}PdCl_2$ has the *cis*-configuration irrespective of the method of preparation of the complex.

In the IR spectrum of V, in the low frequency region there is a very strong broad band 280—290 cm^{-1} corresponding to ν(Pd—Br). The region of 500—1600 cm^{-1}, where the vibrations of the ligand are found, is practically the same as for Ib, which indicates a similar structure of the ligand in Ib and V.

Thus, the conclusion of Hendra and Powell [5] about the *gauche* configuration of diallyl in the complexes of Pd seems to be erroneous. The same structure was proposed by them for the analogous complexes of Pt. As has already been mentioned, this conclusion was based on the non-equivalence of two $=CH_2$ groups in the PMR spectrum of IV. But one cannot find any characteristics of the PMR spectrum of the unstable and poorly soluble complex IV in the original article. The conclusion was then applied by the authors to the compounds II and III on the basis of the similarity of the region 700—1700 cm^{-1} in their IR spectra. However, the PMR spectrum of III, obtained by Cramer [4] is similar to that of Ia [3], which is indicative of the *cis*-configuration of the ligand in III.

We have studied the vibrational spectra of three platinum complexes III, IV and VI (see Fig. 2, Table 2). The whole pattern of IR and Raman spectra of the Pt compounds in the region of the ligand vibrations is analogous to the spectra of Ia. This fact together with Cramer's data permit us to consider the ligand in all complexes of Pt as having the *cis* configuration. In the spectrum of III the frequencies of the Raman doublet, corresponding to ν(C=C), 1505 and 1510 cm^{-1}, are somewhat lower than those of Ia and the splitting between the components became smaller. In the IR spectrum this doublet shows itself as an intensive band at 1512 cm^{-1} with a shoulder at the low frequency side. The frequency of band (ii) is 1252 cm^{-1}, nearly the same as for Ia. In the low frequency region of the Raman spectra of III and IV, unlike to Ia and Zeise's salt, the presence of many strong lines is striking. A comparison of the spectra of III, IV and VI permits us to assign the frequencies 316 and 337 cm^{-1} in the spectra of III to the stretches ν(Pt—Cl), 224 and 214 cm^{-1} in VI to ν(Pt—Br), and 174 cm^{-1} in IV to ν(Pt—I). The bands of Pt—C vibrations are situated in the region of 350—500 cm^{-1}.

The IR and Raman spectra of $(C_6H_{10}RhCl)_2$ (VIII) are given in Fig. 2 and Table 2. The pattern of the ligand spectrum in this case is the same as that for Pd and Pt compounds studied, but the frequencies are somewhat lowered. In particular, the ν(C=C) doublet has the frequencies 1488 and 1505 cm^{-1}, and band (ii) at 1240 cm^{-1}. The strong Raman lines in the region of 350—500 cm^{-1} seem to correspond to ν(Rh—C), and in the region of 250—350 cm^{-1} to ν(Rh—Cl).

On the strength of metal—1,5-hexadiene bond

An attempt is made here to find a relation between the changes observed in the ligand spectra on π-complex formation, the changes in the electron density on the metal atom and the thermal stability of the complex. Using the criterion of Powell, Scott and Sheppard [17], who proposed to consider the summed percentage lowerings of the frequencies of ν(C=C) and β(=CH) in the spectrum

TABLE 2

VIBRATIONAL SPECTRA OF DIALLYLIC COMPLEXES III, VI AND IV OF Pt, AND OF $(C_6H_{10}RhCl)_2$

$C_6H_{10}PtCl_2$ (III)		$C_6H_{10}PtBr_2$ (VI)		$C_6H_{10}PtI_2$ (IV)	$(C_6H_{10}RhCl)_2$ (VIII)	
Raman	IR	Raman	IR	IR	Raman	IR
127 m				137 m	150 s	
			148 w			
171 m				174 s		
199 m			190 m (br)	190 w		
		214 vs	214 m			
228 m		224 vs	224 m			
261 vs	262 s	268 vs	266 w	253 m	256 s	258 s
314 vs	318 vs	315 vs	317 vw	320 vw	314 vs	315 w
334 vs	340 vs					
	363 w		365 w	365 w	353 s	360 w
387 s	390 s	384 vs	380 w			398 m
414 s	418 m	407 vs	408 m	400 m	410 vs	412 m
447 m	450 vw	437 vs	443 vw	442 w	434 vs	436 w
		446 (sh)			468 vs	456 w
508 m	512 s	506 s	507 m			510 m
					529 m	527 w
			593 m	589 m	601 w	594 m
			620 vw			
				758 s	756 vw	742 m
793 w	780 s	788 w	774 s	780 (sh)	776 w	762 w
	797 (sh)					
					828 w	832 w
840 w	845 m		845 w	840 (sh)	851 m	848 vs
856 } m	862 (sh)	861 vs	863 s	856 } s		
860	866 s			860		
		912 w				908 (sh)
932 vw	935 (sh)	938 w	943 m	938 s	920 m	918 s
940 w	945 s				943 w	937 m
976 w	978 w		977 w	981	974 vw	961 (sh)
			999 (sh)	998 } s	985 w	969 s
		1003 w	1009 vs	1010	1005 vw	1001 w
1015 w	1015 vs		1023 s			
1026 w	1030 s	1030 w	1037 w			
1038 w	1042 (sh)					
1068 w	1070 m		1070 m	1068 w	1061 vw	1061 w
1115 w	1119 s		1118 s	1108 m	1108 vw	1108 s
1192 w	1196 m	1192 w	1195 w	1190 w	1185 w	1185 w
1218 m (br.)	1220 m	1218 m	1221 m	1216 w	1207 w	1206 m
					1227 w	1231 } m
1252 s (br.)	1250 } m	1252 vs	1250 } w	1255 w	1245 s	1238
	1258		1258			
1306 w	1308 s	1307 w	1309 s	1310 s	1301 vw	1302 s
1347 vw	1348 m	1362 w	1350 s	1349 w	1335 vw	1330 m
						1340 m
1402 w	1406 s	1405 m	1403 s	1401 m	1389 w	1389 s
1437 w	1437 (sh)	1425 m	1428 (sh)	1420 } m		1420 (sh)
				1428	1439 w	1432 s
1460 w	1462 m	1465 w	1462 m	1460 m	1452 w	1452 } s
1505 m	1507 (sh)	1510 w	1513 m	1510 m	1490 w	1455
						1488 (sh)
1510 m	1516 s					1505 s

of coordinated olefin (compared to a "free" molecule) as a measure of perturbation of the olefin molecule on coordination, we have obtained for the Pd complex the value 9.5%, for Pt 11.6%, and for Rh 13.6% (Table 3). These results are in agreement with the data [21] for 1,5-cyclooctadiene complexes with the same metals and with the usually accepted views about the increasing ability of

TABLE 3

SUMMED PERCENTAGE LOWERINGS OF ν(C=C), THE CHANGES IN ELECTRONIC DENSITY ON THE METAL (ESCA DATA) AND THE DECOMPOSITION TEMPERATURES OF THE DIALLYL COMPLEXES

Complex	Summed lowering of ν(C=C) (%)	ΔE (eV)	Decomp. Temp. (°C)
$C_6H_{10}PdCl_2$	9.5	+0.4	100
$C_6H_{10}PtCl_2$	11.6	+1.5	180
$(C_6H_{10}RhCl)_2$	13.6		160

the metal atoms with d^8 configuration to overlap the π-orbitals of the olefin in a series $Pd^{II} < Pt^{II} < Rh^{I}$.

Modern theoretical ideas about M—olefin bonding based on the Dewar [22] and Chatt and Duncanson [10] scheme, involve two types of interaction: 1, σ-bonding between the filled π orbital of the olefinic ligand and the vacant hybrid orbital of the metal atom, and 2, π-bonding between the filled d-orbitals of the metal atom and the antibonding π^* orbital of the olefin. According to refs. 23 and 24, the lowering of the stretching frequency of carbon—carbon multiple bond on complex formation is mainly due to the second type of interaction (so-called "back donation"). Hence, it follows that the contribution of the back donation for the complexes studied also increases along the series mentioned above. The ESCA results for the compounds of Pd and Pt confirm this conclusion: on going from the complex K_2MCl_4 to $C_6H_{10}MCl_2$, ΔE for the metal atom is +0.4 eV for M = Pd and +1.5 eV for M = Pt (Table 3), i.e. the electron density decreases for both metals, but for Pt the effect is more pronounced than for Pd. Since the partial contribution of Cl atoms into the summed electron density on the metal atom is the same for the complexes of Pd and Pt [8], it can be said that the observed difference in ΔE values may be explained by the greater ability of Pt atom to participate in back donation. All this must lead to greater thermal stability of Pt complex compared to Pd. In fact, the temperature of decomposition of $C_6H_{10}PtCl_2$ (measured by DTA), is 180°, and of $C_6H_{10}PdCl_2$ is 100° *.

From the ESCA results (Table 4), it follows that the distribution of electron density between the ligands (diallyl and chlorine atoms) in $C_6H_{10}MCl_2$ depends on M. The electron density on Cl atoms for the compounds of Pd and Pt is approximately the same ($\approx$ 199 eV). But one can see that on going from K_2MCl_4 to $C_6H_{10}MCl_2$ the electron density has a tendency to increase if M is Pd and to decrease if M is Pt. This means that for the Pd complex a transfer of electronic charge from metal to chlorine, but for the Pt complex the reverse transfer from chlorine to metal, may take place.

When comparing the vibrational spectra of Pt compounds III, IV and VI, one can see that the frequencies of the ligand vibrations depend very little on the nature of the halogen. Thus, the change in electron density of the ligand on coordination is nearly equal for all three complexes. From this together

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* The temperature of decomposition of $(C_6H_{10}RhCl)_2$ is 160°, but it is obvious that this value cannot be compared to those given above because of the different oxidation states of the metal atoms and in view of the dimeric structure of VIII.

TABLE 4

THE CHANGES IN BONDING ENERGY (eV) ON GOING FROM K_2MCl_4 TO $C_6H_{10}MCl_2$ (ESCA DATA)

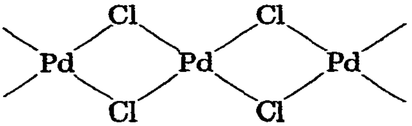
	Pd 3*d*	Cl 2*p*		Pt 4*f*	Cl 2*p*
K_2PdCl_4	338.4	199.0	K_2PtCl_4	73.1	198.9
$C_6H_{10}PdCl_2$	338.8	198.8	$C_6H_{10}PtCl_2$	74.6	199.2
ΔE	+0.4	−0.2		+1.5	+0.3

with the data given in Table 5, it follows that the electron density on the Pt atom remains practically constant on going from the chlorine complex to its bromine and iodine analogues.

On the structure of the intermediate $[C_6H_{10}(PdCl_2)_4]_n$

An interesting but not yet fully resolved problem is the structure of the complex VII, an intermediate formed in the course of the synthesis of the mononuclear complex Ia = II. An erroneous formula $C_3H_6(PdCl_2)_2$ was assigned to this compound previously [3]. But the synthesis of the same intermediate by the reaction with diallyl suggests the presence of the diallylic ligand in VII. The fact that grinding VII (in preparation for recording an IR spectrum) causes decay of the complex with the formation of "free" diallyl (see Experimental) cannot serve as unambiguous evidence for the presence of diallylic ligand. For instance, the decomposition of bis(π-allyl)nickel also leads to diallyl [25], which is absent in the compound itself. Similarly, VII might contain also a π-allylic ligand. However, the IR spectrum of VII in the region of 700—1600 cm^{-1} (Fig. 3, Table 1) does not show the π-allylic bands and is analogous to the spectrum of Ia, differing from the latter only in minor changes in relative intensity of the components of multiple bands. Hence, it can be concluded that the complex VII contains the diallylic ligand in *cis*-configuration.

From the empirical formula it follows that VII must contain also the bridged moiety:



As the data of refs. 7 and 8 show, the presence of bridging halogen atoms leads to an increase of electron density on the Pd atoms. One might think that if such fragments are present in the molecule along with diallylic ligand, two signals would appear in the ESCA spectrum, corresponding to the two different metal

TABLE 5

Pt 4*f* BONDING ENERGIES (eV) FOR DIALLYLPLATINUM COMPLEXES (ESCA DATA)

	Pt 4*f*
$C_6H_{10}PtCl_2$	74.6
$C_6H_{10}PtBr_2$	74.5
$C_6H_{10}PtI_2$	74.4

TABLE 6

Pd 3*d* AND Cl 2*p* BONDING ENERGIES (eV) FOR MONO- AND POLYMERIC Pd COMPLEXES

Complex	Pd 3*d*	Cl 2*p*
K_2PdCl_4	338.4	199.0
$C_6H_{10}PdCl_2$	338.8	198.8
$(PdCl_2)_n$	338.0	199.1
$[C_6H_{10}(PdCl_2)_4]_n$	338.5	199.5

atoms, as in the case for the pink form of Magnus salt [8]. However, there is no broadening of the Pd 3*d* or Cl 2*p* lines, i.e. either Pd or Cl atoms in this complex have only one energetic characteristic. The reasons for this equalizing are not yet clear. The very high value of Cl 2*p* level energy is striking in this spectrum (Table 6). This agrees to some extent with unusual Pd—Cl stretching frequencies for VII. In spite of the fact that in Ia the chlorine atoms are terminal while in VII bridged, the Pd—Cl stretching frequencies lie in the same region of the spectrum, 300—330 cm^{-1}, although we realize that strict comparison may be made only in terms of the force constants of Pd—Cl bonds rather that the IR frequencies of these vibrations.

Such a high value of Cl 2*p* energy level in VII and therefore the decrease in electron density on chlorine atoms is indicative of some additional interactions in the molecule of this polymeric moiety. The results on the thermal stability of VII are in accordance with this hypothesis: the temperature of decomposition of VII increases by 30° over that of Ia. The decay of VII takes place as a simultaneous destruction of the whole molecule rather than a loss of diallyl molecule as the first stage, as in Ia.

Experimental

The IR spectra in the region of 60—4000 cm^{-1} were obtained using UR-20, Perkin—Elmer 457 and FIS-1 spectrophotometers. While preparing samples for IR spectra (during the grinding with KBr, KI or nujol) some of the complexes were found to decompose with the isolation of "free" diallyl, which was easily identified in the spectrum of the pellet or mull. An analogous decomposition took place also in the laser beam during the registration of Raman spectrum, so practice was required before reproducible results were obtainable.

The Raman spectra of solids and CH_2Cl_2 solutions were obtained using a Coderg PH-O and a modified DFS-12 spectrometers equipped with He—Ne lasers of ~ 20 mW. We succeeded in obtaining good Raman spectra only for Ia, II, III, VI and VIII, the other complexes being too unstable in the laser beam.

The ESCA results, mentioned here, were kindly supplied to us by the ESCA group of the Institute of General and Inorganic Chemistry. The spectra were obtained with a Varian VIEE-15 according to a published procedure [7, 8]. The reproducibility of the position of the energy maxima was estimated as 0.1 to 0.2 eV. The compounds II—IV were prepared according to the method given in ref. 1, the complex Ia according to that described in ref. 3.

Preparation of $C_6H_{10}PdBr_2$ *(V)*

Bis(benzonitrile)palladium bromide (0.1 g) was treated with diallyl (2 ml). No solvent was required in this process. The reaction mixture was kept at —10° for 15 h. The dark red crystals of $C_6H_{10}PdBr_2$ were filtered off, washed with cold diallyl, then dried in vacuo. The complex is unstable and readily decomposes in organic solvents and when kept in the air or warmed. Analysis found: C, 21.04; H, 3.20; Br, 45.37; Pd, 30.02. $C_6H_{10}PdBr_2$ calcd.: C, 20.68; H, 2.89; Br, 45.88; Pd, 30.54%.

Preparation of $C_6H_{10}PtBr_2$ *(VI)*

Potassium tetrabromoplatinate (1.45 g) was dissolved in 20 ml of water and filtered. The solution was then treated with diallyl (1 ml). After 5—6 h at 0° yellow-pink crystals were formed, which were separated by filtration, washed with ethanol, ethyl ether, and recrystallized from chloroform and dried in vacuo. Analysis found: C, 16.20; H, 2.64; Br, 36.28; Pt, 44.20. $C_6H_{10}PtBr_2$ calcd.: C, 16.49; H, 2.31; Br, 36.57; Pt, 44.64%.

Preparation of $[C_6H_{10}(PdCl_2)_4]_n$ *(VII) from diallyl*

Bis(benzonitrile)palladium chloride (0.1 g) was dissolved in benzene (20 ml) heated and then filtered. The filtrate was treated with diallyl (0.3 ml). The bright brown precipitate formed immediately, and filtered off, then washed with cold benzene and petroleum ether and dried under reduced pressure (0.3 mm). This compound is insoluble in usual organic solvents and water. Analysis found: C, 9.24; H, 1.42; Cl, 35.71; Pd, 53.26. $[C_6H_{10}(PdCl_2)_4]_n$ calcd.: C, 9.10; H, 1.27; Cl, 35.83; Pd, 53.76%.

Preparation of $(C_6H_{10}RhCl)_2$ *(VIII)*

Rhodium trichloride (0.5 g) and diallyl (1 ml) were shaken together in water/ethanol mixture (1/3, 5 ml) and the precipitate dried in vacuo. The complex is soluble in chloroform, but in several minutes decomposes in this solution. Analysis found: C, 32.50; H, 4.40; Cl, 15.84. $(C_6H_{10}RhCl)_2$ calcd.: C, 32.72; H, 4.57; Cl, 16.10%.

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