Journal of Organometallic Chemistry, 148 (1978) 85—95

ON METAL—π-ALLYL AND METAL—HALOGEN STRETCHING MODES IN THE VIBRATIONAL SPECTRA OF π-ALLYL COMPLEXES OF TRANSITION METALS

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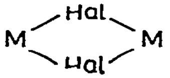
(Received October 5th, 1977)

Summary

The behaviour of metal—π-allyl and metal—halogen stretching frequencies in the spectra of π-allylic complexes of different transition metals has been studied. It is shown that the frequency of the tilting metal—π-allyl vibration ν_t(M—All) (A″) can occupy any of the three possible positions in relation to the other two metal—π-allyl vibrations ν_s(A′) and ν_t(A′). It is found that the increase of the mass of the metal atom M in a series of centrosymmetrical complexes of the type L_2M can lead to an inversion of the frequency sequence of "gerade" and "ungerade" skeleton stretching vibrations. The reasons for coincidence of IR and Raman ν(M—Hal) frequencies in the vibrational spectra of the bridged moieties  are discussed. The force constant *K*(M—All) for homoligand π-allyl complexes has been found to increase in the series Ni ≈ Pd < Pt and Rh < Ir.

Recently we studied the vibrational spectra of homoligand and heteroligand (containing halogens, CO and Cp) π-allyl complexes of Ni, Pd, Pt, Rh, Fe and Mn [1—7]. On the basis of the results obtained and data available in the literature [8—16], we proposed the assignment of internal vibrations of the π-allyl ligand [6] and in the present paper we analyze the behaviour of skeleton stretching vibrations (metal—π-allyl and metal—halogen).

Metal—π-allyl stretchings ν(M—All)

(a) Compounds with only one π-allyl group at the metal atom

The following compounds have been studied by us: $(AllMHal)_2$, where M = Ni, Pd and Hal = Cl, Br, I; $AllFe(CO)_3X$, where X = Cl, Br, I, NO_3; $AllMn(CO)_4$. Complete spectra of $AllCo(CO)_3$ are reported in [11,13] and IR spectra of AllFe-

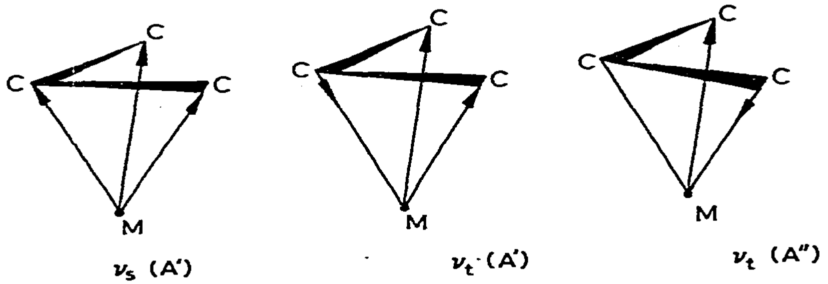


Fig. 1. Metal—π-allyl stretching vibrations.

$(CO)_2NO$ with the polarization data are given in [12].

Assignment of ν(Pd—All) in the spectra of π-allylpalladium halides was first carried out by Shobatake and Nakamoto in 1970 [8]. By analogy with the metal—π-ring system (ring = cyclopentadienyl, benzene) they assumed that only two ν(Pd—All) vibrations should exist: ν_s(Pd—All) and ν_{as}(Pd—All), the latter being considered to be the tilting vibration of the π-allyl plane. However, the analogy with the metal—π-ring system was incorrect in this case since the symmetry of the M—All fragment is lower (C_s) than that of the M—π-ring and the tilting vibration is not degenerate. For any set of coordinates we choose, three ν(M—All) vibrations should exist: a totally symmetrical (of A' species) so called "pure stretching" ν_s(A') vibration with in phase variation of all M—C bonds and two tilting vibrations ν_t of A' and A" species (see Fig. 1). Therefore, two polarized lines corresponding to M—All ν_s(A') and ν_t(A') modes and one depolarized line corresponding to ν_t(A") mode should be observed in the Raman spectrum.

Depolarization ratios of the Raman ν(Pd—All) lines were first measured by Adams and Squire [9] in the spectra of $(AllPdHal)_2$ solutions (Hall = Cl, Br) and then by Sourisseau and Pasquier [14]. In the ν(M—All) region (300—450 cm^{-1}) these authors observed only two polarized Raman lines. However, correctly assuming that there should be three M—All vibrations, they assigned to the remaining ν_t(A") mode a weak band in the IR spectrum with a frequency lying between the frequencies of the polarized Raman lines.

For $(AllPdCl)_2$ we also observed only two (polarized) Raman lines but three IR bands (Fig. 2). For the bromide and iodide * however we obtained all three Raman lines both for solid and solution spectra. The weak depolarized ν_t(A") line appears as a shoulder with its frequency being lower than those of ν_s(A') and ν_t(A') (Fig. 2).

We were unable to obtain the Raman spectra of $(AllNiHal)_2$ due to the decomposition of the substances in the laser beam. IR vibrations were assigned by analogy with $(AllPdHal)_2$. For $AllMn(CO)_4$ all three Raman lines are exhibited in the ν(M—All) region (Fig. 3), the frequency of the depolarized line ν_t(A") being higher than those of ν_s(A') and ν_t(A'). From IR polarization data reported in

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* The spectrum of the iodide (See experimental section) is reported here for the first time.

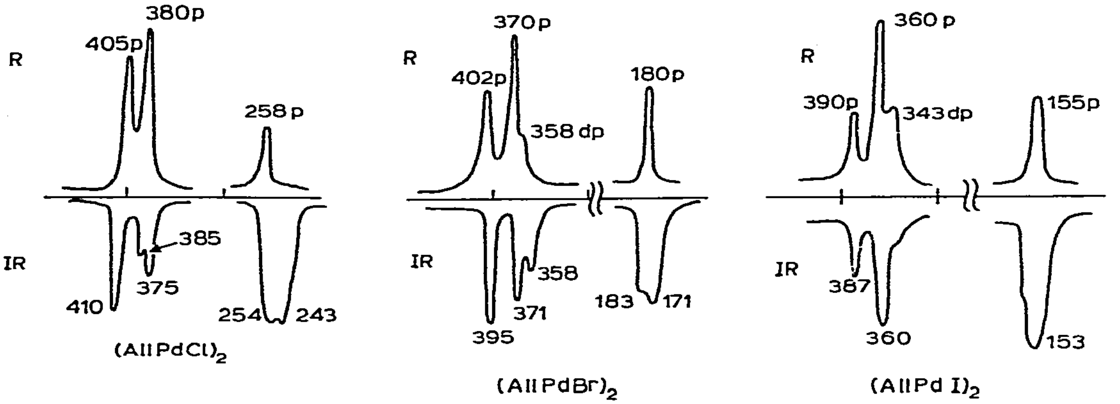


Fig. 2. Skeleton stretching vibrations in the spectra of $(\pi\text{-AllPdHal})_2$; Hal = Cl, Br, I.

[12] it appears that for $\text{AllFe(CO)}_2\text{NO}$ the ν(M—All) frequencies follow the same order. In the spectra of $\text{AllFe(CO)}_3\text{Hal}$, as in the case of $(\text{AllPdCl})_2$, the $\nu_t(A'')$ frequency lies between $\nu_s(A')$ and $\nu_t(A')$ [7]. According to Andrews and Davidson [11], the same sequence of ν(Co—All) frequencies is observed for AllCo(CO)_3. Thus, data obtained for π-allyl compounds of different metals show that the tilting $\nu_t(A'')$ vibration may occupy any of the three possible positions in relation to $\nu_s(A')$ and $\nu_t(A')$. This is an important observation since previously it was accepted that the tilting metal—ligand vibration always has a higher frequency than the "pure stretching" mode. This point of view had appeared as a result of summarizing a few spectra of metallocene and arene π-complexes, then available. However, the latest Raman data on Cp_2Ni [17], Cp_2Mn [18] and Cp_2Mg [19] indicate that the tilting M—Cp vibration may have lower frequency than the „pure stretching" mode. Consequently, the popular point of view that among the metal—π-ligand stretchings, the "pure stretching" vibration should always have the lowest frequency is erroneous.

While the assignment of the $\nu_t(A'')$ mode which appears as a depolarized

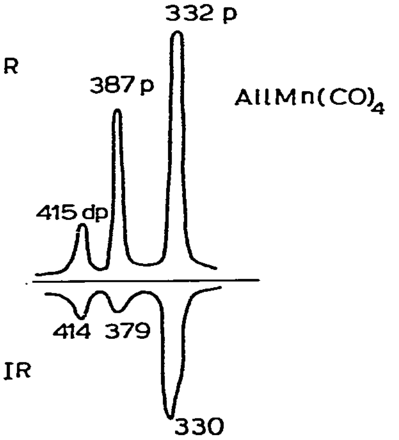


Fig. 3. Mn—π-allyl stretching vibrations in the spectrum of AllMn(CO)_4.

Raman line is straightforward, the assignment of the remaining two ν(M—All) vibrations $\nu_s(A')$ and $\nu_t(A')$ presents certain difficulties, because they belong to the same symmetry species and are both represented by polarized lines.

Adams and Squire [9] assigned the polarized line with the lowest frequency in the spectra of $(AllPdHal)_2$ (Hal = Cl, Br) to $\nu_s(A')$ on the basis of the above mentioned analogy with the metal—π-ring systems (assignment I). However, recently Sourisseau and Pasquier proposed the reverse assignment (assignment II) for similar complexes of Ni and Pd [14,20], based on comparison of measured and calculated isotopic ratios ρ for ν(Pd—All) frequencies in $(\pi\text{-}C_3H_5PdCl)_2$ and $(\pi\text{-}C_3D_5PdCl)_2$ spectra, considering these vibrations as translation and rotations of the π-allyl plane. However this approximation does not take into account the coupling of ν(M—All) with out-of-plane CH vibrations, which should noticeably affect the value of ρ. Since experimental values of ρ for $\nu_s(A')$ and $\nu_t(A')$ (1.08 and 1.14) differ only slightly, the validity of this approach is questionable.

To assign the ν(M—All) vibrations of A′ species we propose to use the criterion of intensity of the corresponding Raman lines. It seems evident from a simple qualitative consideration that for the "pure stretching" ν_s mode variation of molecular polarizability should be greater than for the tilting vibration. Therefore, the strongest Raman line should correspond to $\nu_s(A')$, i.e. we agree with assignment I.

(b) Compounds with two π-allyl groups at the metal atom

We have studied homoligand All_2M (M = Ni, Pd, Pt) [3,4] and heteroligand complexes $(All_2RhHal)_2$ [5] and $All_2Fe(CO)_2$ [7]. In general, *bis*(π-allyl) compounds should have 6 ν(M—All) vibrations. For centrosymmetrical *trans*-All_2M compounds these vibrations are distributed as follows:

$$\Gamma_{C_{2h}} = 2\ A_g(\nu_s, \nu_t; \text{Raman, p}) + A_u(\nu_t, \text{IR}) + B_g\ (\nu_t; \text{Raman, dp}) + 2\ B_u\ (\nu_s; \nu_t; \text{IR})$$

The assignment of these vibrations shown in Fig. 4, is based on their IR and Raman activity and on depolarization ratios of the Raman lines. Note that in this case the value of $\nu_t(B_g)$ lies between the values of ν_s and $\nu_t(A_g)$.

It is of interest to follow the behaviour of ν(M—All) frequencies with increase of the mass of the metal atom. Since the frequencies of "gerade" vibrations are independent of the metal mass, the fact that frequencies of Raman active ν(M—All) modes are practically the same in the spectra of All_2Ni and All_2Pd and are higher in the All_2Pt spectrum indicates close values of K(M—All) force constants for All_2Ni and All_2Pd and a higher force constant for All_2Pt.

The frequencies of "ungerade" vibrations depend on the metal mass and this dependence determines the relative disposition of IR and Raman frequencies (Fig. 4). For All_2Ni the IR frequencies corresponding to "ungerade" vibrations are higher than the Raman frequencies corresponding to "gerade" vibrations. On going from All_2Ni to All_2Pd Raman frequencies retain their values, while IR frequencies are shifted to lower values due to increase of the metal mass and, by chance, coincide with the Raman frequencies. This leads to an apparent violation of the mutual exclusion rule. On going further to All_2Pt, Raman frequencies increase due to higher K(M—All) values while IR frequencies are under the competitive influence of mass increase and higher K(M—All) value and, as a result, are practically not displaced in relation to All_2Pd.

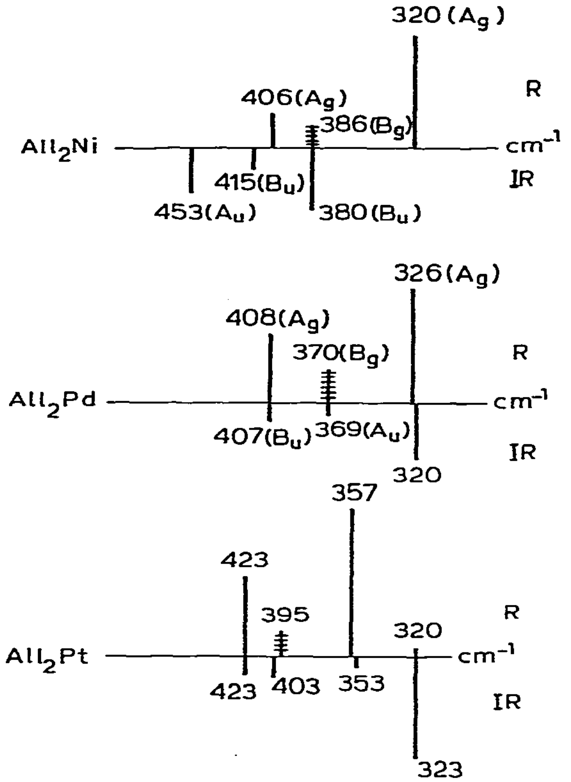


Fig. 4. Metal—π-allyl stretching vibrations in the spectra of All$_2$M (M = Ni, Pd, Pt). I = p; ‡ = dp.

Thus, a gradual increase of the metal atom mass in a series of π-complexes with central symmetrical structure may lead to an inversion of the frequency sequence of "gerade" and "ungerade" skeleton vibrations. Evidently, this phenomenon is not peculiar only to π-allyl complexes and should be taken into account during analysis of spectra of various π-complexes.

According to X-ray data [21], the π-allyl groups in $(\text{All}_2\text{RhHal})_2$ are *cis*-arranged and the local symmetry of Rh environment is C_2, consequently all ν(Rh—All) vibrations should be both Raman and IR active. In fact, all Raman lines in the spectra of $(\text{All}_2\text{RhCl})_2$ and $(\text{All}_2\text{RhBr})_2$ (Fig. 5) have IR counterparts with the exception of the most intense line of the $\nu_s(A')$ mode whose IR counterpart is very weak in the spectrum of the chloride and absent in the bromide spectrum. It should be noted that low intensity of the IR band corresponding to the totally symmetrical metal—ligand vibration which is not forbidden in IR by selection rules, is often encountered in the spectra of transition metal π-complexes (see, for instance, [22]). The assignment of ν(Rh—All), given in Fig. 5, is described in [5]. The 285 cm^{-1} IR band of medium intensity in the bromide and chloride spectra that has a weak Raman counterpart could have been assigned to the missing ν_t vibration if it were not present in the All_3Rh spectrum (see below). An unambiguous assignment of this band is difficult since no one of the possible assignments can be adequately argumented.

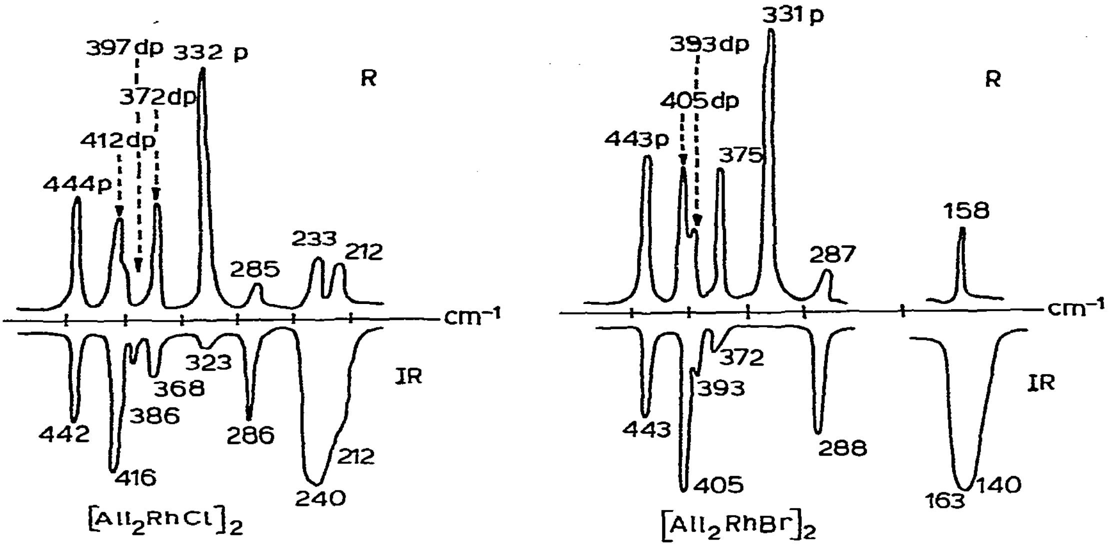


Fig. 5. Skeleton stretching vibrations in the spectra of (π-$All_2RhHal)_2$; Hal = Cl, Br.

Unlike bis(π-allyl) compounds in which the two π-allyl groups kinematically interact, for $All_2Fe(CO)_2$ in the region of ν(Fe—All) a pattern typical of monoallyl compounds is observed (Fig. 6): three Raman lines (2 polarized and one depolarized) and their IR counterparts, i.e. ν(Fe—All) vibrations obey the local symmetry of an Fe—All moiety (C_s). This may indicate that the AllFeAll angle is close to 90° and conforms with PMR data on the *cis*-structure of this complex. The approximately equal intensity of the IR bands of symmetrical and antisymmetrical ν(CO) vibration [7] also agrees with the *cis*-structure of $All_2Fe(CO)_2$ [23].

(c) Compounds with three π-allyl groups at the metal atom

Of such compounds, All_3Rh [5,15] and All_3Ir [15] have been studied. In this

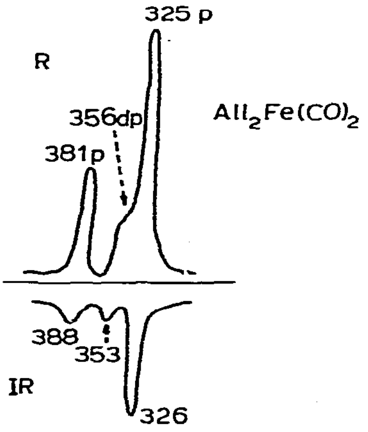


Fig. 6. Fe—π-All stretching vibrations in the spectra of $All_2Fe(CO)_2$.

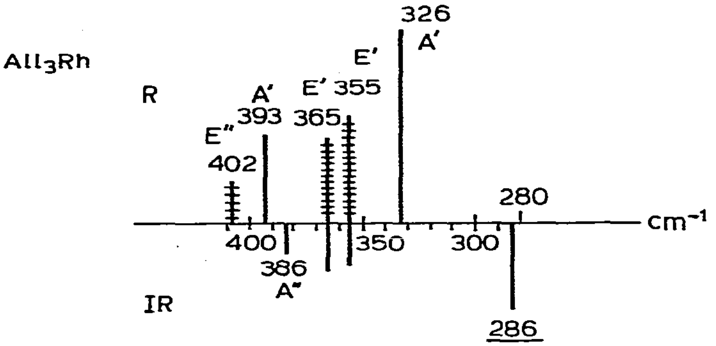


Fig. 7. Skeleton stretching vibrations in the spectrum of All_3Rh. I = p; ‡ = dp.

case there should be 9 ν(M—All) vibrations.

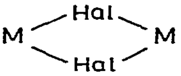
The spectral pattern in the ν(Rh—All) region obtained for All_3Rh (Fig. 7) is in very good agreement with C_{3h} symmetry:

$\Gamma_{C_{3h}} = 2\ A'\ (\nu_s, \nu_t; \text{Raman, p}) + A''\ (\nu_t; \text{IR}) + 2\ E'\ (\nu_s, \nu_t; \text{Raman, dp; IR}) + E''\ (\nu_t; \text{Raman, dp})$.

For this compound the ν(Rh—All) vibrations of different π-allyl groups noticeably interact. The straightforward assignment of these vibrations to various symmetry species is provided by the specificity of selection rules in this case [5].

In the All_3Ir spectra, obtained by Andrews and Davidson [15] the IR bands in the 350—450 cm^{-1} region and depolarized Raman lines which should correspond to ν(Ir—All) are absent. Only two polarized Raman lines at 349 and 413 cm^{-1} are observed, which correspond apparently to ν_s and ν_t respectively. Note that the frequencies of these vibrations are higher than in the All_3Rh spectrum, indicating increase of the K(M-All) force constant on going from Rh to Ir.

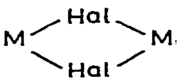
Metal—halogen vibrations

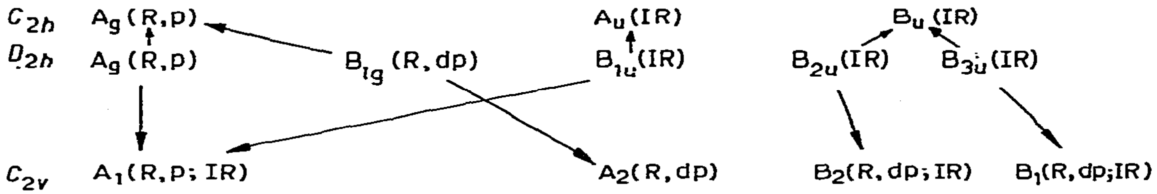
The separately considered planar  ring with equal M—Hal bonds has a D_{2h} symmetry and its 6 normal vibrations are distributed as follows:

$\Gamma_{D_{2h}} = 2\ A_g + B_{1g} + B_{1u} + B_{2u} + B_{3u}$.

One of the A_g vibrations is a bending vibration of the ring and the B_{1u} mode is an out-of-plane ring deformation. Their frequencies should be lower than those of the remaining "pure stretching" A_g and B_{1g} ν(M—Hal) modes and the modes of the B_{2u} and B_{3u} species which are mixed stretching and bending vibrations. Vibrations of the planar cycle should obey the mutual exclusion rule.

If adjacent bonds in the bridge are not identical (as, for instance, in $(All_2RhCl)_2$ [21]), the symmetry of the cycle is lowered to C_{2h}, the number of Raman and IR active vibrations is retained, and only the depolarization ratio of one Raman line must be changed.

The non-planar  cycle has a C_{2v} symmetry. For these three symmetry groups the following correlation exists:



In the case of C_{2v} point symmetry all vibrations should be Raman active and all, except for A_2, IR active. Therefore, there is a theoretical possibility of distinguishing between planar and non-planar bridges on the basis of spectral data.

Such an approach is obviously approximate as bridge vibrations in real systems are coupled with vibrations of other ligands. However, vibrations that mainly involve metal—halogen bonds may be easily distinguished from metal—ligand vibrations by the mass-dependence of the former in the sequence Hal = Cl, Br, I.

In the spectra of all the π-allyl and π-crotylmetal halides studied (Fig. 2, Table 1) instead of the four expected ν(M—Hal) frequencies (two Raman lines and two IR bands that do not coincide with the first), we observed as a rule a strong broad IR band split into two components (B_{2u} and B_{3u}), and one Raman line (polarized in the case of $(AllPdCl)_2$) corresponding to the A_g vibration. In the case of bromides and chlorides the separation between two IR band components is 10—15 cm^{-1} for Ni and Pd complexes and up to 30 cm^{-1} for Rh complexes. The frequency of the Raman line falls within the range of IR frequencies, i.e. an apparent violation of the mutual exclusion rule is observed.

IR and Raman frequencies of ν(M—Hal) modes also coincide in the spectra of norbornadienyl complexes [24] and of several CdL_2Hal_2 complexes [25]. On this basis the last authors proposed for the Cd environment not a polymeric octahedral but a tetrahedral structure with terminal but not bridged Cd—Hal bonds.

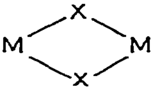
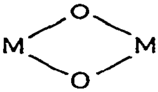
However the analysis of the approximate analytical expressions that determine

TABLE 1

VIBRATIONAL SPECTRA OF $(\pi\text{-}CH_3C_3H_4PdX)_2$ IN THE LOW FREQUENCY REGION (600—60 cm^{-1})

$(\pi\text{-}CH_3C_3H_4PdCl)_2$		$(\pi\text{-}CH_3C_3H_4PdBr)_2$		$(\pi\text{-}CH_3C_3H_4PdI)_2$	
IR	R	IR	R	IR	R[a]
530s		529vs	529s	532vs	
448s		442s	445w, p	446s	
414m	415s, p	410m	406vs, p	405s	396vs, p
366s	353m, dp	360m	364m, dp	358m	348m, dp
300vw		295vw		287w	
255vs	262vw	177s (br)	183vw	147s	
204m					
106w		108vw			
92w		82vw		71m	

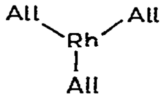
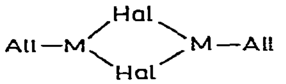
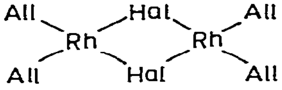
[a] This Raman spectrum is incomplete due to strong stray light of the sample.

the ν(M—Hal) frequencies, taking into account their coupling with ν(M—All), shows that the difference between vibration frequencies of different symmetry species is determined first of all by the cosine of the HalMHal angle (α) and, secondly, by the force constant of M—Hal bonds coupling (h). At α values approaching 90° and at small values of h (according to published data [26], h values for four-membered cycles amount to not more than 5% of K(M—Hal) values) vibrations of different symmetry species may have very close frequency values. This seems to explain the spectral pattern observed for the complexes studied and for other bridged cycles. Baran [26] for  and Wing and Callagan for [27] noticed the dependence of the frequency difference of bridge stetching modes on the value of α.

Thus, the fact whether the ν(M—Hal) frequencies in IR and Raman spectra coincide or not cannot serve as a criterion for distinguishing between structures with bridged or terminal M—Hal bonds or between planar or non-planar bridge structures. It only shows whether the HalMHal angle deviates from 90°.

The strength of M—All bonds

As it is well-known that the change of the force constant of a given bond in a series of isostructural molecules reflects the change in the bond strength, it was interesting to follow the variation of M—All bond strength in the compounds considered in the present work. As shown above, even from the frequencies of ν(M—All) Raman lines in the spectra of "pure" π-allyl complexes it is evident that the M—All force constant varies in the sequences Ni ≈ Pd < Pt and Rh < Ir. To compare K(M—All) in "pure" π-allyl complexes and in π-allylmetal halides we calculated it for models (in the latter model the AllRhAll angle was assumed

All—M—All, ,  and 

to be equal to 180°). Calculations were carried out in the point-mass approximation using frequencies of pure stretching vibrations, i.e. assuming that the plane of the π-allyl group vibrates as a whole in relation to the metal atom. The coupling of ν(M—All) and ν(M—Hal) modes was taken into account. Since it is impossible to distinguish between alternate assignments of IR active ν(M—Hal) frequencies ($B_{2u} < B_{3u}$ or vice versa) on the basis of available data, calculations were carried out for both assignments.

It is evident from data presented in Table 2 that for both assignments the calculated values of K(M—All) for π-allylmetal halides are higher than for "pure" π-allyl complexes. Hence, the data obtained agree with Brown and Owens' results [28] on quantum-mechanical calculations by the SCCCMO method according to which the strength of the metal—π-allyl bond increases with the atomic number of the metal within the same group of the periodic table and when electron-acceptor Hal atoms are attached to the metal atom.

TABLE 2

K(M—All) FORCE CONSTANTS FOR All_2M AND $(AllMX)_2$

Complex	K(M—All) × 10^6 cm^{-2}		
	assignment I $B_{2u} > B_{3u}$		assignment II $B_{2u} < B_{3u}$
All_2Ni		3.06	
$(AllNiCl)_2$	4.15		3.38
$(AllNiBr)_2$	4.62		3.43
$(AllNiI)_2$	4.11		4.11
All_2Pd		3.09	
$(AllPdCl)_2$	4.27		3.56
$(AllPdBr)_2$	4.50		3.68
$(AllPdI)_2$	4.34		4.34
All_2Pt		3.78	
All_3Rh		3.52	
$(All_2RhCl)_2$		3.87	
$(All_2RhBr)_2$		3.82	

Experimental

Raman spectra were measured, using Coderg PH-O spectrometer equipped with He-Ne laser (10—40 mW). IR spectra were taken using UR-20 and FIS-1 infrared spectrophotometers.

The spectra of solid $(AllPdI)_2$ were: Raman: 3060vw (br), 3030vw, 3010vw, 2995vw, 1485vw, 1458vw, 1380w, 1226m, 1198m, 1017s, 1002(sh), 958m, 940m, 911w, 756w (br), 497s, 389s, 360s, 349(sh), 155s. Infrared: (in KBr pellett and Nujol mull 3073vw, 3042w, 2940vw, 1888m, 1842m, 1483vw, 1460w, 1380m, 1226w, 1198w, 1018s, 997m, 952m, 933s, 920m, 755m (br), 497s, 387m, 360m, 349(sh), 107(sh), 95s, 79m.

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