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Nuclear Magnetic Resonance Spectroscopy of Organometallic Allyl Compounds

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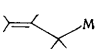
The NMR spectroscopic data for organometallic allyl and related derivatives have been examined. It is suggested that allyl compounds of transition metals be classified solely as σ- and π-derivatives and NMR spectroscopic criteria for the assignment of the test compounds to one of these types have been formulated. The effects of the structural non-equivalence of allyl ligands in a series of compounds, certain types of isomerism of allyl derivatives and also their possible lack of stereochemical rigidity have been considered. The validity, from the standpoint of NMR experiments, of the hypothesis of the σ-π transformations of allyl derivatives of transition metals in the presence of bases has been discussed. Hypotheses have been put forward concerning the geometry of the allyl compounds of certain non-transition metals.
The bibliography includes 171 references.

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I. INTRODUCTION

Depending on the geometry of the allyl–metal (a transition or non-transition metal) bond, allyl derivatives can be divided into two basic types: (1) compounds with the usual localised σ-bond [structure (I)]; (2) compounds with a non-classical delocalised bond [structure (II)].



(I)
σ-Bond



(II)
Delocalised bond

Allyl derivatives of the σ-type (I) are more characteristic of the chemistry of non-transition metals, while compounds with a delocalised bond (II), usually referred to as the π-bond[1], are typical with transition metals. There is no rigorous correspondence between the nature of the metal (transition or non-transition) and the bond type [(I) and (II)]. A fair number of transition metal derivatives with an allyl–metal σ-bond have been synthesised. On the other hand, structures with a delocalised bond (II) are known for non-transition metals, but, in order to regard them as π-complexes, a group-theoretical justification is necessary. Together with organometallic compounds containing an unsubstituted or substituted allyl group, it is natural to consider also compounds of certain other classes in which the allyl fragment is part of an open or closed carbon chain. In the discussion on derivatives with a delocalised bond, such grouping permits the consideration from one standpoint of all compounds where this bond is formally formed by three electrons from the three carbon atoms of the ligands.

Nuclear magnetic resonance (NMR) spectroscopy has proved to be the most important physicochemical instrument for the discovery and comprehensive investigation of complexes of the π-allyl type. For example, the non-classical structure of certain allyl (and also π-benzyl and trimethylenemethane) transition metal derivatives was initially proposed on the basis of NMR studies[2–4] and only subsequently confirmed by diffraction methods[5–7]. The isomerism in the series of allyl derivatives, various rearrangements, and many other structural and chemical problems have been successfully investigated by NMR spectroscopy. During the last decade, numerous spectroscopic data have accumulated and probably in the immediate future the NMR method will provide much information about compounds of this type.

However, for a number of reasons the data obtained are not always interpreted with sufficient rigour. As a result, certain conclusions which "follow from NMR data" and which have been widely adopted in the literature, actually proved to be incorrect. Apart from other reasons, this was because in studies of organometallic allyl compounds the entire "arsenal" of the NMR method was not employed. For example, until now no studies have been made of such important characteristics as $^{13}C-^{1}H$ spin–spin coupling, although the constants $J_{^{11}C-^{3}H}$ provide information about the valence state of the carbon atoms in the allyl ligand. Moreover, in the discussion of the screening of the proton in the π-allyl ligand the effect of the magnetic anisotropy of other ligands, for example triphenylphosphine, is as yet rarely taken into account.

All these considerations led us to undertake the present review. We must stipulate that the method chosen for the treatment of the subject, namely the use of data based on only one physicochemical procedure, dictated both the principles governing the selection of facts and the manner of their presentation. As a result, we have to concentrate attention only on the conclusions which follow unambiguously from NMR spectroscopic data. Clearly, the final

answer to the majority of the problems considered can be obtained only by considering together results obtained by several physicochemical methods.

II. COMPOUNDS WITH A LOCALISED σ-BOND

NMR spectroscopic studies have been made on a number of organometallic σ-allyl derivatives[1,8-17] and related compounds containing the σ-allyl fragment—cyclopentadienyl[18-24], benzyl[3,25-28], and indenyl[19,29-32] derivatives. In almost all cases NMR spectroscopy permits fairly reliable identification of the σ-allyl type. The relevant spectroscopic characteristics are presented in Table 1. For comparison, data for certain other organometallic allyl compounds are also included.

The ^{1}H NMR (PMR) spectra of σ-allyl derivatives (Fig. 1) show at least three groups of signals (intensity ratios 1 : 2 : 2) characteristic of the normal allyl system ($AKLX_2$, in the limiting case $ABCX_2$):

=CH—	CH_2=	—CH_2M
δ 6.0—6.6 p.p.m.	δ 3.5—5.0 p.p.m.	δ 1.5—2.8 p.p.m.

The lines due to the most screened aliphatic CH_2 protons (X_2) are split by CH vinyl protons, which to a first approximation gives rise to a doublet in the spectrum.

The vinyl protons of the =CH_2 (KL) group are non-equivalent and therefore produce a poorly resolved multiplet in the spectrum. As a result of splitting by all the remaining protons in the allyl fragment, the vinyl =CH proton (A) gives rise in the spectrum to a distinct asymmetric multiplet, typical for vinyl compounds, located in the region of the weakest fields.

It follows from the data in Table 1 that the screening of individual groups of protons in each compound differs somewhat from the corresponding values in propene.

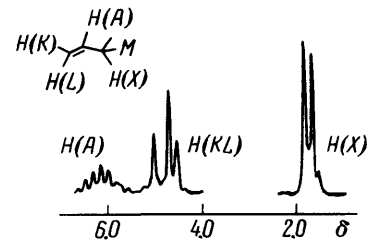
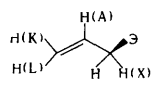
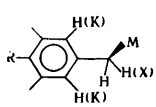
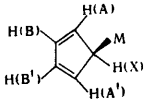
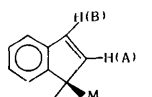


Figure 1. NMR spectrum of the compound σ-$C_3H_5Mn(CO)_5$ ($AKLX_2$ spin system)[1].

Table 1. Parameters of the PMR spectra of σ-allyl derivatives of the elements.

Type of molecule and type of spectral system of allyl component of spectrum	Compound	δ_H, p.p.m. rel. to TMS*			$J_{HH'}$, Hz		Conditions of measurement (solvent, temp., °C)	References
		H(A)	H(K, L) H(B)	H(X)	AK (*cis*)	AL (*trans*)		
 $AKLX_2$	$C_3H_5Mn(CO)_5$	6.15	4.77	1.85	10	17		1
	$C_3H_5Fe(CO)_2$-π-C_5H_5	6.16	4.59	2.07	9.2	17.1		8
	$C_3H_5Mo(CO)_3$-π-C_5H_5	6.0	3.5	2.27				9
	$C_3H_5W(CO)_3$-π-C_5H_5	~6.0	4.53	2.32			C_6H_{12}	10
	$C_3H_5Rh(CO)Cl_2[P(C_6H_5)_3]_2$	6.58	4.82	2.8			$CDCl_3$	12
	$C_3H_5IrCl_2[P(CH_3)_2C_6H_5]_3$	6.2	4.90	2.70			$CDCl_3$	11
	$(C_3H_5)_4Si$	5.62	4.70	1.50			<165	14
	$(C_3H_5)_3B$	5.65	4.70	2.05			<—40°	14
	$(C_3H_5)_4Sn$	5.88	4.83 (K) 4.72 (L)	1.88	9.39	16.90		15
	$C_3H_5Ge(CH_3)_3$	5.94	4.79 (K) 4.92 (L)	1.74				16
	$(C_3H_5)_2Hg$	5.98		1.86	9.52	16.75	[$^2H_8$]THF	17
	C_3H_6	5.73	4.88 (K) 4.97 (L)	1.72	10.02	16.81	CCl_4	33
	$C_6H_5CH_2Mo(CO)_3$-π-C_5H_5		7.13	2.88			CS_2	3
	4-$CH_3C_6H_4CH_2Mo(CO)_3$-π-C_5H_5		7.04	2.92				25
	4-$CH_3C_6H_4CH_2W(CO)_3$-π-C_5H_5		7.07	2.99			$CDCl_3$	25
	$(C_6H_5CH_2)_4Ti$		6.42	2.57			[$^2H_8$] toluene	27
	$(C_6H_5CH_2)_4Zr$		6.38	1.53			C_6D_6	28
	$(C_6H_5CH_2)_4Sn$			2.22			$CHCl_3$	26
	$C_6H_5CH_3$			2.34			CCl_4	34
 $AA'BB'X$	σ-$C_5H_5Fe(CO)_2$-π-C_5H_5	~6.0	~6.3	3.5			CS_2, —80	18
	σ-$C_5H_5Cr(NO)_2$-π-C_5H_5	6.28	6.5				CS_2, —110	19
	σ-$C_5H_5Si(CH_3)_3$	6.48		3.23				22
	$(\sigma\text{-}C_5H_5)_2Ge(CH_3)_2$	6.63		3.51				22
	C_5H_6	6.42		2.90				34
 ABX	$C_9H_7Fe(CO)_2$-π-C_5H_5	6.72	6.53	3.97			$CDCl_3$, 25	19
	$(C_9H_7)_2Hg$	6.76		3.81	~5.7		<—41	29
	$C_9H_7Sn(CH_3)_3$	6.80	6.58	3.87			CS_2, —37	30
	$C_9H_7Ge(CH_3)_3$	6.65		3.50			<134	30
	$C_9H_7Si(CH_3)_3$	6.73	6.41	3.29			<180	30
	C_9H_{10}	6.14	6.67	2.99	5.88			35

* Tetramethylsilane (Ed. of Translation)

However, these differences do not make it necessary to take into account additional factors apart from those already known: the electronegativity of the metal, the magnetic anisotropy of the C–M bond, and the anisotropies of the individual fragments of the molecule. The coupling constants J_{HH} (*cis*) and J_{HH} (*trans*) of the compounds under considerations, including transition metal derivatives, in fact agree with the corresponding constants for propene. Nor are any other spectroscopic differences observed between σ-allyl derivatives of transition and non-transition metals. Furthermore, one may conclude that, under the conditions (temperature, solvent) where NMR spectroscopy indicates a σ-allyl structure of the compounds considered, no signs of coordination of the double bond of the allyl fragment to the metal atom are observed.

The available data permit the formulation of the principal spectroscopic characteristics of organometallic allyl compounds with a localised σ-bond: (1) the non-equivalence of the CH_2 groups; (2) the equivalence of the protons in the aliphatic CH_2 group and their non-equivalence in the olefin group; (3) the agreement of the vicinal coupling constants J_{HH} (*cis*) ≃ 9–10 Hz and J_{HH} (*trans*) = 17 Hz with the corresponding constants for propene and other allyl derivatives.

The PMR spectra of σ-benzyl, σ-indenyl, and σ-cyclopentadienyl derivatives of transition and non-transition metals are also very similar to the spectra of the corresponding hydrocarbons (toluene, indene, and cyclopentadiene). In all cases the aliphatic protons are the most screened and the observed spectrum fully agrees with expectation for a spin system with a C–M σ-bond. It should also be noted that the signals due to aliphatic protons, geminal relative to the metal atoms, are located in a fairly narrow region of the spectrum for each of the above classes of compounds:

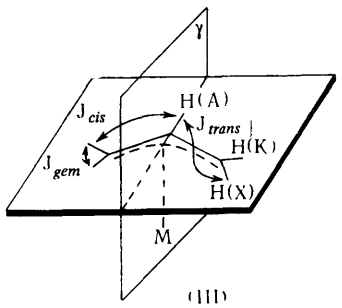
$CH_2{=}CH{-}CH_2M$	$C_6H_5CH_2M$	C_5H_5M	C_9H_7M
δ 1.5—2.8 p.p.m.	δ 2.2—3.0 p.p.m.	δ 3.2—3.5 p.p.m.	δ 2.9—4.0 p.p.m.

This evidently can be used as a test for the formation of a localised bond.

III. DERIVATIVES WITH A DELOCALISED BOND

The PMR spectra of the compound π-$C_3H_5Co(CO)_3$ with a delocalised bond were investigated for the first time in 1960 by Heck and Breslow[2]. The PMR spectra of allyl derivatives of transition metals with a delocalised C_3H_5–M bond were investigated in greater detail by McClellan et al[1]. The number of studies which in one form or another relate to the NMR spectroscopy of π-allyl compounds increases steadily. Spectroscopic data are now available both for compounds containing allyl groups only [$(C_3H_5)_nM$, M = Ni, Pd, Zr, Hf, Th, Rh, Ir, Pt, U, etc.)][36-44] and for mixed compounds containing, apart from the π-allyl ligands, one or several other groups: a halogen[1,45-47], carbonyl[1,2,48-50], π-cyclopentadienyl[1,47,54,55], a halogen and carbonyl[56-60], a halogen and π-cyclopentadienyl[54,61], carbonyl and π-cyclopentadienyl[8-10,51-53], etc. Spectroscopic data are also being quoted for π-allyl complexes in which the transition metal atom is coordinated to phosphines, pyridine, dimethyl sulphoxide, the acetylacetonate ion, and similar basic ligands[11,12,46,62-73,82].

Historically the NMR spectra of non-transition metal derivatives with a postulated delocalised bone [structure (II)] were investigated earlier than those of the π-allyl complexes of transition metals. Thus, as early as 1959, Nordlander and Roberts[74] observed in the PMR spectrum of C_3H_5MgBr characteristics the interpretation of which did not exclude the possible existence in this compound of one of the forms of the delocalised C_3H_5–Mg bond:



(III)

Table 2 lists certain spectroscopic characteristics of the π-allyl derivatives of transition metals. In the PMR spectra of compounds with an unsubstituted ligand, as in the case of σ-complexes, there are as a rule three groups of signals with intensity ratios of 1 : 2 : 2 (Fig. 2). However, the spin system of the AK_2X_2 spectrum indicates a greater symmetry of the allyl–M group in compounds of the π-type. In particular, it follows from the spectrum that each of the two signals in a strong field (K_2X_2) no longer refers to an individual CH_2 group, as in the σ-structure, but to an individual type of proton from each CH_2 group—*cis* or *trans*†.

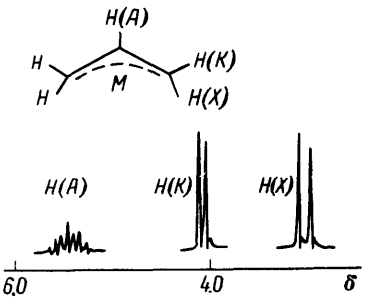
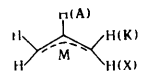
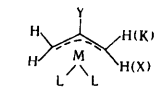
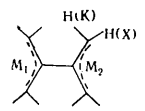
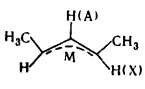
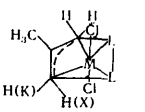
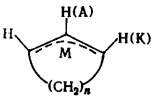
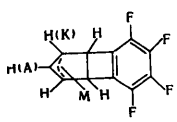


Figure 2. NMR spectrum of the compound $(\pi\text{-}C_3H_5PdCl)_2$ (AK_2X_2 spin system)[66].

The results led to the conclusion that in derivatives of π-type [structure (III)] a delocalised bond is formed and all the carbon atoms of the allyl fragment are in a state of sp^2-hybridisation (strictly speaking, in order to assess the valence state of the carbon atoms of the π-allyl ligand, it is also necessary to have data on $^{13}C-{}^1H$ spin–spin coupling). Then both C–C bonds of the ligands prove to

† Here and subsequently we are considering the position of the terminal protons relative to the central proton or the group replacing it [structure (III)]. The terms *"cis"* and *"trans"* were introduced for these compounds in 1959 by Nordlander and Roberts[74] and are used in the discussion of both allyl and π-olefin, π-butadiene, π-pentadienyl, and similar complexes. Two years later[1] the terms *"syn"* and *"anti"* were introduced, but have not been widely adopted by investigators of π-complexes (with the exception of allyl complexes).

Table 2. Parameters of the PMR spectra of transition metal derivatives with a symmetrical π-allyl–M bond.

Type of molecule and type of spectral system of allyl component of spectrum	Compound	δ_H, p.p.m.rel. to TMS			J_{HH}, Hz		Conditions of measurement (solvent, temp., °C)	References
		H (A)	H(K) (*cis*)	H(X) (*trans*)	*cis*	*trans*		
1	3	3	4	5	6	7	8	9
 AK_2X_2	$(C_3H_5PdCl)_2$	5.45	4.02	2.95	7.1	12.1	$CHCl_3$	47
	$(C_3H_5PdI)_2$	5.40	4.35	3.05	6.3	11.8	$CHCl_3$	47
	$C_3H_5PdC_5H_5$	5.68	4.37	3.19	5.0	10.0	$CDCl_3$	1
	$(C_3H_5)_2Pd$, two types of symmetrical π-allyl groups	5.06	4.14	2.40	7.6	13.0	$CDCl_3$	36
		4.93	3.90	2.56	7.6	13.0	—20°	
	$(C_3H_5NiBr)_2$	4.3	2.3	1.2	7.0	13.3	C_6H_6	75
	$C_3H_5NiC_5H_5$	3.70	3.09	1.88	3.0	11.0		1
	$C_3H_5NiCH_3$	5.33	2.76	2.25			TMS, —60	76
	$(C_3H_5)_2Ni$, two types of symmetrical π-allyl groups	5.03	3.79	1.67	7.0	14.0	$CDCl_3$	36
		4.55	3.58	2.20	7.0	14.0	—40°	
	$C_3H_5Mn(CO)_4$	4.7	2.8	1.8	7.0	12.0	C_6H_6, 160	48
	$C_3H_5Co(Co)_3$	4.91	3.07	2.15	6	10		1
	$C_3H_5Mo(CO)_3(CH_3CN)_2Cl$	4.44	3.59	1.01	6.0	9.0	C_6H_5Cl	77
	$C_3H_5FeC_5H_5(CO)$	4.16	2.67	1.68	8.0	11.0	C_6H_6	8
	$(C_3H_5)_3Rh$, three types of symmetrical π-allyl groups	5.26	2.87	2.53	7.0	14.0	$CFCl_3$	38
		4.17	2.68 or 2.62	1.33	6.5	11.0	—74	
		3.50	2.62 or 2.68	1.71	6.5	11.0		
	$(2\text{-}CH_3C_3H_4PdCl)_2$	—	3.83	2.83	—	—	$CHCl_3$	47
	2-$CH_3C_3H_4$Pdacac	—	3.52	2.66	—	—	CCl_4	46
	$2\text{-}CH_3C_3H_4Rh[P(C_6H_5)_3]_2$	—	2.46	2.27	—	—	C_6H_5Cl	78
	$(2\text{-}ClC_3H_4PdCl)_2$	—	4.27	3.26	—	—	$CDCl_3$, 34	68
	2-ClC_3H_4Pdacac	—	4.55	3.12	—	—	$CDCl_3$, 34	68
	$2\text{-}ClC_3H_4Co(CO)_3$	—	3.83	2.92	—	—		1
 K_2X_2	$(C_5H_5NiC_3H_4)_2$	—	3.05	1.3			C_6D_6, 30	79
	$C_5H_5NiC_3H_4$—$C_3H_4PdC_5H_5$	—Ni	2.75	1.15			C_6D_6, 30	79
		Pd	3.65	2.15				
	$(C_5H_5PdC_3H_4)_2$		3.65	2.24			$CDCl_3$	72
	$(acacPdC_3H_4)_2$		4.01	2.81			$CDCl_3$	72
 AX_2	$(C_3H_5PdCl)_2$	5.14	—	3.62	—	10.7		80
	$C_5H_5Co(CO)_3$					9.8	CDCl, 33	81
 K_2X_2	$2\text{-}CH_3C_3H_4IrCl_2[P(C_6H_5)_3]_2$		4.10	3.20	—	—	$CDCl_3$, 34	11
	$2\text{-}CH_3C_3H_4RhCl_2[As(C_6H_5)_3]_2$		4.15	3.74	—	—	$CDCl_3$, —60	82
	$2\text{-}CH_3C_3H_4RhCl_2[Sb(C_6H_5)_3]_2$		4.39	3.15	—	—	$CDCl_3$, —50	82
 AK_2	n=2, $C_8H_7NiC_5H_5$	5.13	3.96	—			C_6H_6	83
	n=2, $C_5H_7Cr(CO)_2C_5H_5$	5.10	4.00	—			C_6H_6	51
	n=3, $(C_5H_9PdCl)_2$	5.51	5.22	—				84
	n=3, $C_8H_9Rh[P(C_6H_5)_3]_2$	5.25	3.60	—	6.6	—	C_6H_5Cl	78
	n=5, $C_9H_{13}Co$-*cyclo*-octa-1,5-diene	5.5	3.3		8	—	C_6D_6	85
	n=5, $C_8H_{13}Rh[P(C_6H_5)_3]_2$	5.25	3.47		8.0	—	C_6H_5Cl	78
	$C_{11}H_5F_4NiC_5H_5$	5.02	3.85					86

be equivalent and the metal is located symmetrically relative to the terminal carbon atoms. Subsequently these conclusions were confirmed by diffraction data (see, for example, Refs. 5, 80, 87, and 88).

The H(A) proton bound to the central carbon atom proves to be least screened in all cases. Its signal consists of a complex symmetrical multiplet due to splitting by the two pairs of terminal protons. Two other signals are due to the *cis*-protons H(K) and *trans*-protons H(X). To a first approximation, each of them consists of a doublet due to splitting by the central atom. In a more detailed investigation of these "doublets" it is possible to observe a fine structure due to the interaction of the non-equivalent geminal protons H(K) and H(X). The corresponding coupling constant J_{HH} (*gem*) usually does not exceed 1.5 Hz [36,41,62,66] but in the case of substituted compounds of the allyl type higher splittings for geminal protons are also known: 2 Hz for 2-ClC_3H_4Pdacac [68] and

3 Hz for π-$C_6H_5CH_2Mo(CO)_2C_5H_5$. [3] We may note that for the compound $(CH_2)_3CFe(CO)_3$ this value reaches up to 5 Hz. [4]

As in π-complexes of other types, the proton spin–spin coupling constants for π-allyl complexes J_{HH} (*cis*) = 3–8 Hz and J_{HH} (*trans*) = 10–15 Hz (Table 2) are much lower than for the initial olefins [for example in the case of ethylene J_{HH} (*cis*) = 11.5 Hz and J_{HH} (*trans*) = 19.1 Hz [89]] and the corresponding σ-allyl derivatives. Complex formation is the evident explanation of this effect.

However, it should be emphasised that, despite the lowering of the absolute values of the constants J_{HH} of all three types, the sequence of their relative values established previously[34,90] in the olefin series is strictly maintained:

$$J_{HH}\,(trans) > J_{HH}\,(cis) > J_{HH}\,(gem).$$

This finding permits an unambiguous assignment of the signals due to *cis*- and *trans*-protons in the spectroscopic study of each new π-complex.

The experimental data so far accumulated (Table 2) show that in π-allyl complexes the *cis*-protons H(K) are less screened than the *trans*-protons H(X). The range of variation of the screening of the individual groups of protons in π-complexes is much wider than in derivatives of the σ-type.

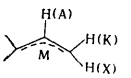
H(A)	H(K)	H(X)
$5.68 \geqslant \delta \geqslant 3.5$	$4.4 \geqslant \delta \geqslant 2.7$	$3.2 \geqslant \delta \geqslant 1.3$

This can probably be accounted for by the greater sensitivity of the π-allyl ligand to the characteristics of the complex-forming metal. Differences in experimental conditions can also play a decisive role: Table 2 includes for certain compounds data for screening in benzene solutions, although the use of this solvent can seriously distort the results. Evidently, as information accumulates on the spectra of the π-allyl derivatives of an increasing number of metals, the range of variation of the screening of protons of each type may become extended. At the same time, there is also a possibility that the range of variation will be found to be narrower in repeated NMR measurements under standard conditions, particularly when NMR spectroscopic data for the compounds in solvents such as benzene, toluene, etc. are excluded. We may also note that, although the ranges of variation of the chemical shifts of the individual groups of protons overlap to a considerable degree, for each specific π-complex the sequence of increasing screening is as a rule maintained: H(A) < H(K) < H(X).

Thus, using as an example compounds containing an unsubstituted π-allyl group, it is possible to formulate a number of criteria for the π-coordination of the transition metal atom to the ligand: (1) the equivalence of both CH_2 groups and the non-equivalence of the protons in each; (2) the shift of the signals of all the protons towards stronger fields compared with the σ-allyl complexes, particularly for *trans*-protons; (3) a sharp reduction of the J_{HH} (*cis*) and J_{HH} (*trans*) constants.

At a fairly low temperature, the PMR spectrum [91] of C_3H_5Li resembles the spectra of the π-allyl complexes of transition metals (Table 3). It consists of three signals and corresponds to the AK_2X_2 spin system. All the necessary spectroscopic criteria of the delocalised bonds were observed: the equivalence of the CH_2 groups, the non-equivalence of the *cis*- and *trans*-protons, and the lowering of the constants J_{HH} (*cis*) and J_{HH} (*trans*). The only difference between the spectra of C_3H_5Li and the π-allyl complexes, for example $(C_3H_5)_4Zr$, consists in the reversal of the positions in the spectrum of the signals due to the *cis*- and *trans*-protons: in contrast to transition metal π-complexes, the *cis*-protons in allyl-lithium are the most screened. Thus one may conclude that, under conditions where the spectrum of allyl-lithium was measured (Table 3), a delocalised bond of type II and not a σ-bond is formed, the metal atom being located symmetrically relative to both CH_2 groups.

Table 3. Comparison of the spectroscopic parameters of zirconium and lithium derivatives with a delocalised allyl–M bond.



Spectrocopic parameters, conditions of measurement		Compound $(C_3H_5)_4Zr$ [36]	Compound C_3H_5Li [91]
δ_H, p.p.m. rel. to TMS	H (A)	5.18	6.38
	H (K)	3.28	1.78
	H (X)	1.90	2.24
J_{HH}, Hz	*cis*	8.5	8.6
	trans	15.5	15.2
Solvent		$CFCl_3$	$[^2H_8]$THF
Temperature		–74°	–87°

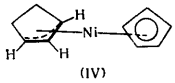
The NMR spectrum of the π-allyl complex becomes significantly simplified after symmetrical substitution in the ligand: substitution of the central proton [1,11,46,47,68,82], substitution of both *cis*-protons by identical groups [80,81,92,93], and substitution of both *trans*-protons with formation of a π-enyl ring [47,51,78,83,84,94–96]. The chemical shifts and the spin–spin coupling constants of the remaining protons in general differ little from the corresponding values for π-complexes with an unsubstituted ligand.

Table 4. Chemical shifts of cycloheptatrienyl protons.

Compound	Solvent	Temp., °C	δ_H, p.p.m. rel. to TMS H_1	H_2	H_3	H_4	References
$C_5H_5Fe(CO)C_7H_7$	$[^2H_8]$ toluene	–50	2.44	4.32	6.05	5.20	100
	$CDCl_3$		3.08	4.75	6.10	5.15	100
$C_5H_5Mo(CO)_2C_7H_7$	CCl_2F_2–$[^2H_8]$ toluene	–107	1.13	3.76	6.20	5.19	101
	$CHCl_2F$	–118	2.32	4.59	6.50	5.40	101
	$CHCl_2F$ $[^2H_8]$ toluene	–118	2.00	4.37	6.36	5.36	101
	$CFCl_3$–CS_2	–110	2.10	4.27	6.0	5.0	102
$Co(CO)_3C_7H_7$	CF_2Cl_2	–140	3.50	4.95	~6.5	~5.8	102
C_7H_8			2.19	5.27	6.09	6.51	103

We may note a characteristic feature of the π-enyl complexes associated with the sensitivity of the spin–spin coupling constants to ring size [97–99]. The J_{HH} (*cis*) constants for π-enyl rings are lower than those for the non-complex molecules, as can be seen from a comparison of

the corresponding values, for example, for compounds (IV) and (V). However, the absolute values of these constants are significantly lower for both types of compounds than in the case of open-chain systems—π-allyl complexes and olefins[78,96]. Thus the J_{HH} (*cis*) constants for the π-enyl complexes may not fall in the range of values found for the π-allyl compounds:



(IV)



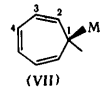
(V)

$J_{HH}(cis)$ = 2.7 Hz (Ref.96) $J_{HH}(cis)$ = 5.4 Hz (Ref.97)

For certain stereochemically non-rigid cycloheptatrienyl molybdenum and cobalt compounds (Table 4), the existence of a π-allyl bond has been postulated [structure (VI)] [104-106]:



(VI)



(VII)

However, recent studies[101,102], including one on the corresponding iron derivative[100], show that at fairly low temperatures the NMR spectra of these compounds agree better with the instantaneous formation of a C_7H_7-M σ-bond [structure (VII)]: the aliphatic proton proves to be most highly screened and the chemical shifts of each of the three pairs of olefinic protons are similar to the corresponding values for cycloheptatriene. To resolve this contradiction, it is evidently necessary to carry out structural studies. However, it should be emphasised that discrepancies between the actual structures of organometallic compounds and those expected on the basis of the effective atomic number rule are being increasingly observed. This can be illustrated, for example, by the structure of the indenyl compound of samarium for which NMR data indicate a localised C–Sm σ-bond[31], although a delocalised π-bond had been suggested, by analogy with the corresponding cyclopentadienyl derivatives of the lanthanides.

IV. PROTON SCREENING IN π-ALLYL COMPLEXES

A shift of the PMR signals to the "aliphatic" region of the spectrum is observed on formation of π-complexes by aromatic and olefinic ligands of a wide variety of types[107]. Since the effect itself has not so far been fully interpreted quantitatively, its discussion for π-allyl compounds must be restricted to certain qualitative considerations. As usual[34,90], it is natural to assume that the magnetic screening of protons is determined mainly by the relation between two factors: the simultaneous effect of the anisotropy of the magnetic susceptibility of the adjacent atoms and bonds and the changes in electron density at the given hydrogen atom.

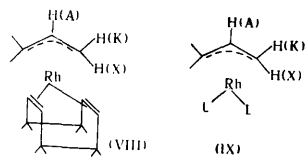
The effect of the anisotropy of the magnetic susceptibility on the screening of protons in the π-allyl ligand may include both the effect of the magnetic anisotropy of the ligand itself and the effect of the transition metal atom and other groups bound to it. One of the main causes of the shift towards stronger fields of the signals due to the protons in olefinic derivatives on formation of π-allyl compounds is the change in the magnetic anisotropy of the multiple bonds on complex formation[108].

The magnetic anisotropy of the double bond, which leads to a shift of the proton signal towards weaker fields compared with its "true" position (i.e. when only local screening is taken into account), is known[34,90] to make a considerable contribution to the screening of olefin protons. On formation of the π-allyl complex the contribution of this effect diminishes, which is shown in the spectra by a shift of the signals of the protons investigated towards stronger fields, although their screening then merely approaches the "true" value.

The magnetic anisotropy of the transition metal, particularly the presence in the latter of filled *d* levels, can have a significant effect on the screening of the protons of the coordinated ligand. This effect is clearly revealed by the fact that in all π-allyl complexes the *trans*-protons located close to the transition metal atom are screened more than the *cis*-protons. This type of feature is not characteristic only of allyl-lithium (Table 3), where a non-transition metal is involved in the formation of a delocalised bond[91].

The magnetic anisotropy of other ligands bound to the transition metal atom can also influence the screening of the protons. For example, when the chemical shifts of the protons in two allylrhodium derivatives [(VIII) and (IX), Table 5] are compared, it is evident that the replacement of cyclo-octa-1,5-diene by two triphenylphosphine groups alters the screening of the allyl protons in different ways. Then the central proton is screened to a greater extent, while the terminal protons are in fact descreened, a particularly pronounced effect being observed for *trans*-protons located closest to the source of perturbation. One cause of this behaviour is probably the fact that the effect of the magnetic anisotropy of the triphenylphosphine groups is greater than the effect of cyclo-octa-1,5-diene.

Table 5. Changes in the screening of the protons in the π-allyl derivatives of rhodium as a function of the structure of the compound.



(VIII)

(IX)

$L = P(C_6H_5)_3$

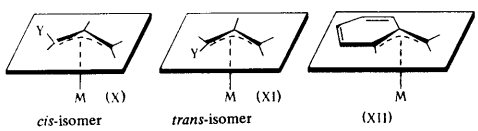
Type of proton	δ_H, p.p.m. rel. to TMS (VIII)(Ref.109)	(IX)(Ref.78)	$\Delta\delta$
H (A)	5.17	4.95	0.22
H (K)	2.65	2.74	−0.09
H (X)	1.67	2.19	−0.42

It follows from the data in Table 2 that in certain cases a shift of the signal due to the protons in the π-allyl ligand towards strong fields, relative to that of the protons of the non-coordinated olefin, reaches 3–4 p.p.m. Such a shift cannot be explained without postulating that, apart from the influence of the magnetic anisotropy of neighbouring atoms and bonds, the change in the local screening of the ligand protons, caused by the partial transfer of electron density from the metal atom to the ligand (M → L), also has a definite effect. This is evidently a reflection of the electropositive nature of the metal compared with carbon atoms. Unfortunately, it is very difficult to isolate this factor against the background of the experimentally observed overall effect.

It is quite likely that the displacement of electron density from the metal to the ligand is accompanied by its non-uniform distribution in the π-allyl group. Possibly this is why in the complexes examined the central proton proves to be least screened compared with others. A more pronounced screening of the terminal protons may be evidence of an enhanced electron density at the corresponding carbon atoms. Consequently, if electrophilic substitution reactions involving a π-allyl ligand are discovered, the point of attack in such reactions will be primarily the terminal carbon atoms. However, in choosing model systems for such reactions, it is necessary to observe certain conditions. Such models must evidently be characterised not only by the presence of an excess electron density in the ligand but also by a fairly pronounced inertness of the molecule towards possible competing reactions (a strong allyl–M bond, the absence of labile M–halogen bonds, etc.). It may be that in fact an unsuitable choice of models is the reason why all known attempts to achieve electrophilic substitution in a π-allyl ligand (see, for example, Rubezhov[110]) have so far proved unsuccessful.

V. ASYMMETRIC ALLYL COMPOUNDS WITH A DELOCALISED BOND

Like any other symmetrical system, a π-allyl complex may lose, as a result of some perturbation, the plane of symmetry γ passing through the metal and the central carbon atom [structure (III)]. As a result, the two "arms" of the π-allyl ligand may become non-equivalent. One may point to several sources of perturbation, which lead to a non-uniform distribution of electron density in a π-allyl ligand. In the simplest case this is a substituent Y joined to one of the terminal carbon atoms [structures (X) and (XI)].



An asymmetric π-complex of this type, crotylcobalt tricarbonyl, was investigated by the NMR method earlier than others[111]. Subsequently many other asymmetric π-allyl complexes were described[41,55,66,76,112–116]. Some of them are listed in Table 6. Lithium derivatives with asymmetric allyl ligands are also known[117].

It follows from the data in Table 6 that in the complexes under consideration the *trans*- (and *cis*-) protons of the same ligands can have different chemical shifts and somewhat different constants for spin–spin coupling to the central proton (Fig. 3).

The π-benzyl and π-thienyl derivatives of a number of transition metals constitute an interesting class of asymmetric π-allyl complexes[3,25,118,119]. In these compounds asymmetry is an inseparable property of the molecules: three carbon atoms of the ligand form with the metal a delocalised π-allyl bond in such a way that one of its "arms" belongs to the ring [structure (XII)]. At a low temperature, when the geometry of these compounds is fixed, the protons of the CH_2 group are non-equivalent. In particular in π-$C_6H_5CH_2Mo(CO)_2$–π-C_5H_5 the chemical shifts of these protons at −30°C differ approximately by 1 p.p.m. The proton on the part of the ring involved in the π-allyl bond becomes much more screened than the others and acquires a chemical shift uncharacteristic of aromatic protons [δ = 5.2 p.p.m. for π-$C_6H_5CH_2Mo(CO)_2C_5H_5$]. Because of the structural characteristics of molecules of this class, there is only one piece of spectroscopic evidence for the asymmetry—the difference between the screening of the two *trans*-protons.

Groups external to the allyl ligand and also the low symmetry of the entire molecule can also give rise to the asymmetry of the π-allyl ligand. However, in compounds where these factors may operate, the possibility or impossibility of asymmetry is not evident in all cases. We shall examine two examples of the occurrence of asymmetry of this type in π-allyl complexes of two classes—planar square and octahedral complexes.

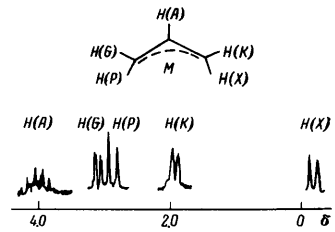
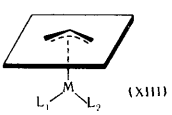


Figure 3. NMR spectrum of the compound (π-$C_3H_5)_4Mo$; four equivalent asymmetric π-allyl ligands (AGKPX spin system)[41].

Complexes of the platinum group metals (XIII) have been investigated fairly comprehensively. When $L_1 = L_2$ [for example, $(C_3H_5PdCl)_2$, [46,47,66,93] $(C_3H_5NiBr)_2$, [75] etc.], they have a spectrum of the AK_2X_2 type, characteristic of a symmetrical π-allyl ligand. Evidently asymmetry may arise only when the substituents are non-equivalent ($L_1 \neq L_2$), which leads to the corresponding non-equivalence of the *cis* and *trans*-protons and the appearance in the spectrum of five signals of equal intensity (AGKPX spin system).



However, the possibility of asymmetry is not realised in all cases (Table 6). For example, when the groups L_1 and L_2 do not differ very much in their electronic effects, the spectrum characteristic of symmetrical complexes is maintained. As already stated, the chemical shifts of protons may be influenced not only by changes in electron density but also by the magnetic anisotropy of adjacent groups. In many cases the asymmetry of the allyl group is due precisely to this factor. For example, the spectra of compounds C_3H_5PdClL correspond to the symmetrical allyl group (AK_2X_2) [66] when L = dimethyl sulphoxide (DMSO) and to an asymmetric ligand (AGKPX, Table 6) when $L = E(C_6H_5)_3$ (E = P, As, or Sb), whose basicity is close to that of dimethyl sulphoxide. Probably in this case the magnetic anisotropy of the aromatic rings of the substituents is in fact of decisive importance.

When the π-complexes have an octahedral structure, the number of situations favouring asymmetry is much greater.

For example, we shall consider the conditions under which the π-ligand in derivatives of the type $(\pi\text{-}C_3H_5)_2ML_1L_2$ (Table 7) may become asymmetric.

If the compound has the *trans*-configuration and the ligands L_1 and L_2 are identical or different, then both allyl groups must be symmetrical and equivalent. Correspondingly the NMR spectrum should show only one set of signals associated with the spin system AK_2X_2. For the *cis*-configuration of the molecule and identical ligands L_1 and L_2, the terminal CH_2 groups of both equivalent allyl ligands become non-equivalent. In consequence, the NMR spectrum should show a group of signals of the system AGKPX, characteristic of an asymmetric π-allyl ligand. Such a spectrum was observed, for example, in the study

Table 6. Parameters of the NMR spectra of metal derivatives with an asymmetric π-allyl–M bond.

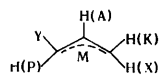
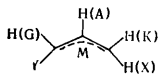
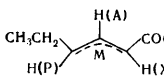
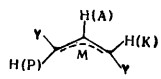
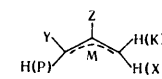
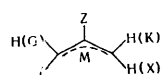
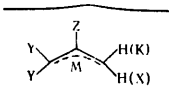
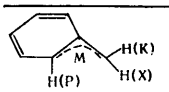
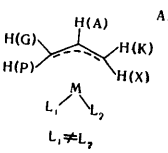
Type of molecule and type of spectral system of allyl component of spectrum	Compound	δ_{HH}, p.p.m.rel. to TMS			J_{HH}, Hz		Conditions of measurement (solvent, temp., °C)	References
		H(A)	H(G,K) (*cis*)	H(P, X) (*trans*)	*cis*	*trans*		
Source of perturbation in allyl group								
 AKPX	(1-ClCH$_2$C$_3$H$_4$PdCl)$_2$	5.45	4.02	3.03(X)	6.9	12.0	CHCl$_3$	46
	1-CH$_3$C$_3$H$_4$Co(CO)$_2$P(π-C$_3$H$_5$)$_2$	4.42	2.17	2.60(P) 1.35(X)	6.2	10.4 9.0	C$_6$D$_6$	115
 AGKX	1-CH$_3$C$_3$H$_4$Co(CO)$_2$				7.1 6.8	12.3		81
	1-CH$_3$C$_3$H$_4$Rh[P(C$_6$H$_5$)$_3$]$_2$	~4.9	3.35(G) 2.47(K)	2.01	6 6.9	14.0	C$_6$H$_5$Cl 30	78
	1-ClC$_3$H$_4$Co(CO)$_2$	5.99	4.68 3.35	2.38	8	11		1
 APX	1-C$_3$H$_5$-3-COC$_6$H$_5$C$_3$H$_3$Mn(CO)$_4$	5.77		3.59(P) 3.13(X)		10.1 10.0	CDCl$_3$	120
 AKP	1,3-(CH$_3$)$_2$-C$_3$H$_3$Co(CO)$_2$				7.2	11.3		81
 KPX	(1-CH$_2$-2-Cl-C$_3$H$_3$PdCl)$_2$	—	4.04	3.05	—	—	CDCl$_3$	68
	(1-t-C$_4$H$_9$-2-CH$_2$C$_3$H$_3$PdCl)$_2$		3.62	2.67(P) 3.48(X)	—	—		121
 GKX	(1-t-C$_4$H$_9$-2-CH$_2$C$_3$H$_3$PCl)$_2$	—	4.44	3.87(P) 3.47(X)	—	—		121
 KX	[1,1(CH$_3$)$_2$-2-ClC$_3$H$_2$PdCl]$_2$	—	4.18	3.44				68
	π-C$_5$H$_5$CH$_2$Mo(CO)$_3$C$_5$H$_5$	—	2.82	1.81(X) 5.2(P)			CFCl$_3$, —30	3
Source of perturbation outside allyl group								
 AK_2X_2	C$_3$H$_5$PdCl·DMCO	5.81	4.29	3.43	6.7	11.6	CDCl$_3$ —20	66
	C$_3$H$_5$NiBr·P(C$_6$H$_5$)$_3$	5.1	3.38	2.45	6.5	14.5	C$_6$H$_5$Cl 30	62

Table 6 (contd.).

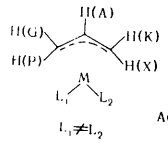
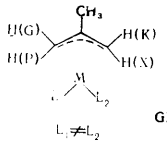
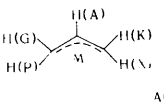
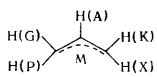
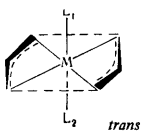
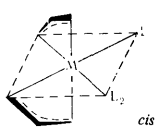
Type of molecule and type of spectral system of allyl component of spectrum	Compound	δ_{HH}, p.p.m.rel. to TMS			J_{HH}, Hz		Conditions of measurement (solvent, temp., °C)	References
		H(A)	H(G,K) (*cis*)	H(P,X) (*trans*)	*cis*	*trans*		
 AGKPX	$C_3H_5PdCl\cdot P(C_6H_5)_3$	5.58	4.69 3.07	3.70 2.82	6.0 7.0	12.0 13.5	$CDCl_3$, —30	66
	$C_3H_5PdCl\cdot As(C_6H_5)_3$	5.50	4.70 3.25	3.65 2.83	6.0	13.5 11.5	$CDCl_3$, —50	66
	$C_3H_5NiCH_3\cdot P(C_6H_5)_3$	5.00	3.61 2.88	2.71 1.91				76
 GKPX	$2\text{-}CH_3C_3H_4PdCl\cdot As(C_6H_5)_3$	—	4.54 3.82	3.57 2.78	—	—	$CDCl_3$, —72	122
	$2\text{-}CH_3C_3H_4PdCl\cdot P(C_6H_5)_3$	—	4.52 2.85	3.59 2.79	—	—	—20	112 116
	$2\text{-}CH_3C_3H_4PdSnCl_3\cdot P(C_6H_5)_3$		4.48	3.32				
 AGKPX	$(C_3H_5)_4Mo$	4.08	3.11 1.93	2.88 —0.20	8.5 9.1	11.5 13.3	$CDCl_3$, 30	41
	$[(C_3H_5)_2RhCl]_2$	4.76	5.08 2.50	4.02 1.82	6.0 6.8	10.8 12.0	$CDCl_3$, —20	113
	$(C_3H_5)_2Fe(CO)_2$	4.16	2.04 3.13	1.01 1.90	6.5	12.3	$[(CH_3)_3Si]_2O$, —67	49
	$(C_3H_5)_2Ru(C_8H_{12})$	~4.2	4.79 1.70	3.65 —0.03	6	12.0 10.5	$CDCl_3$, 34	123
	$(C_3H_5)_2RhCl\cdot As(C_6H_5)_3$,	5.02	4.50 1.88	3.13 0.71	6.0 7.0	10.3 11.5	$CDCl_3$, 30	41
	Two types of asymmetric π-allyl groups	4.46	4.27 3.54	3.22 2.91	5.8 7.2	11.0 11.6		

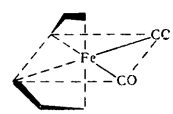
Table 7. Structure and suggested NMR spectra of the compounds $(\pi\text{-}C_3H_5)_2ML_1L_2$.



Structure of compound			
geometrical configuration	characteristics of L_1 and L_2	Characteristics of π-allyl groups	Suggested type of NMR spectrum
 *trans*	$L_1 = L_2$	two equivalent symmetrical allyl ligands: H(G) = H(K), H(P) = H(X)	AK_2X_2
	$L_1 \neq L_2$	ditto	AK_2X_2
 *cis*	$L_1 = L_2$	two equivalent asymmetric allyl ligands: H(G) ≠ H(K), H(P) ≠ H(X)	AGKPX
	$L_1 \neq L_2$	two non-equivalent asymmetric allyl ligands: H(A) ≠ H (A'), H(G) ≠ H (G'), H(K) ≠ H (K'), H(P) ≠ H (P'), H(X) ≠ H (X')	AGKPX + +A'G'K'P'X'

of $(\pi\text{-}C_3H_5)_2Ru\text{-}\pi\text{-cyclo-octa-1,5-diene}$[123] and $[(\pi\text{-}C_3H_5)_2RhCl]_2$ at a temperature below −20°C.[113]

In turn the observation of the spin system AGKPX in the spectrum of the compound $(\pi\text{-}C_3H_5)_2ML_1L_2$ with $L_1 = L_2$ may be regarded as evidence for the *cis*-arrangement of the allyl group. Such a case probably occurs in the $(\pi\text{-}C_3H_5)_2Fe(CO)_2$ molecule[49]: at −67°C the spectrum corresponds to the system AGKPX (the alternative description of the spectrum by two AK_2X_2 sets in which the screening of the central protons of two types of allyl groups is fortuitously identical is less likely) which permits the assignment to the compound of the *cis*-structure (XIV):



(XIV)

The spectrum is most complex for the *cis*-configuration with $L_1 \neq L_2$, since in this structure both asymmetric π-allyl groups become non-equivalent. In the spectra of such compounds two sets of signals of the AGKPX system should be observed. This type of situation has indeed been observed in a spectroscopic study of $(\pi\text{-}C_3H_5)_2RhClAs(C_6H_5)_3$ and similar compounds[41].

The number of examples may be increased. Thus the application of the double resonance technique makes it possible to establish[41] that in $(C_3H_5)_4Mo$ there are four asymmetric and equivalent π-allyl ligands (Fig. 3). However, it is much more difficult to arrive at a conclusion concerning the structure of this compound.

Examination of the spectroscopic data for allyl derivatives with asymmetric ligands shows that, despite the appreciable differences in screening, these complexes retain all the spectroscopic features of the π-structure: the screening of the central proton does not alter significantly; the signals of the *trans*-protons are as a rule located in the region of stronger fields than those of *cis*-protons; the constants J_{HH} (*cis*) and J_{HH} (*trans*) differ significantly from one another and are of the same order of magnitude as for asymmetric π-complexes.

The idea of the possible formation of asymmetric π-allyl compounds has been most clearly formulated only in the last two or three years [41,66,67,76,82,113,124,125]. At one time these derivatives were classified as compounds with a mixed bond type – the so called π, σ-complexes [structure (XV)] [58,68,112,126]. However, subsequently this view met certain objections [48,113,125].



(XV)

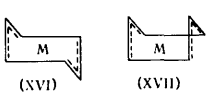
In this connection, it is necessary to emphasise that the available NMR spectroscopic data indicate only a certain asymmetry in the distribution of electron density in a delocalised allyl – M bond, while the π-structure is retained. There are no data indicating a more far-reaching rearrangement of these compounds, including the formation of complexes of the π, σ-type.

VI. ISOMERISM OF π-ALLYL COMPLEXES

The characteristics of the π-allyl bonds, the considerable coordinating capacity of transition metals, and finally the retention under certain conditions of a stable steric orientation of the π-allyl ligand relative to the coordination centre are all factors which give rise to a great variety of π-allyl complexes. In recent years quite a number of examples of different types of isomerism and non-equivalence of allyl ligands have been found with the aid of NMR spectroscopy.

The simplest type is the *cis – trans* isomerism in complexes with asymmetric π-allyl ligands [structures (X) and (XI)]. Isomers of this kind are known for many metals and may be successfully identified by NMR methods even in mixtures [78,81,111,114,121].

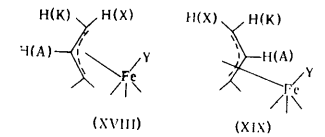
An interesting type of isomerism was observed in the study of the derivatives $(\pi\text{-allyl})_2M$ (M = Pd, Ni, or Pt, i.e. metals capable of forming planar square complexes). Two sets of signals (due to the AK_2X_2 spin system for the unsubstituted ligand and K_2X_2 for the ligand substituted at the central carbon atom) have been found in the NMR spectra of these compounds in proportions depending on the metal, temperature, the nature of the medium, and the substituent at the central carbon atom [36,42,53,127–130]. This phenomenon was explained by the fact that such compounds may exist in solution not only in form (XVI), characteristic of the solid state [88], but also in the isomeric form (XVII) [127]:



(XVI) (XVII)

The rotational isomers of the compounds $C_3H_5Fe(CO)_3Y$ (Y = Cl, Br, I, or NO_2) have been investigated [59]. In the crystal such molecules have the structure (XVIII) [131]. Therefore the NMR study of their solutions shows, with increasing electronegativity of Y (I < Br < Cl < NO_2), a shift towards weaker fields of the signals due to the H(A) and H(K) protons most remote from the substituent (Table 8). This behaviour is not shown solely in the case of *trans*-protons H(X), the screening of which is determined not only by the electron density at the terminal carbon atoms but also by the influence of the magnetic anisotropy of the nearest substituent. In the spectra of compounds with Y = halogen, less intense signals of another isomer, which according to the authors has the structure (XIX), were found in addition to the signals due to the isomer (XVIII). In the spectra of these isomers a shift towards weaker fields with increasing electronegativity of Y is observed for signals of the *cis*- and *trans*-protons and corresponds, in accordance with structure (XIX), to signals of the central proton H(A). The content of the isomer in the mixture depends appreciably on the steric hindrance due to the substituent Y: for Y = NO_2, the isomer does not exist.

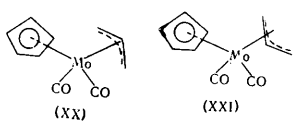
Table 8. Chemical shifts of protons of different types in the compounds $C_3H_5Fe(CO)_3Y$ (according to data of Nesmeyanov et al. [59]).



(XVIII) (XIX)

Y	δH p.p.m. rel. to HMDSO*						Solvent
	H (A)	H(K) (*cis*)	H(X) (*trans*)	H (A)	H(K) (*cis*)	H(X) (*trans*)	
	XVIII			XIX			
I	4.55	4.13	3.77	5.90	3.75	2.24	CCl_4
Br	4.85	4.28	3.41	5.7	3.94	2.58	CS_2
Cl	5.11	4.48	3.21	5.80	4.22	2.63	$CDCl_3$
NO_2	5.31	4.70	2.63	—	—	—	$CDCl_3$

An analogous situation was observed in the NMR spectra of the compounds π-allyl – $Mo(CO)_2$ – π-C_5H_5. [13,52] It was found that the relative amounts of the isomers (XX) and (XXI) depend on steric factors determined by the substituent at the central carbon atom of the allyl ligand:



(XX) (XXI)

An interesting example of the non-equivalence of allyl ligands was observed in the study of triallylrhodium. It was found that at a low temperature (−74°C) the three symmetrical allyl ligands are non-equivalent (in the spectrum there are three groups of AK_2X_2 signals in proportions of 1 : 1 : 1). [38] It was suggested (following Green and Nagy [132]) that each ligand occupies two coordination sites and thus the triallylrhodium molecule may have the form of a trigonal prism or an octahedron [38,40].

VII. STEREOCHEMICAL NON-RIGIDITY OF ORGANOMETALLIC ALLYL COMPOUNDS.

The advances of organometallic chemistry in the last decade led to the synthesis of a multiplicity of compounds of most varied and sometimes unexpected types. Among these, there are quite a few systems where stereochemical non-rigidity was observed or is possible in principle. The terminological aspect of this problem has not yet been clearly resolved. Therefore we shall adopt the convention that the concept "stereochemical non-rigidity" will be applied to two basic types of intramolecular rotation (recognising, of course, the non-rigorous nature of such subdivision in many cases): intramolecular rotation and metallotropy.

For organometallic compounds, including allyl derivatives, it is possible to indicate several types of intramolecular motion, which are analogous to those in the usual organic derivatives, for example rotation about the C–M σ-bond in σ-allyl compounds. However, there is a possibility in principle also of processes specific to organometallic compounds, the nature of which is fairly difficult to predict and the study of which provides much information about the structure and properties of such compounds. In the classification of intramolecular dynamic processes in organometallic allyl compounds it is most natural to use as a basis the spin system of the allyl component of the NMR spectrum.

1. INTRAMOLECULAR ROTATION.

a. Processes with Retention of the AK_2X_2 Spin System.

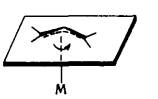
We shall isolate in a separate group those cases where in a certain temperature range the spin system of the allyl part of the spectrum is not simpler than AK_2X_2. One should evidently include here both asymmetric derivatives where the asymmetry of the allyl ligands disappears with increasing temperature (in the sense AGKPX → AK_2X_2) and compounds with a symmetrical C_3H_5–M bond in which the dynamic process is accompanied by the retention of the formal AK_2X_2 spin system.

For example, it is possible to assign to this group the asymmetric complex $[(C_3H_5)_2RhCl]_2$ in the spectrum of which the four separate signals due to each of the four terminal protons merge into two pairs of signals as the temperature is raised from −20° to 90°C. Under these conditions, there is hardly any change either in the position in the spectrum or the form of the signal due to the proton attached to the central carbon atom of the allyl ligand[41]. Apparently an analogous phenomenon is observed in the NMR spectrum of the compound $(C_3H_5)_2Fe(CO)_2$: on raising the temperature from −67° to 20°C, the set of signals of the AGKPX spin system is transformed into the set of signals of the AK_2X_2 system[49].

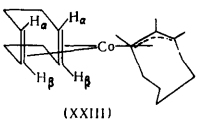
Compounds of the type $2\text{-}RC_3H_5Mo(CO)_2C_5H_5$ (R = H, CH_3, etc.) constitute stereochemically non-rigid systems where the temperature-dependent spectroscopic changes are accompanied by the retention of the spin system. Probably at temperatures exceeding 80–90°C the rate of mutual transformations of the isomers (XX) and (XXI) increases so much that each can no longer be observed spectroscopically as a separate entity. As a result the spectrum contains no longer two but only one set of signals of the AK_2X_2 system[52,53]. Allyl compounds of molybdenum with a more complex structure were examined by Trofimenko[133].

An analogous phenomenon was observed[31] in the study of the spectra of triallylrhodium. The signals of the protons in two of the three nonequivalent π-allyl groups merged into a common system of lines on raising the temperature from −67° to 10°C. In the case of diallylnickel a change in temperature affected the NMR spectrum in such a way that, on transition from −40°C (in $CDCl_3$) to 60°C (in benzene), the ratio of the intensities of the two groups of AK_2X_2 signals associated with the isomers (XVI) and (XVII) gradually changed from 3 : 1 to 2.2 : 1. [36]

The stereochemically non-rigid systems considered have a common characteristic. Neither the removal of the asymmetry of the π-allyl ligand in one isomeric form {in $[(C_3H_5)_2RhCl]_2$ and $(C_3H_5)_2Fe(CO)_2$, etc.} nor the mutual transformation of the isomers [(XX) and (XXI), (XVI) and (XVII), etc.] is accompanied by the equalisation of the chemical shifts of the *cis*- and *trans*-protons. The dynamic process satisfying this condition may be only the rotation of the π-allyl group about the axis joining the metal atom to the central carbon atom of the ligand [structure (XXII)]. This type of process was observed for the first time by Becconsall and O'Brien[38] in a study of the temperature variation of the triallylrhodium spectrum:



(XXII)



(XXIII)

It must be emphasised that this type of dynamic process was observed for derivatives of significantly different transition metals: rhodium, iron, molybdenum, and nickel. It is quite possible that it occurs also in many other π-allyl compounds, but is observed only in those few systems where there are structural factors which retard it and make possible its spectroscopic study. The compounds investigated exhibit in this sense a similarity with complexes where there is a C_nH_n–M π-bond (C_nH_n is a cyclic ligand with n = 4, 5, 6, or 7) and in which the rotation of the ligand about the n-fold axis has been reliably established.

We may quote an opposite example. In the spectrum of π-cyclo-octenyl-π-cyclo-octa-1,5-diene derivative of cobalt (XXIII) the α- and β-protons of the diene ligand are magnetically non-equivalent in the temperature range between −88° and 60°C. [85] The most acceptable explanation of this finding is that there is no rotation about the π-enyl–cobalt bond. However, we may note that in the spectrum of $\pi\text{-}C_3H_5$–Rh–π-cyclo-octa-1,5-diene the signals of all the diene protons are equivalent[109].

b. Processes with Degeneration of the Spin System to AX_4.

All the compounds in which the allyl component of the NMR spectrum is simplified on raising the temperature to such an extent that the *cis*- and *trans*-protons become indistinguishable ($AK_2X_2 \rightarrow AX_4$) will be assigned to this group of stereochemically non-rigid allyl systems. This type of phenomenon was observed[36,37,44,124], for example, in the NMR spectrum of tetra-allylzirconium. While at a low temperature (−74°C) the spectrum has a form characteristic of a π-allyl complex with symmetrical ligands (AK_2X_2 spin system), on raising the temperature the doublets due to the *cis*- and *trans*-protons initially broaden, then approach one another, and finally merge at −40°C, the width of the signal in the transition region being independent of the concentration of the compound[124]. When the temperature is raised further to −10°C, the signal, which is now associated with all four terminal protons, consists of a distinct doublet, while the signal due to the central proton consists of a quintet (at a low temperature this is a nonet) (Fig. 4). Thus at −10°C the spectrum already belongs to the AX_4 spin system. This shows that under such conditions the terminal protons of all the allyl groups of tetra-allylzirconium are equivalent. The following factors are important for the understanding of the mechanism of this process: (1) when the spectrum changes from AK_2X_2 to AX_4, the screening of the central proton remains unchanged; (2) at −10°C the doublet due to the terminal protons occupies a position in the spectrum intermediate between those of the doublets of the *cis*- and *trans*-protons in the low-temperature spectrum; (3) the

$J_{H(A)-H(X)}$ coupling constant for the AX_4 spectrum is equal to half the sum of the constants J_{HH} (*cis*) and J_{HH} (*trans*) for the AK_2X_2 spectrum.

An analogous spectral pattern was observed in the study of certain other symmetrical allyl derivatives with a delocalised C_3H_5-M bond: tetra-allylthorium (AK_2X_2 at 10°C and AX_4 at 80°C) [37], tetra-allylhafnium (the AX_4 spin system is already observed at −72°C) [36], and allyllithium (the $AK_2X_2 \rightarrow AX_4$ transition occurs at about −87°C) [91]. Above 90°C the $AK_2X_2 \rightarrow AX_4$ transition is also observed in the spectrum of the compound $[(C_3H_5)_2RhCl]_2$ but this is probably a not altogether apt example, since the pattern may be complicated by the dissociation of the Rh−Cl bond[41].

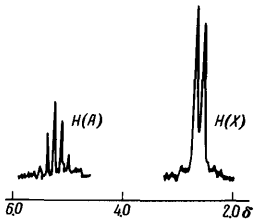
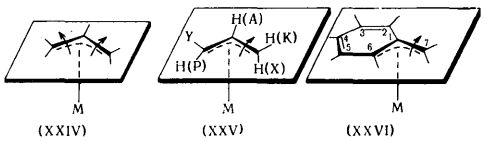


Figure 4. NMR spectrum of the compound $(\pi\text{-}C_3H_5)_4Zr$ at −20°C (AX_4 spin system)[36].

The averaging out of the chemical shifts of the *cis*- and *trans*-protons and of the spin−spin coupling constants has been frequently observed also in the NMR study of asymmetric derivatives with a delocalised allyl−M bond, in particular in the study of the phenylallyl compounds of alkali metals[117]. Thus on raising the temperature the distinct signals associated with the two H(K) and H(X) protons, non-equivalent at 5°C in the $1\text{-}C_6H_5C_3H_4Li$ spectrum, begin to broaden and gradually approach one another and at 90°C become spectroscopically indistinguishable, the process being reversible [structure (XXV)]:



(XXIV) (XXV) (XXVI)

Probably the temperature-dependent averaging out of the chemical shifts of the *cis*- and *trans*-protons is determined to some extent by the 1.5 bond order of the delocalised allyl−M bond. It may be supposed that the degree of its double-bond character will be variable and will depend on the nature of the substituent in the ligand and at the metal, on the electron-donating capacity of the metal, and many other factors. Thus under certain conditions the 1.5 order of the delocalised bond can apparently only hinder internal rotation about the C⋯C bonds but cannot prevent it altogether.

Thus the temperature-dependent effects observed in the study of the NMR spectra of the allyl compounds under consideration may be caused entirely by changes in the rate of internal rotation of the CH_2 groups about bonds joining them to the central carbon atom [structures (XXIV) and (XXV)] [36,37,124]. It is useful to note that such effects have so far been observed in compounds of both transition (zirconium and thorium) and non-transition (lithium) metals, where on formation of a delocalised bond the *d* electrons of the metal cannot participate in the formation of dative bonds with the ligand[37], which would favour the fixation of its position in space relative to the metal atom. In the spectra of the derivatives of many other metals, for which the formation of dative bonds is not excluded, the temperature-dependent changes were not observed {the spectra of $C_3H_5Mo(CO)_4$ at 160°C [48], $(C_3H_5PdCl)_2$ at 150°C [48], $(C_3H_5)_4Mo$ at 170°C [41], and $C_3H_5Rh[P(C_6H_5)_3]_2$ at 130°C [78] have been investigated}.

A reversible change in the allyl component of the spectrum was observed in the study of the π-benzyl derivatives of molybdenum, tungsten, and palladium, [3,25,119]. For example, in $\pi\text{-}C_6H_5CH_2Mo(CO)_2\text{-}\pi\text{-}C_5H_5$ the screening of the CH_2 protons is averaged out when the temperature is raised from −30° to 64°C. There are also corresponding changes in the signals of the phenyl protons. Under these conditions, the average chemical shift of each pair of protons [CH_2-, 2−6, and 3−5; structure (XXVI)] is exactly equal to half the sum of the initial shifts[3]. King and Fronzaglia[3] suggested that this effect is caused by the rotation of the benzyl ligand about the 1−7 axis. They did not exclude also alternative mechanisms, in particular a mechanism with a postulated intermediate formation of a σ-type compound. The latter mechanism has been supported by Cotton and Marks[25]. We may note that in the spectra of certain π-thienyl derivatives of molybdenum no changes were observed in the temperature range between −60°C and 105°C [118].

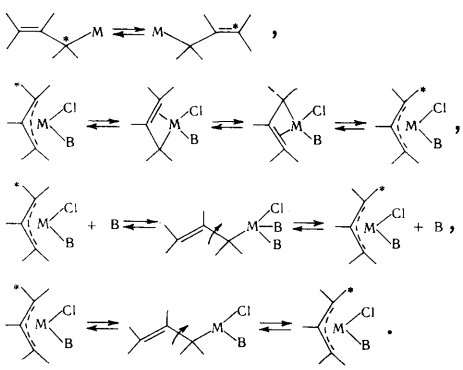
VIII. SPECTRA OF π-ALLYL COMPOUNDS IN THE PRESENCE OF BASES

In 1961 Chien and Dehm[134] observed that, when the solvent is changed (chloroform replaced by dimethyl sulphoxide), the NMR spectrum of $(C_3H_5PdCl)_2$ alters sharply. In the case of an unsubstituted π-allyl ligand this transformation consists of a change of the spin system of the allyl components of the spectrum from AK_2X_2 to AX_4; corresponding changes have also been observed for 1- and 2-substituted allyl groups. Subsequently quite a few papers have been published on these changes, which were observed in the NMR spectra of the π-allyl derivatives of palladium, platinum, rhodium, and other transition metals under the influence of bases (sulphoxides, phosphines, arsines, stibines, etc.)[13,48,62,66,67,69,78,82,112,114,122,124-126,135-139].

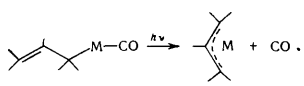
Formally these are the same changes which occur in the spectrum of tetra-allylzirconium on raising the temperature, i.e. the equalisation of the screening of the *cis*- and *trans*-protons is accompanied by a simplification of the spin system of the spectrum ($AK_2X_2 \rightarrow AX_4$ for symmetrical π-allyl derivatives and $AGKPX \rightarrow AK_2X_2 \rightarrow AX_4$ for asymmetric derivatives). In fact the situation is much more complex‡.

‡ In recent years the term "dynamic allyl" [37] has been frequently used in the literature to designate a new (apart from the σ- and π-allyl derivatives) type of allyl compound. Usually this term designates any situation (associated with the solvent, temperature, etc.) which leads to the appearance in the NMR spectrum of an AX_4 spin system. However, examination of the corresponding data shows that a new "dynamic" type of allyl compound does not exist, just as compounds of the π,σ-type apparently do not exist. In fact there is only a group of phenomena, frequently of a different nature, which have the same spectroscopic effect. Therefore further use of the concept "dynamic allyl" does not appear to be justified.

Chien and Dehm[134] suggested that the π-allyl derivatives of palladium are wholly converted into the σ-form on dissolution in a solvating medium and in this form can in fact undergo the rearrangement (1) put forward by Nordlander and Roberts[74] in the discussion of the spectra of the allyl derivatives of magnesium. However, subsequently it was found that mixed compounds of $(\pi\text{-allyl-PdCl})_2$ with dimethyl sulphoxide and other bases (phosphines, etc.), i.e. compounds of the type C_3H_5PdClB, are, in fact not σ- but π-allyl complexes—symmetrical or asymmetric[48,66,112,137]. Therefore the observed effects were explained not by complete transformation of the compound into the σ-form but by the formation of σ- or π, σ-complexes at a very low concentration, which is, however, sufficient to promote the interchange of the *cis*- and *trans*-protons [Eqns. (2)–(4), M = Pd or Ni][48,69,112,125,126]. Moreover, Becconsal and O'Brien[154] pointed out that these effects can be accounted for by rotation about the C–C bond.



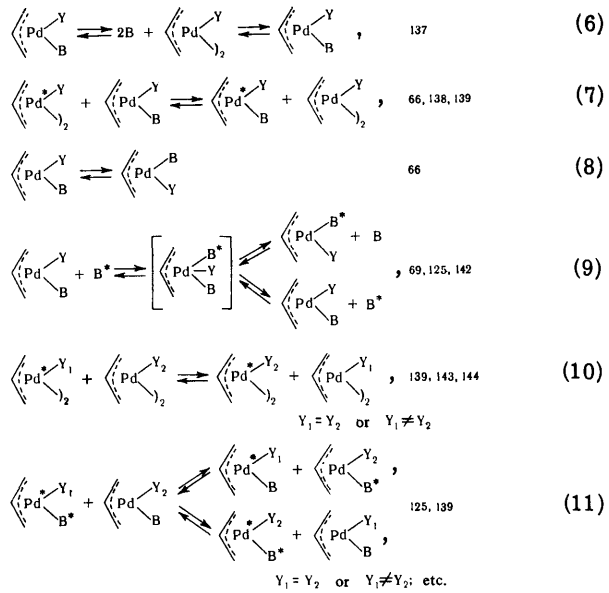
Among the various mechanisms of the rearrangement of the π-allyl derivatives of transition metals to σ- or π, σ-complexes, proposed to account for their spectroscopic behaviour in the presence of bases [Eqns. (1)–(4)], the mechanism of type (3) is particularly successful. Essentially this mechanism represents the π-σ transformation of the molecules investigated with retention of the coordination number of the transition metal owing to the simultaneous formation of an M–B bond and constitutes a special process, the converse of the transformation of the σ-allyl derivatives of iron, manganese, molybdenum, and tungsten into π-allyl derivatives[1,8–10]:



Therefore it might have been expected that the allyl compounds of "pentacoordinate palladium" or nickel isolated in a pure form are in fact σ-complexes. For nickel, such $C_3H_5NiClB_2$ complexes were obtained (B = phosphine or phosphite), but their investigation did not confirm the above hypothesis. It was found that the spectra of derivatives with ligands such as $P(OC_6H_5)_3$ and $P(C_6H_5)_3$ do not differ from those of the corresponding π-allyl derivatives of tetracoordinate nickel: the AK_2X_2 spin system was transformed into AX_4 only in the case where B = $P(C_2H_5)_3$.[62] An analogous conclusion follows from the spectroscopic data for and the structural investigation of other allyl compounds of pentacoordinate nickel[140,141].

Strictly speaking, the spectral spin system AX_4 is too symmetrical to indicate unambiguously any one dynamic process. In principle, several such processes are compatible with a spectrum of type AX_4. Moreover, in solutions of π-allyl derivatives of palladium, nickel, rhodium, and certain other metals in the presence of bases, the exchange reactions (6)–(11) occur or can occur (here M = Pd; X = halogen, SCN, etc.; B = DMSO, phosphine, amine, etc.).

These reactions do not relate directly to π–σ rearrangements and in any case can occur without the participation of allyl–M bonds. However, they can also cause the merging of the signals due to the *cis*- and *trans*-protons in the NMR spectrum[41,66,69,137,143].



It must be emphasised that the structure of the transition state in reactions (6)–(11), their stereochemical results, and similar problems associated with their mechanism have only now begun to be seriously investigated by various procedures including the NMR method[143]. For example, it has been found that the rate of exchange depends on temperature, the concentrations of the π-allyl compound and the base, and other factors. A clear similarity of these compounds (lability of the M–X bonds, their capacity for exchange reactions, etc.) to organic derivatives of non-transition metals, for which exchange reactions have been investigated fairly thoroughly by the NMR method (see, for example, Brown[145]) has also been observed.

Thus the problem of the causes responsible for the changes observed in the NMR spectra of certain π-allyl derivatives of transition metals under the influence of bases remains at present unresolved. Such a cause may be the internal rotation of the allyl ligand about the C–C bond, which is facilitated by the donor–acceptor interaction between the metal and the base. Another cause may be exchange reactions of types (6)–(11). Finally the changes may arise also as a result of π–σ rearrangement, but so far no evidence has been obtained by the NMR method indicating the formation of a σ-complex under the action of bases which would not be susceptible to some other interpretation.

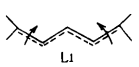
IX. THE NATURE OF THE ALLYL–METAL BOND IN CERTAIN NON-TRANSITION METAL (LITHIUM, MAGNESIUM, ZINC, AND CADMIUM) DERIVATIVES.

According to NMR spectroscopic data, an allyl–Hg σ-bond is formed in allyl derivatives of mercury[17,91,146,147]. Triallylboron below −65°C [14,148] and other allyl compounds of boron[149,150] have similar structures. However, the spectroscopic behaviour of allyl-lithium suggests the formation of a delocalised bond in this compound[91]. In the study of the derivatives of certain other non-transition metals with an allyl–M bond (M = Li, [117,151-153] Mg, [74,154-157] Zn, [158,159] or Cd [160]) it was found that, as in the case of allyl-lithium, close to room temperature the NMR spectrum has an AX_4 spin system for compounds with an unsubstituted ligand and the corresponding spectral pattern for substituted ligands.

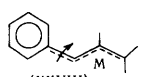
To explain the spectrum of allylmagnesium bromide, Nordlander and Roberts[74] examined three possibilities: (1) the establishment of rapid equilibrium between two σ-structures [Eqn. (1)]; (2) the formation of a structure with a delocalised allyl–M bond in which there is rapid rotation about C–C bonds [structure (XXIV)]; (3) the formation of an ionic bond.

In principle, neither Roberts[161] nor other investigators (see, for example, Lanpher[162]) excluded the possibility of the formation of a delocalised bond of type (II) by non-transition metals. However, since the bond order in such compounds should be greater than unity, Nordlander and Roberts[74] disregarded the second and third possibilities and subsequently interpreted their experimental data only from the standpoint of the formation of a σ-structure undergoing rapid 1,3-transformations [Eqn. (1)]. This view was also adopted by many other investigators[151,153], although in recent years it encountered objections from supporters of the formation of an ionic bond[91,117,158,160].

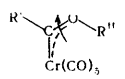
During the last decade extensive data have accumulated in the literature on the NMR spectra of allyl derivatives of transition and non-transition metals. The hypotheses concerning the structures of these compounds have also undergone a definite change. Moreover, experimental spectroscopic studies on organic and organometallic compounds showed that, when the order of the bond under consideration is greater than unity and less than 2, rotation about it is not precluded, for example in the compounds (XXVII), [163] (XXVIII, M = Li), [117] (XXIX) [164], and even in classical olefinic derivatives[165]:



(XXVII)



(XXVIII)



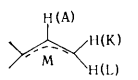
(XXIX)

Therefore it appears necessary to reconsider the possibilities proposed by Nordlander and Roberts[74] and to determine which of them is most acceptable in the light of the available facts.

It has been suggested[91] that in C_3H_5Li the delocalised bond is ionic. Probably this involves some exaggeration. It is known that organic derivatives of lithium do not dissociate into ions. For example, the C_5H_5Li molecule, like C_5H_5Na, has the C_{5v} symmetry and not D_{5h} as might have been expected if it dissociated into ions (a D_{5h} symmetry has been established for C_5H_5M with M = K, Rb, or Cs) [166]. An analogous result was obtained in a study of the Li-NMR spectra of fluorenyl-lithium[167]. In certain organolithium derivatives the metal–carbon bond may be significantly covalent [for example, in a study of the tetramer $(CH_3Li)_4$ it proved possible to observe $^{13}C-^{7}Li$ spin–spin coupling [168,169]]. Thus it is probably more justifiable to speak not of an ionic but of a fairly polarised bond (in the sense allyl$^{\delta-}$–M$^{\delta+}$). Then the allyl derivatives of the metals considered may be discussed from a single standpoint. We shall assume that magnesium, zinc, cadmium, and similar metals, as well as lithium, are capable of forming a delocalised allyl–M bond. We shall also postulate that the delocalised bond in any real compound is always polar to some extent and the degree of its polarity depends on the electropositivity of the metal, the nature of the substituents in the ligand and the metal, the nature of the medium, and other factors.

Apart from the effect of other factors, the steric stability of the allyl–M fragment in transition metal derivatives can be achieved also as a result of the participation of the metal *d* electrons in a dative interaction. For allyl compounds of non-transition metals, such a stabilising factor may be the amount of double-bond character of the C–C bonds of the ligand, which in turn is a function of the electropositive properties of the metal.

Table 9. Chemical shifts of the methylene protons in certain allyl compounds of non-transition metals.



Compound	Solvent	$\delta_{H(K,L)}$	Electronegativity of metal E_M [170]
C_3H_5Li	THF	2.17[91]	1.0
$(C_3H_5)_2Mg$	THF	2.45[157]	1.2
$(C_3H_5)_2Zn$	C_6D_6	2.96[158]	1.6
$(C_3H_5)_2Cd$	THF	2.86[160]	1.7

Table 9 shows that the screening of the terminal protons in non-transition metal derivatives varies in parallel with their electropositivity:

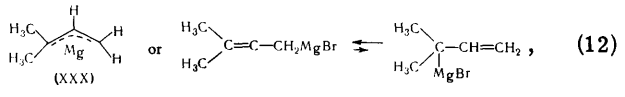
$$\underset{\text{enhancement of screening and the electropositivity of the metal}}{\longleftarrow} \quad Li > Mg > Zn \sim Cd$$

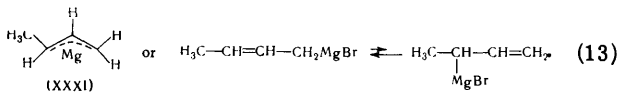
Consequently, the amount of double-bond character in the allyl group should decrease from lithium to zinc and cadmium with a corresponding increase in the rate of internal rotation. The experimental data do not contradict this conclusion. On lowering the temperature to −87°C, "freezing" of internal rotation [structure (XXIV)] is observed in the spectrum of allyl-lithium. Spectroscopically this is shown by a separation of the signals due to the *cis*- and *trans*-protons and in a change of the spin system of the spectrum ($AX_4 \rightarrow AK_2X_2$) [91]. For cadmium and magnesium derivatives, such "freezing" has not so far been achieved even at a lower temperature (diallylmagnesium at −120°C in tetrahydrofuran[157], allylmagnesium bromide at −80°C in ethyl ether[156], and diallylcadmium at −100°C in tetrahydrofuran[160] have been investigated).

Over a wider range of variation of the amount of double-bond character, observations are also consistent with predictions. Thus, while for allyl derivatives of lithium, including asymmetric derivatives[117], internal rotation may be "frozen" by varying the temperature, in

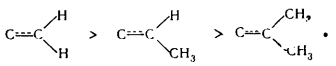
studies on asymmetric allyl derivatives of more electropositive metals [potassium and sodium—structure (XXV)] internal rotation was not observed even at a fairly high temperature[117].

We may note that for allyl compounds of magnesium and cadmium it is possible to raise the "freezing temperature" of the spectral pattern, for example by introducing into the ligand electron-donating substituents capable of increasing the amount of double-bond character of the C—C bonds. This phenomenon was observed, in particular, by Roberts and coworkers[155] in a spectroscopic study of 1,1-dimethylallylmagnesium bromide (XXX): when the temperature is reduced to only −26°C, the splitting of the signal due to the methyl protons into two components, associated with the *cis*- and *trans*-groups, is already observed:





The molecular structures of 1-$CH_3C_3H_4MgBr$ and 1,1-$(CH_3)_2C_3H_3MgBr$ merit special examination. The spectra, investigated by Roberts and coworkers[154,155], are fully consistent with the structures (XXXI) and (XXX) with a delocalised allyl−M bond if it is assumed that the rate of rotation about the bond of order 1.5 varies in the sequence



Roberts and coworkers interpreted the spectra obtained in a different way. They suggested that each of the compounds considered constitutes one of two possible non-equivalent σ-structures, which are interconverted at a high rate. To reconcile this possibility with the observed spectral patterns, it was suggested that equilibria (12) and (13) are almost entirely displaced to the left.

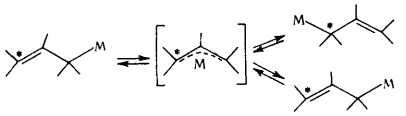
However, whereas previously both possibilities [delocalised structures (XXX) and (XXXI) or equilibria (12) and (13)] might have been regarded as at least equally probable, although only one of them had been considered, further investigations[91,117,163-165] show that there is no justification for rejecting the very possibility of rotation about a C—C bond of order 1.5. There are no other objections to the formation of a delocalised bond. On the other hand, equilibria (12) and (13) are not altogether consistent with the spectroscopic and chemical features of the compounds examined. For example, the NMR spectra undergo hardly any changes when the temperature is reduced [if one disregards the splitting of the signal due to the methyl groups in the spectrum of 1,1-$(CH_3)_2C_3H_3MgBr$], although the screening of the CH_2 protons cannot fail to change under these conditions. The assumption that equilibria (12) and (13) are almost completely displaced to the left over the entire temperature range investigated is inconsistent with the results of the analysis of the decomposition products, for example, butenylmagnesium bromide[161].

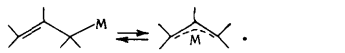
Investigations in the next few years, in particular structural studies by diffraction methods, will show which view is closer to the truth. However, even if the hypothesis of the formation of a delocalised bond in the allyl compounds of lithium, magnesium, zinc, and cadmium is confirmed, there will remain many other problems the solution of which is at present not evident: association of the compounds considered, the role of the solvent in the formation of a σ- or delocalised structure, the relation between the intramolecular and intermolecular bonds, etc.

X. METALLOTROPY IN ALLYL DERIVATIVES OF NON-TRANSITION METALS

It is not claimed that the view put forward in the preceding section is of completely general validity. It merely shows how the possibility of two interpretations (on the basis of the published NMR data) of the structures of the allyl derivatives of magnesium, zinc, and cadmium—with a localised or a delocalised bond—gives rise as a consequence to two interpretations of the dynamic behaviour of these compounds—a metallotropic 1,3-transition [Eqn. (1)] or rotation about the C—C bond of order 1.5 [structures (XXIV) and (XXV)].

Continuing this analysis, we also find it necessary to conclude that the mechanism of metallotropic transformations of those derivatives for which a σ-structure could be reliably demonstrated§ is not also not unambiguous. There are at least two possibilities;





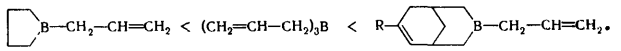
The only difference between them is in fact that in one case the formation of a delocalised bond is suggested in the transition state and in the other in the ground state [Eqns. (14) and (15)].

As a rule the mechanism represented by Eqn. (14) is considered, in particular in the discussion of the NMR spectra of the allyl derivatives of boron[14,150]. It was found that below −65°C the spectrum of triallylboron has an $AKLX_2$ spin system corresponding to the allyl−boron σ-bond. On raising the temperature to room temperature, the signals of both methylene groups become broader and on further increase to 135°C two symmetrical signals of the AX_4 spin system appear. In the high-temperature spectrum the chemical shift of the methylidyne proton H(A) remains virtually unchanged but the form of the signal becomes simplified. The chemical shift of the protons H(X) amounts to approximately half the sum of the shifts of the methylene protons of both types in the low-temperature spectrum ($KLX_2 \rightarrow X_4$). In the study of other allyl derivatives of boron similar changes in the NMR spectrum were found.

Certain characteristics of the rearrangement of the allyl compounds of boron have been elucidated[14,150]. In particular, it has been found that the rate of rearrangement of triallylboron in carbon tetrachloride or cyclohexane is independent of concentration, which indicates that the

§ For example the allyl derivatives of boron[14,148-150], diallylzinc in solvating media at a low temperature[37,171], indenyl derivatives of mercury at −41°C [29] and of tin(IV) at −37°C [30], etc.

rearrangement is intramolecular. Solvating solvents (tetrahydrofuran and in particular pyridine), which are capable of being coordinated to a vacant orbital of boron, appreciably retard the rearrangement. The rate of the process depends also on the structural characteristics of the compound:



These data lead to the suggestion[14] that the 1,3-transition (it can hardly be called metallotropic because boron is not a metal) in allyl derivatives of boron takes place via a transition state with a delocalised allyl–boron bond [Eqn. (14)]. However, it must be emphasised that the available NMR spectroscopic data do not yet allow a distinction to be drawn between a rearrangement of this type and the interconversions of the two forms of the compound considered in which there is a localised or a delocalised bond [Eqn. (15)]. This applies also to the rearrangement of the indenyl derivatives of tin[30], mercury[29], and similar systems. Probably future spectroscopic investigations will demonstrate the reality of both processes or it will be possible to choose between them.

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