by an alkyl substituent. Both elements of symmetry are lost, and a correlation diagram can no longer be constructed by the usual procedure. However, common sense dictates that the reaction must still be forbidden to a first approximation. In terms of the above approach some of the elements in H_A which were previously equal will now be slightly different and the φ_A will now be slightly different combinations of the original basis set atomic orbitals than the φ_B. However, since φ_A and φ_B are formed from the same basis set, a given φ_A can always be written as a linear combination of the φ_B's. Similarly, Ψ_A can be written as a linear combination of eigenfunctions Ψ_B. Evaluation of $\Psi_A\mathcal{H}_B\Psi_A$ will give $aE_0 + bE_1 + cE_2 + \cdots$ where E_0, E_1, $\cdots$ are the ground-state and excited-state energies of the products, respectively. In the present case the coefficient of one of the excited-state energies will be very much larger than all the other coefficients, and this could be interpreted to mean that the reaction is almost forbidden.

This approach can be applied particularly easily to the square-planar substitution reaction considered previously. It has been shown that this reaction leads to rotation of the plane by $\pi/3$. It is more convenient to consider $\Psi_B\mathcal{H}_A\Psi_B$, *i.e.*, to use the final wave functions and the initial Hamiltonian. The wave functions for a $\pi/2$ rotation have been given in Figure 2. Those for a $\pi/3$ rotation can be expressed in terms of the original wave functions and the $\pi/2$ rotated wave functions, *i.e.*

$$\varphi_B = \cos \pi/3\ \varphi_0 + \sin \pi/3\ \varphi_{\pi/2} = \frac{1}{2}\varphi_0 + \frac{\sqrt{3}}{2}\varphi_{\pi/2}$$

Since the $\pi/2$ rotation leads to a forbidden reaction, it is readily shown that

$$\Psi_B\mathcal{H}_A\Psi_B = \frac{1}{4}E_0 + \frac{3}{4}E_1$$

Thus qualitatively the reaction is expected to be slower than the fully allowed tetrahedral substitution (for which $\Psi_B\mathcal{H}_A\Psi_B = E_0$) but faster than the forbidden *cis–trans* isomerization (for which $\Psi_B\mathcal{H}_A\Psi_B = E_1$).

It is unlikely that arguments of this kind will have more than qualitative significance but they may find a place in rationalizing what are at first sight rather puzzling observations such as the greatly enhanced rate of ligand exchange in tetrahedral d^8 complexes compared to square planar. Application of similar arguments to the isomerization and substitution reactions of complexes of higher coordination number is under consideration and will be reported in due course.

Acknowledgment. The author is indebted to Drs. J. P. Jesson and E. L. Muetterties for helpful discussions.

Nuclear Magnetic Resonance Study of Asymmetric π-Allylic Complexes: ((allyl)$_2$RhCl)$_2$, (allyl)$_2$RhCl(C$_6$H$_5$)$_3$P, (allyl)$_2$RhCl(C$_6$H$_5$)$_3$As, and (allyl)$_4$Mo

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Abstract: Nuclear magnetic resonance has been employed to investigate the structures of ((allyl)$_2$RhCl)$_2$, (allyl)$_4$Mo, and (allyl)$_2$RhClL where L = (C$_6$H$_5$)$_3$P and (C$_6$H$_5$)$_3$As. The spectra are of the AGMPX type, corresponding to asymmetric π bonds and indicating that the two terminal carbon atoms of the allyl group are bonded unequally to the metal atom. The nmr parameters, chemical shifts, and coupling constants are listed and discussed in terms of the various structures. The temperature dependence of the spectra yielded further information on the intermediates involved in the conversion of static-to-dynamic systems.

Recent reports[1-12] have shown that nuclear magnetic resonance (nmr) may be utilized to classify allyl metal complexes with respect to symmetry and bonding. Three distinct types have been proposed: (1) symmetrical π, indicated by an AM$_2$X$_2$ spectrum and exemplified by ((allyl)PdCl)$_2$,[4] Ni(allyl)$_2$, Zr(allyl)$_4$, and Pd(allyl)$_2$;[8] (2) σ, indicated by an ABCX$_2$ spectrum, with only two unambiguous examples reported, (allyl)Co(CN)$_5$[11] and (allyl)Mn(CO)$_5$;[12] and (3) dynamic, indicated by an AX$_4$ type and exemplified by numerous examples including substituted allyl compounds[2,13] for

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(1) J. C. W. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961).

(2) J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

(3) K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim.*, **85**, 1077 (1966).

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(6) H. C. Volger and K. Vrieze, *J. Organometal. Chem.* (Amsterdam), **9**, 527 (1967).

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(12) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

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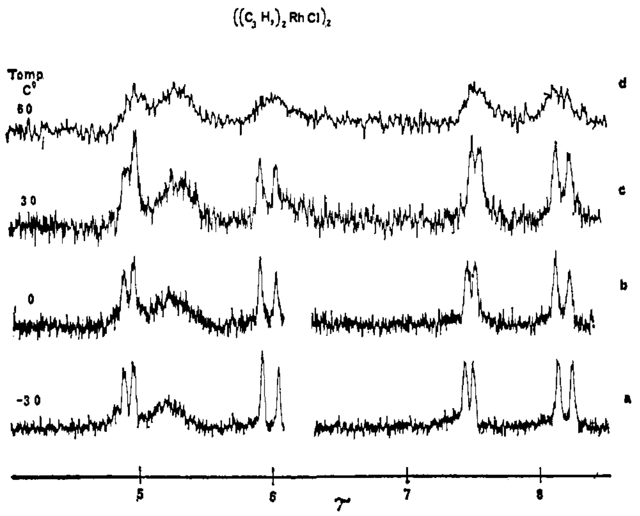
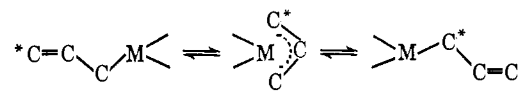


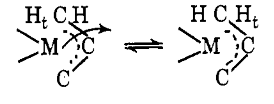
Figure 1. Temperature dependence of the nmr spectrum of ((allyl)$_2$RhCl)$_2$ in solution in CDCl$_3$.

which the AX$_4$ pattern is usually observed at elevated temperatures and compounds of type M(allyl)$_n$ such as Zr(allyl)$_4$[8] and Hf(allyl)$_4$ which yield AX$_4$ spectra at relatively lower temperatures. In addition to the classification of allyl compounds and of equal importance, as indicated by the amount of discussion and speculation in the literature, are (1) the mechanism for the conversion of static-to-dynamic systems, and (2) the structures of intermediates.[9,10,13–17]

Two mechanisms have been proposed: (1) a π to σ equilibration which may involve three species



and (2) a process involving rotation about the C–C bonds.



The first process appears to be favored by most investigators, but the supporting evidence is certainly not well defined.[18–21] The second mechanism, recently proposed by Becconsall and coworkers,[8,22] is attractive and appears to be supported by the nmr parameters for the two forms of Zr(allyl)$_4$. Since in this system, for which the conversion of AM$_2$X$_2$ and AX$_4$ spectra is observed, the chemical shift of the A proton is not significantly altered, the X$_4$ resonance is an average of the resonant frequencies of the M$_2$ and X$_2$ nuclei, and J_{AX} for the dynamic system is half the sum of J_{AM} and J_{AX} for the AM$_2$X$_2$ system. Nevertheless, the C–C rotation mechanism has been criticized by Davison and Rode,[17] but the data cited are insufficient and probably not pertinent.

Recently[7,9,10,13–15,21] a fourth type of allyl group or subgroup, that of an asymmetric π, yielding an AGMPX spectrum has been suggested. Most of these systems contain only one allyl group per metal atom and yield relatively simple spectra at low temperatures, but the temperature dependence and the interpretation of the spectra are complicated by the dissociation of the various ligands such as DMSO, (C$_6$H$_5$)$_3$P, and (C$_6$H$_5$)$_3$As. This study concerns itself with the structures of some complex allyl systems falling in the asymmetric π class, the temperature dependence of their spectra, and the relevance of the observations in terms of the various mechanisms proposed for the dynamic form.

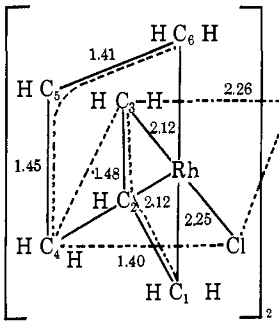
Experimental Section

The nmr spectra were obtained using Varian HA-100 and A-60 spectrometers equipped with variable-temperature accessories. CDCl$_3$, C$_6$D$_6$, and o-C$_6$H$_4$Cl$_2$ were used as solvents, and tetramethylsilane was included as an internal reference and field-locking signal.

The dimer ((allyl)$_2$RhCl)$_2$ was prepared by the reaction of allyl chloride with (Rh(CO)$_2$Cl)$_2$,[23] while Mo(allyl)$_4$ was prepared according to the method of Wilke, *et al.*[24] (C$_6$H$_5$)$_3$P and (C$_6$H$_5$)$_3$As were obtained from Alfa Inorganics, Inc., and used without further purification.

Results and Discussion

((allyl)$_2$RhCl)$_2$. A preliminary note on the X-ray analysis of bisallylrhodium chloride dimer by McPartlin and Mason[14] yielded structure I. The bond-length data could be interpreted in terms of a σ-bonded complex, structure II, but the conformation of the two methylene groups relative to the plane containing the allyl carbon atoms could not be determined by crystallographic techniques.



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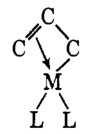

II

The nmr spectrum of bisallylrhodium chloride dimer in solution in CDCl$_3$, as obtained at −20°, is shown in Figure 1a and is consistent with structure I. The spectrum corresponds to an AGMPX type indicating that the four allyl groups are equivalent and that the terminal carbon atoms of each allyl group are bonded unequally to the metal atom. The nmr parameters are listed in Table I. They are not consistent with a σ-bonded allyl group, structure II, but rather a near-planar π-bonded allyl group. This is indicated by (1) the small coupling of the geminal protons, <0.5 Hz, suggesting

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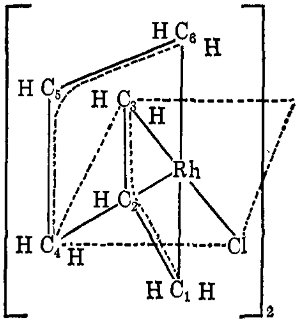
Table I. Nmr Parameters of Bisallylrhodium Chloride Dimer



Solvent	Temp, °C	Chemical shift, τ $1,6_{cis}$	$2,5$	$1,6_{trans}$	$3,4_{cis}$	$3,4_{trans}$	Coupling constants, Hz
$CDCl_3$	−20	4.92	5.24	5.98	7.50	8.18	$J_{cis,1,2} = 6.8$ $J_{trans,1,2} = 12.0$ $J_{cis,3,2} = 6.0$ $J_{trans,3,2} = 10.8$
o-$C_6H_4Cl_2$	30	5.13	5.50	6.10	7.76	8.26	$J_{cis,1,2} = 7.0$ $J_{cis,3,2} = 6.0$ $J_{trans,1,2} = 12.2$ $J_{trans,3,2} = 10.8$
	150		5.40		1, 3, 4, and 6 6.78		$J_{1,2} = J_{23} = 9.0$ $J_{Rh,2} = 2.3$

that the H–C–H angle is about 120°, and (2) the small differences between $J_{cis,1,2}$ and $J_{cis,2,3}$, and $J_{trans,1,2}$ and $J_{trans,2,3}$.

The temperature dependence of the nmr spectrum of bisallylrhodium chloride dimer is of particular significance. With increasing temperature the asymmetric π-allyl system should yield different spectra depending upon the type of equilibration, providing the dimer does not dissociate to monomers. For the first mechanism, a π-to-σ equilibration, an AX_4 spectrum should result. At the initiation of the equilibration, the intermediate should yield a spectrum showing collapse of the resonances for one end of the allyl group, while the other resonances remain relatively sharp.[3] This appears reasonable since the *trans* effects of $(C_6H_5)_3P$ and the allyl group are quite similar as indicated by the bond distances in $((allyl)_2RhCl)_2$ and $(allyl)PdCl$-$P(C_6H_5)_3$.[3] For an equilibration involving C–C rotation only, the AGMPX spectrum should convert into an AM_2X_2 spectrum as the temperature is increased. The temperature dependence of the nmr spectrum of bisallylrhodium chloride dimer in solution in $CDCl_3$ and o-$C_6H_4Cl_2$ is shown in Figures 1 and 2. In o-$C_6H_4Cl_2$, the resonances are sharp at room temperature and broaden at about 70°, and the terminal CH_2 resonances appear to coalesce to an AM_2X_2 type at 90°. This could result from C–C rotation, but the lack of resolution of the A resonance at this temperature seems to indicate that this is not the case. If the spectra were interpreted in terms of a π-to-σ process, then the terminal protons should collapse at different rates, providing the observations reported by Vrieze, *et al.*,[3] are representative of the initial steps. However, Figure 2 suggests that this is not the case; the resonances for the terminal protons collapse at the same rate. The nmr parameters for the two systems, AGMPX and AX_4, are quite similar to those reported by Becconsall and coworkers[8,22] for $Zr(allyl)_4$. The chemical shift of proton A changes only slightly as the spectrum changes from an AGMPX to an AX_4 system; the chemical shift of the X_4 resonance is very close to the average for the GMPX resonances, and J_{AX} for the AX_4 system is equal to $^1/_4(J_{AG} + J_{AM} + J_{AP} + J_{AX})$ for the AGMPX system. The most probable equilibrations seem to involve dimer dissociation coupled with some type of allyl rearrangement. Dissociation alone would not give rise to an AX_4 spectrum, but the combination of dimer–monomer equilibrium and either C–C rotation or a π-to-σ conversion could produce the observed pattern. Consequently, the evidence does not lend support for either of the two previously proposed mechanisms.

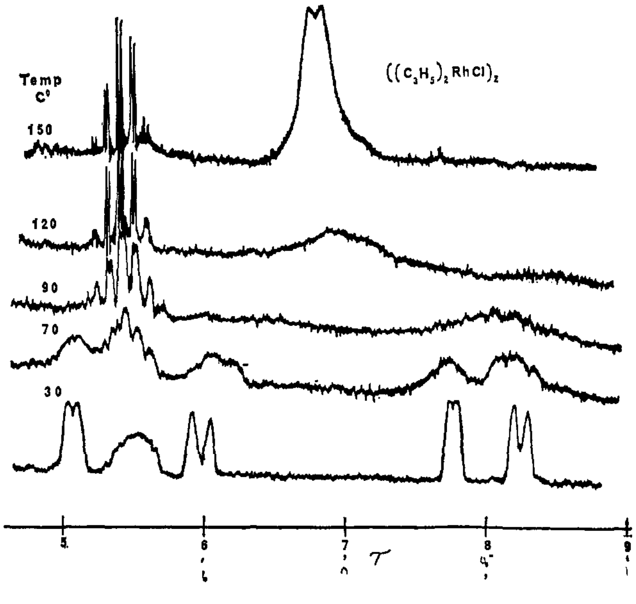


Figure 2. Temperature dependence of the nmr spectrum of $((allyl)_2RhCl)_2$ in solution in o-$C_6H_4Cl_2$.

Further evidence on the classification of asymmetric π-allylic systems was obtained from an nmr study of the $(C_6H_5)_3P$ and $(C_6H_5)_3As$ derivatives of bisallylrhodium chloride dimer. These results together with those for $Mo(allyl)_4$ are discussed in the following section. The

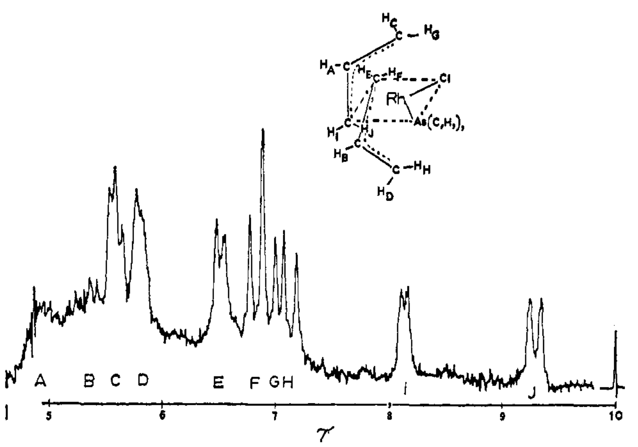


Figure 3. Nmr spectrum of (allyl)$_2$RhCl(C$_6$H$_5$)$_3$As in solution in CDCl$_3$ obtained at 30° and 100 MHz.

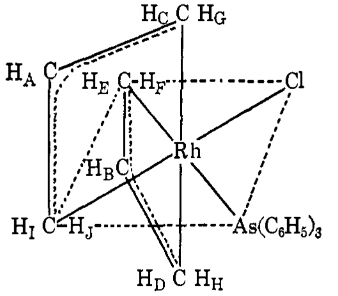
latter compound was prepared in an attempt to simplify the system with respect to the number of probable equilibrations.

Systems ((allyl)$_2$RhCl)$_2$ + (C$_6$H$_5$)$_3$P and (C$_6$H$_5$)$_3$As. A reaction mixture of (C$_6$H$_5$)$_3$As and ((allyl)$_2$RhCl)$_2$ (2 moles of (C$_6$H$_5$)$_3$As per mole of dimer) in solution in CDCl$_3$ at 30° gives a complex nmr spectrum as shown in Figure 3. For reaction mixtures containing less than 2 moles of (C$_6$H$_5$)$_3$As per mole of dimer, the spectra show sharp resonances for the dimer and derivative suggesting the following reaction

$$[(\text{allyl})_2\text{RhCl}]_2 + 2\text{L} \longrightarrow 2(\text{allyl})_2\text{RhClL}$$

and that the two do not interact below 35°. The nmr spectrum is interpretable in terms of two asymmetric π-allylic groups, and the assignments were based on (1) the downfield positions and splitting patterns of resonances A and B, (2) spin decoupling which shows that A is coupled to CGIJ and B to EFDH, and (3) the magnitudes of the various coupling constants which readily differentiate between *cis* and *trans* protons and to a certain extent facilitate the assignment of the terminal protons. The differentiation of allylic protons relative to carbon atoms 1, 2, and 3 or 4, 5, and 6 was based on the results for the (C$_6$H$_5$)$_3$P derivative and is discussed in the following section.

Table II. Nmr Parameters for (allyl)$_2$RhClAs(C$_6$H$_5$)$_3$



Solvent	Temp, °C	Chemical shift, τ		Coupling constant, Hz	
CDCl$_3$	30	A 4.98	F 6.78	J_{AI} = 6.0	J_{BE} = 5.8
		B 5.34	G 6.87	J_{AJ} = 10.3	J_{BF} = 11.0
		C 5.50	H 7.09	J_{AC} = 7.0	J_{IC} = 2.2
		D 5.73	I 8.12	J_{AG} = 11.5	J_{DE} = 2.0
		E 6.46	J 9.29	J_{BD} = 7.2	J_{RhC} = 4.0
				J_{BH} = 11.6	J_{RhD} = 2.0

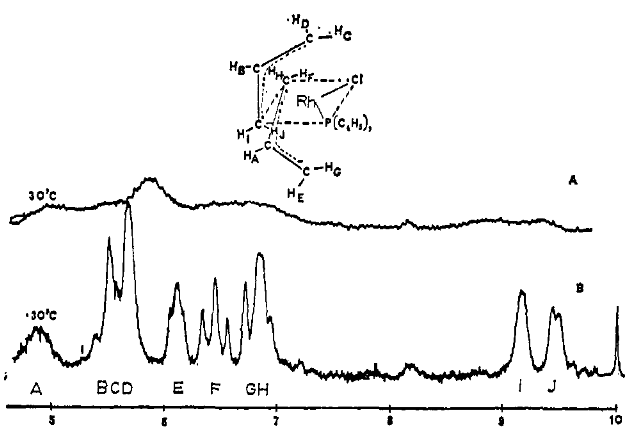


Figure 4. Nmr spectrum of (allyl)$_2$RhCl(C$_6$H$_5$)$_3$P in solution in CDCl$_3$ obtained at 100 MHz: (A) 30°, (B) −30°.

The nmr parameters are listed in Table II and are quite similar to those for the dimer. Two additional couplings were observed between protons I and C and D and E of 2.2 and 2.0 Hz, respectively. These small couplings provide further evidence for the near-planar structure of the allyl group.[25,26]

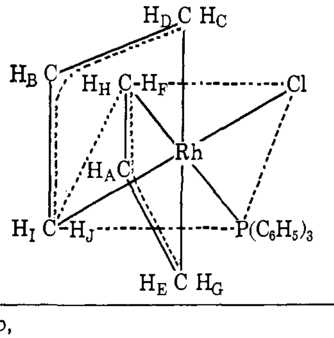
The temperature dependence of the nmr spectrum of (allyl)$_2$RhCl(C$_6$H$_5$)$_3$As is rather complex as anticipated. Even so, a number of significant points were obtained: (1) an AX$_4$ spectrum is observed at high temperatures and (2) the parameters for the AX$_4$ system are close to the average values observed for the static asymmetric π system.

A reaction mixture of (C$_6$H$_5$)$_3$P and ((allyl)$_2$RhCl)$_2$ (2 moles of (C$_6$H$_5$)$_3$P per mole of dimer) in CDCl$_3$ yielded at 30° a complex spectrum as shown in Figure 4A. This spectrum is characteristic of those obtained for a number of reaction mixtures containing various ratios of dimer to ligand. The broad bands suggest the following equilibration

$$[(\text{allyl})_2\text{RhCl}]_2 + 2\text{L} \rightleftharpoons 2(\text{allyl})_2\text{RhClL}$$

which shifts to the adduct as the temperature is de-

Table III. Nmr Parameters for (allyl)$_2$RhClP(C$_6$H$_5$)$_3$



Solvent	Temp, °C	Chemical shift, τ		Coupling constant, Hz	
CDCl$_3$	−30	A 4.86	F 6.42	J_{AE} = 6.4	J_{BI} = 5.0
		B 5.60	G 6.71	J_{AH} = 7.0	J_{BD} = 7.0
		C 5.60	H 6.88	J_{AG} = 12.0	J_{BJ} = 9.0
		D 5.68	I 9.10	J_{AF} = 11.0	J_{BC} = 12.0
		E 6.11	J 9.48	J_{EH} = 1.5	J_{FP} = 11.0
				J_{ID} = 2.2	J_{HP} = 6.0
					J_{EP} = 3.0

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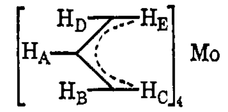
(26) S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964).

creased to −30° (Figure 4B). The spectrum of the low-temperature species is quite similar to that for the $(C_6H_5)_3As$ adduct, and the basis for the assignment is essentially the same. The preferential coupling of phosphorus to protons in the *trans* position,[27] which allows an assignment of the allylic protons to the respective carbon atoms, gives rise to the assignments listed in Table III. As the temperature is increased the spectrum of $(allyl)_2RhCl(C_6H_5)_3P$ converts into a broad AX_4 pattern, and this is further complicated by decomposition.

$Mo(allyl)_4$. The nmr spectrum of $Mo(allyl)_4$ has been reported by Wilke, *et al.*[24] They obtained five resonances with an area ratio of 1:1:1:1:1 and proposed two interpretations: (1) two sets of symmetrical π-bonded allyl groups, indicating that two of the allyl groups are bonded differently than the other two, or (2) four equivalent asymmetrical π-bonded allyl groups, indicating that the two terminal carbon atoms of each allyl group do not interact with the molybdenum atom in the same way. The nmr spectrum, as shown in Figure 5a, is consistent with the previous report, and the parameters as listed in Table IV agree with the latter interpretation. The coupling constants were confirmed by spin decoupling (frequency sweep), and the results are illustrated in Figure 5b. The irradiation of proton D, τ 8.07, removes the 1.6-Hz coupling from resonance B and the small 0.8 Hz coupling from E. Clearly these interactions confirm the latter interpretation.

Table IV. Nmr Parameters for $Mo(allyl)_4$ in $CDCl_3$



Chemical shift, τ	Coupling constants, Hz
A 5.92	J_{AB} = 9.1
B 6.89	J_{AC} = 13.3
C 7.12	J_{AD} = 8.5
D 8.07	J_{AE} = 11.5
E 10.20	J_{BD} = 1.6
	J_{DE} = 0.8

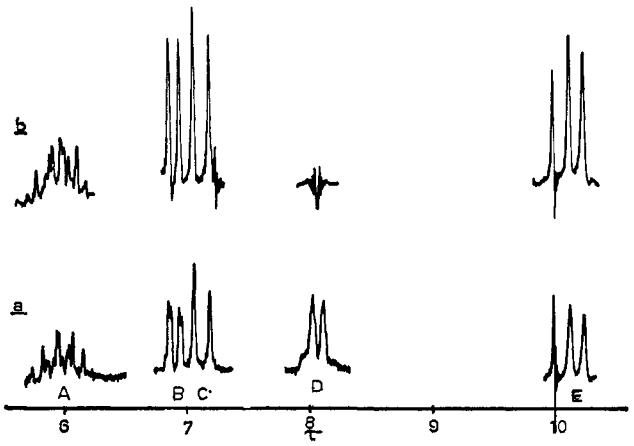


Figure 5. Nmr spectrum of $Mo(allyl)_4$ in solution in $CDCl_3$ obtained at 30°: (a) normal, and (b) decoupled.

The temperature dependence of the nmr spectrum of $Mo(allyl)_4$ should differentiate between the two mechanisms for the conversion of static to dynamic allyl systems. Unfortunately, the spectrum shows no indications of equilibrating even at 170°, where decomposition of the compound begins.

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