Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

COMPLEXES OF ALLENES WITH PLATINUM(II) AND RHODIUM(I)

K. VRIEZE, H. C. VOLGER AND A. P. PRAAT
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.) (The Netherlands)

(Received October 1st, 1969)

SUMMARY

The π-allene–metal linkage in compounds of tetramethylallene (TMA) and 1,1-dimethylallene (1,1-DMA) with platinum(II) and rhodium(I) has been investigated. The compounds were: the dimers $[(\text{TMA})\text{PtCl}_2]_2$ and $[(1,1\text{-DMA})\text{PtCl}_2]_2$, prepared by reaction of the allene and $[(\pi\text{-C}_2\text{H}_4)\text{PtCl}_2]_2$; the monomers $(\text{TMA})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_4\text{-}p\text{-X})$, ($\text{X}=\text{NH}_2$, CH_3, C_2H_5, H, Br, CN), and $(1,1\text{-DMA})\text{Cl}_2\text{Pt}(\text{NC}_5\text{H}_5)$, prepared from the respective dimers and (substituted) pyridines; and $(\text{Acac})\text{Rh}(\text{TMA})_2$ (Acac = acetylacetonato), prepared from the allene and $(\text{Acac})\text{Rh}(\pi\text{-C}_2\text{H}_4)_2$.

In all these cases NMR results confirmed that the allene group is linked to the metal atom by one of its double bonds. They also indicated that in the TMA-platinum compounds there is a monomolecular reaction in which the metal atom moves back and forth from one double bond to the other. With the monomeric TMA–platinum compounds a linear relation is found between the logarithm of the rate of movement of the metal atom and the Hammett σ_p parameter of the pyridine substituent.

INTRODUCTION*

In compounds in the series $\text{L}_2\text{Cl}_2\text{Rh}(\pi\text{-methallyl})$, the π-metallyl group, which is *trans* to both ligands L[1], has been found[2,3] to undergo a π–σ reaction (*i.e.* conversion from its initial state to a transition state reminiscent of a σ-allyl intermediate) for which the activation energy decreased as the electron-donor capacity of the Group V ligands increased. Although the bonding in π-allyl and π-olefin metal complexes can be described in the same terms, this trend in the mobility of the formally negatively charged π-allyl anion was not to be expected for π-olefin or similar neutral molecules in metal complexes. This suggested that an investigation of the π-olefin–metal linkage might be worth while. Some information had already been collected on π-olefin–platinum compounds[4,5], but the reactions involved here were not generally monomolecular, which made comparison rather difficult. As the reactions involved in the π-allene–platinum compound were found to be monomolecular, we decided to concentrate on the fairly stable π-allene–platinum linkages. This would allow us to

---

* Abbreviations used: 1,1-DMA = 1,1-dimethylallene; TMA = tetramethylallene; Acac = acetylacetonato; DMP = 2,4-dimethyl-1,3-pentadiene.

investigate theories about the movement of the allene group and metal atom with respect to each other. These theories are based on experimental data published for $Fe(CO)_4(TMA)$[6], and recently for $(PPh_3)_2Pt(allene)$[7,8], $(PPh_3)_2ClRh(\pi\text{-allene})\cdot\frac{1}{2}CH_2Cl_2$[8], and $[Ir(diphosphine)(CH_2{=}C{=}CH_2)]^+Cl^-$[8], which have indicated that the allene is linked to the metal atom by one of its double bonds*. In the light of this it has been suggested that two movements can be distinguished:

(*a*) a rotational movement of the allene on an axis passing through the centre of the coordinated double bond linked to the metal, and

(*b*) a "helical" movement of the metal atom from one double bond to the other.

Movements of type (a) have been observed in π-olefin compounds such as $(\pi\text{-}C_5H_5)Rh(\pi\text{-}C_2H_4)_2$[9,10], (2,4,6-trimethylpyridine)$Cl_2Pt[\pi\text{-}(CH_3)HC{=}CH_2]$[4] and (Acac)-ClPt(π-olefin)[11], while movement (b) has been suggested in the case of $(OC)_4Fe(TMA)$[6].

For the present investigation** we prepared a number of compounds of allenes with Pt^{II} and Rh^{I} and studied the influence of various ligands on the movement of the allene group such as occurs in a monomolecular reaction.

EXPERIMENTAL

Preparation of $[(TMA)PtCl_2]_2$ *and* $[(1,1\text{-}DMA)PtCl_2]_2$

Tetramethylallene (0.2 g) was added to a suspension of $[(C_2H_4)PtCl_2]_2$[13] (0.6 g) in 25 ml benzene in an atmosphere of dry, oxygen-free nitrogen. The platinum compound dissolved with liberation of ethylene gas, while the colour changed from yellow to orange-red. After filtration and dry-freezing of the filtrate, orange $[(TMA)PtCl_2]_2$ was isolated. The compound is a non-conductor in acetone. (Found: C, 23.6; H, 3.4; Cl, 18.8; Pt, 55.6. $C_{14}H_{24}Cl_4Pt_2$ calcd.: C, 22.2; H, 3.3; Cl, 19.6; Pt, 53.9%.) Recrystallization in carbon tetrachloride yielded crystalline $[(TMA)PtCl_2]_2\cdot CCl_4$.

By an analogous procedure the orange $[(1,1\text{-}DMA)PtCl_2]_2$ was obtained from 1,1-dimethylallene (0.27 g) and $[(C_2H_4)PtCl_2]_2$ (1.2 g). (Found: C, 15.0; H, 2.1; Cl, 18.1; Pt, 60.4. $C_{10}H_{16}Cl_4Pt_2$ calcd.: C, 18.0; H, 2.3; Cl, 21.3; Pt, 58.4%.)

It was also attempted to prepare $[(H_4C_3)PtCl_2]_2$ and $[(TMA)PdCl_2]_2$ from the appropriate allene and $[(C_2H_4)PtCl_2]_2$ and $[(C_2H_4)PdCl_2]_2$[14], respectively. However, the first reaction yielded an unidentified compound and from the product of the second reaction the π-allyl compound $\{[\pi\text{-}(CH_3)_2CC(Cl)C(CH_3)_2]PdCl\}_2$ was isolated. The latter compound had been formed previously from $(benzonitrile)_2PdCl_2$ and tetramethylallene[15,16].

Preparation of $(TMA)Cl_2Pt(NC_5H_4\text{-}p\text{-}X)$ *and* $(1,1\text{-}DMA)Cl_2Pt(NC_5H_5)$

These compounds were prepared by addition of an equimolar amount of the (substituted) pyridine to $[(TMA)PtCl_2]_2$ or $[(1,1\text{-}DMA)PtCl_2]_2$ in 5 ml $CHCl_3$ and subsequent treatment of the solution with pentane. The yellow product obtained in each case was then washed with pentane.

---

* This is further supported by crystallographic data recently published for $(PPh_3)_2IRh(\pi\text{-}C_3H_4)$[32], $(Acac)Rh(1,1\text{-}DMA)_2$[33] and $(CO)_2Rh_2(Acac)_2(\pi\text{-}C_3H_4)$[33]. In the last-mentioned compound the allene is linked to two Rh-atoms.

** A preliminary communication on this work appeared recently[12].

TABLE 1

RESULTS OF ELEMENTARY ANALYSIS

Compound	Analysis: found (calcd.) (%)				
	C	H	Cl	N	Pt
(TMA)Cl₂Pt(NC₅H₄-p-X)					
$X=NH_2$	32.3	4.0	15.6	7.2	42.0
	(31.6)	(4.0)	(15.5)	(6.2)	(42.7)
$X=CH_3$	34.2	4.3	15.4	3.6	44.0
	(34.3)	(4.0)	(15.6)	(3.1)	(43.0)
$X=C_2H_5$	35.1	4.2	14.9	3.2	~37
	(35.9)	(4.4)	(15.1)	(3.0)	(41.6)
X=H	32.5	3.9	16.1	3.2	41.0
	(32.6)	(4.0)	(16.1)	(3.1)	(44.2)
X=Br[a]	25.5	3.1	16.1	1.8	
	(28.0)	(3.0)	(13.6)	(2.6)	(37.5)
X=CN	33.2	3.4	15.4	6.4	41.0
	(33.5)	(3.5)	(15.2)	(6.0)	(41.8)
(1,1-DMA)Cl₂Pt(NC₅H₅)					
	28.5	3.0	17.3	3.2	47.0
	(29.0)	(3.2)	(17.2)	(3.4)	(47.2)

[a] Found: Br, 10.3. Calcd.: Br, 15.3%.

The $(TMA)Cl_2Pt(NC_5H_5)$ was also prepared by an alternative method involving addition of tetramethylallene (0.26 g) dropwise to a suspension of 0.5 g *trans*-$(C_2H_4)Cl_2Pt(NC_5H_5)$[17] in 5 ml methanol. The complex dissolved, ethylene gas was liberated, and after a short time yellow $(TMA)Cl_2Pt(NC_5H_5)$ crystallized. (Found: C, 32.4; H, 3.8; Cl, 15.7; N, 3.1. $C_{12}H_{17}Cl_2NPt$ calcd.: C, 32.6; H, 3.1; Cl, 16.1; N, 3.1%.)

Preparation of (Acac)Rh(TMA)₂

Addition of tetramethylallene (0.25 g) to a suspension of $(Acac)Rh(\pi\text{-}C_2H_4)_2$ (0.4 g) in 12 ml methanol at room temperature in a dry, oxygen-free nitrogen atmosphere led to dissolution of the complex, with evolution of ethylene gas. After three h the solution was placed in an icebox. After a few days orange crystals developed, which decomposed very rapidly in air. The formula $(Acac)Rh(TMA)_2$ was ascertained by NMR spectroscopy (in $CDCl_3$) and single-crystal X-ray studies[18,*].

When carried out at 55–60° the reaction yielded a dark red air-susceptible compound. The composition of this compound was found to be (Acac)Rh(DMP) (DMP=2,4-dimethyl-1,3-pentadiene). This was ascertained by NMR spectroscopy, and by introduction of carbon monoxide into solutions of the complex in $CHCl_3$, which immediately led to the formation of reddish green needles of $(Acac)Rh(CO)_2$[19] and free 2,4-dimethyl-1,3-pentadiene.

---

[*] Racanelli *et al.*[33] recently reported isolating $(Acac)Rh(TMA)_2$ as a liquid, which indicates, in view of our results, that their compound was probably impure.

TABLE 2

NMR ABSORPTIONS OF (ACAC)Rh(DMP) AND DMP

Compound	δ^a (intensity)						
	=CH–	$=CH_2$		$=C(CH_3)_2$		$=C(CH_3)$–	$-CH_3$(Acac)
(Acac)Rh(DMP)	4.27(1)	2.64(1)	1.82(1)	1.22(3)	0.86(3)	2.14(3)	1.98(6)
DMP	5.58(1)	4.77(1)	4.84(1)	1.76[b]		1.76[b]	

[a] Chemical shift (ppm from TMS). [b] Broad signal (total intensity 9).

Spectroscopic measurements

The NMR spectra of the rhodium and platinum complexes were recorded on a Varian spectrometer (HA 100 and DP 60), using $CDCl_3$ as solvent. Low temperatures were obtained with variable Varian dewar inserts.

The kinetic measurements on the platinum compounds were carried out on the two low-field methyl signals at about 2.20 and 2.60 ppm (δ) respectively, using the formula appropriate to the slow exchange region[20]. The natural line widths were in the range of 3.0–3.5 Hz.

RESULTS

Complexes of allene with Pt^{II}

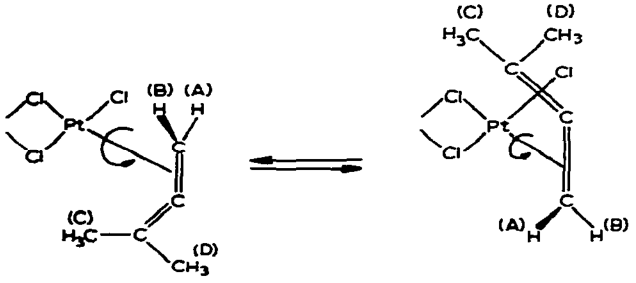
Dimeric compounds. The NMR spectrum of $[(TMA)PtCl_2]_2$ in $CDCl_3$ at $-70°$ showed the presence of four inequivalent methyl groups at 1.48 $[J(Pt-CH_3) \approx 44-48$ Hz], 1.58 $[J(Pt-CH_3) \approx 44-48$ Hz], 2.21 and 2.72 ppm (δ). (The chemical shift of the methyl groups of free tetramethylallene is 1.62 ppm.) In view of their high fields, and also because of the presence of the $^{195}Pt-CH_3$ coupling, the first two absorptions must be assigned to the two methyl groups linked to the coordinate double bond.

Analogously, one may conclude from the NMR spectrum of $[(1,1\text{-DMA})PtCl_2]_2$ that the allene is bonded with its $C=CH_2$ part to the Pt-atom $[\delta(CH_2=C) = 4.04$ ppm, $J(Pt-H) = 52.0$ Hz]. This was confirmed by the two methyl groups linked to the non-coordinate double bond absorbing at approximately the same magnetic fields [2.22 and 2.62 ppm; $J(H-CH_3) = 1.4$ Hz] as the analogous methyl groups in $[(TMA)PtCl_2]_2$. It should be noted that the chemical shifts of free 1,1-dimethylallene are 4.44 ppm ($C=CH_2$) and 1.63 ppm $[C=C(CH_3)_2]$, while $J(H-CH_3) = 3.1$ Hz[21].

The interesting point to note about the NMR spectrum of $[(1,1\text{-DMA})PtCl_2]_2$ is that the two protons of the coordinate $C=CH_2$ group absorb at the same magnetic field even at $-70°$, which would not be expected, considering the inherent asymmetry of the dimeric compounds and the inequivalence of the CH_3 groups of the coordinate $C=C(CH_3)_2$ group in the tetramethylalleneplatinum dimer. It may therefore well be that even at low temperatures the DMA group rotates about the Pt–allene bond.

Inspection of models shows that due to this rotation the positions of hydrogen atoms (A) and (B) are interchanged, but not the positions of methyl groups (C) and (D) because the H–C–H plane is perpendicular to the $H_3C-C-CH_3$ plane.

At temperatures above $-70°$ no changes were observed in the NMR spectrum



of $[(1,1\text{-DMA})PtCl_2]_2$. In the case of $[(TMA)PtCl_2]_2$, however, the four methyl signals coalesced to one signal at the weighted average $[J(Pt-CH_3)=23.0$ Hz$]$ at room temperature. As the $Pt-CH_3$ coupling is retained, the rearrangement must be intramolecular, and as the rate $(1/\tau)$ is independent of the concentration, it is very likely monomolecular. A similar coalescence was reported for $(OC)_4Fe(TMA)$ by Ben-Shoshan and Pettit[6], who suggested a movement of the $(OC)_4Fe$ moiety from one double bond to the other and *vice versa*. They also reported an activation energy of about 9 kcal/mole, which is of the same order of magnitude as the value found for our Pt-dimer[12] (7 kcal/mole).

In connection with these movements mention should be made of the work on the structure of $[(TMA)_2PtCl_2]_2-CCl_4$ done by Hewitt and De Boer[22], who demonstrated that the tetramethylallene is linked to the Pt-atom by one double bond. They further found that

(*a*) the coordinate C=C bond and the non-coordinate bond have approximately the same length (1.36 Å), and are slightly longer than in the free allene (1.31 Å)[23];

(*b*) the tetramethylallene group is no longer linear as in the free molecule, but shows an angle of 151° between the two double bonds;

(*c*) the CH_3-C-CH_3 planes at the two ends of the allene are virtually perpendicular to each other, as in the free molecule;

(*d*) the Pt–C distances are not equal; they are 2.29 Å $[Pt-C(CH_3)_2]$ and 2.07 Å (Pt–central-C).

The coalescence of the methyl signals can only be explained by assuming that the Pt-atom moves across the central carbon atom from one π-orbital to the other, which orbitals are orthogonal to each other.

Monomeric complexes. The NMR spectra of compounds $(TMA)Cl_2Pt(NC_5H_4\text{-}p\text{-}X)$ $(X=NH_2, CH_3, C_2H_5, H, Br, CN)$ at $-70°$ in $CDCl_3$ show three methyl signals with intensities in the ratio 1/1/2 at about 2.60, 2.20 and 1.90 ppm, respectively (see Table of ref. 12), the last-mentioned peak having a $^{195}Pt-CH_3$ coupling of about 44 Hz. In this series we observed only small differences both between the chemical shifts and between the coupling constants, which indicates very similar stereochemical arrangements and bond distances. The equivalence of the methyl groups linked to the coordinate double bonds is very likely due to the symmetry of the compounds with respect to a plane through the N–Pt-coordinated allene perpendicular to the plane of the molecule.

At temperatures higher than $-70°$ the three methyl signals broaden and finally coalesce to one signal at room temperature. The reactions are intramolecular and independent of added pyridine, because in the temperature range of measurement (below −40°) the Pt-coupling is retained both on the CH_3-signal and on the peak of the *ortho*-protons of the substituted pyridine (see Table of ref. 12).

Rate measurements in the slow-exchange region showed that (a) the rates are independent of the concentration of the complex and (b) the rates decrease with increasing basicity of the (substituted) pyridine (see Fig. of ref. 12). In fact a plot of the logarithm of $1/\tau$ *vs.* the Hammett σ_p parameter is a straight line.

At temperatures above −40° the complexes of the (substituted) pyridine ligands start dissociating, the kinetically most labile complexes being the ones with the ligands having the strongest electron-withdrawing substituents. This is in agreement with what was observed for $(\pi\text{-olefin})Cl_2Pt(NC_5H_4\text{-}p\text{-}X)^5$, for which complex the exchange reaction was shown to be bimolecular, since the disappearance of the Pt-coupling on the *ortho*-protons of the pyridine was formed to be accelerated by the addition of excess pyridine.

The allene ligand itself is strongly bonded to the Pt-atom, since it did not give any sign of dissociation even at +80° and/or in the presence of excess free tetramethylallene. This is in contrast with the situation for the much more labile Pt–π-olefin bond in $(\pi\text{-olefin})Cl_2Pt(NC_5H_4\text{-}p\text{-}X)^5$.

Finally, the rates of rearrangement of the allene group were investigated for mixtures of $[(TMA)PtCl_2]_2$ and $(TMA)PtCl_2(C_5H_5N)$. Both for the monomer and for the dimer these rates were found to be virtually independent of the concentration of both components. This is in sharp contrast with what has been observed, for example, for mixtures of $[(\pi\text{-}C_4H_7)PdCl]_2$ and $(\pi\text{-}C_4H_7)PdCl(L)^{24}$ and mixtures of $[(diene)MCl]_2$ and $(diene)MCl(L)^{25}$ (M=Rh, Ir; L=PPh_3 and $AsPh_3$), for which both "monomer–dimer" reactions and ligand exchange ractions were found.

Complexes of allene with Rh(I)

The allene part of the NMR spectrum of $(Acac)Rh(TMA)_2$ consists of four methyl signals at 0.83 [$J(Rh–CH_3)=2.0$ Hz], 1.49 [$J(Rh–CH_3)\sim 1$ Hz], 1.96 and 2.44 ppm (δ)*. The high field chemical shifts with the Rh-coupling are assigned to the methyl groups linked to the coordinate double bond.

No temperature dependence of the methyl signals was observed in the range of −70° to +50°. In this connection it is of interest to mention some relevant details of the molecular structure[18]. Each of the two TMA ligands is linked to the Rh-atom by one double bond. The Rh–C distances are 2.03 Å [$Rh–C(CH_3)_2$] and 2.18 Å [Rh–C(centre)], the angle between the two double bonds being 147.2°. The CH_3–C–CH_3 planes at the two ends of the allene molecules are again approximately perpendicular to each other.

The absence of allene movements in the temperature range studied may be due to steric factors as well as to strong Rh-allene bonding. An indication of the latter could be the bond length of the coordinate double bond, which shows stronger π-backbonding than in the Pt-compound. This is not unexpected, considering that the formal charge of Rh^I is lower than that of Pt^{II}.

At temperatures higher than +50° (in $CDCl_3$) the rhodium complex slowly decomposed. In this connection it is interesting to note that during the preparation

---

* For comparison we might add that the CH_3-absorptions of $(OC)_4Fe(TMA)$ occur at 1.77, 1.98 and 2.03 ppm (δ) with intensities in the ratio 2|1|1.

of the complex at temperatures of 55–60°, which resulted in the formation of (Acac)-Rh(DMP)*, a hydrogen shift occurred, which probably proceeded via an intermediate rhodium–hydride species. This reaction was not further investigated.

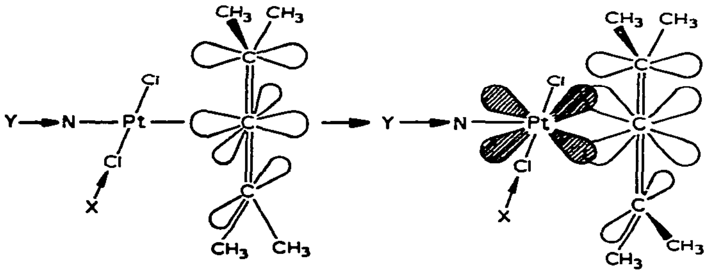
DISCUSSION

An interesting point that needs some further discussion is the bonding in the complexes during the rotational movement of olefins and allenes and the "helical" movement in Pt–allene compounds.

The initial state of the metal–olefin linkage is described by an interaction of the empty 6*s*, 6*p*- and $5d_{x^2-y^2}$-orbitals of Pt^{II} with the filled bonding π-orbital of the olefin (σ-interaction) and by an interaction of the filled $5d_{xz}$-orbital of Pt^{II} with the empty antibonding π^*-orbital of the olefin (π-interaction).

With regard to the rotational movements of the coordinated olefin about the metal–olefin σ-bond, we may describe the transition state by the same σ-interaction, while there is a π-interaction between the filled $5d_{xy}$-orbital of the metal with the π^*-orbital of the olefin[5,11,26]. As the σ-bonding interactions occur both in the initial and in the transition state, it is to be expected that different π-bonding contributions in these two states and different overall electronic densities on the metal atom lead to different activation energies. Insufficient experimental details are known, however, to test this hypothesis, although it seems to be confirmed by the use of different substituents on the olefin[11].

With regard to the helical movement of the allene group, we propose two configurations for the transition state and intermediate state:



Transition state Intermediate state

In the transition state, the interaction with the highest bond order is probably the σ-interaction between σ-type orbitals of the Pt-atom and a *p*-orbital of the central carbon.

In the intermediate state, which is halfway the reaction path and may be representative of the minimum of the saddle in the energy diagram, two *p*-orbitals of the central carbon donate electrons to various empty Pt-orbitals.

The question now is what the effect will be on the initial and transition states, if in the series $(TMA)Cl_2Pt(NC_5H_4\text{-}p\text{-}X)$ we move to more strongly electron-withdrawing substituents, *i.e.* from $X=NH_2$ to $X=CN$. As the bond strength increases

---

* In the reaction of tetramethylallene with $Fe_2(CO)_9$ Ben-Shoshan and Pettit[6] isolated in addition to $(OC)_4Fe(TMA)$ also $(OC)_3Fe(DMP)$.

with an increasing overlap integral S, and decreases with increasing energy difference ΔE between ligand and metal orbitals to be mixed, we have to take into account both overlap and energy phenomena.

When going from $X=NH_2$ to $X=CN$, the size of the orbitals probably becomes smaller with increasing positive charge on the metal. A decreasing orbital overlap is therefore expected in the initial state of both σ- and π-interactions, while in the transition state the σ-orbital overlap (there is no π-orbital overlap) will become smaller. The initial state may therefore be more destabilized than the transition state, mainly due to changes in π-orbital overlap in the initial state, which causes a decrease in activation energy for more strongly electron-withdrawing substituents.

As to energy it is not unreasonable to assume that the energy of the Pt-orbitals is about halfway between the energies of the π- and π^*-orbitals of the allene. An increase in electronegativity of the pyridine causes a downward shift of the Pt level relative to the allene π- and π^*-levels. We believe that this leads to a better energy match for the σ-levels and a poorer energy match for the π-levels. As a consequence, σ-bonding may increase both in the initial and in the transition state, while π-bonding may decrease in the initial state. From energy considerations alone one may thus tentatively infer that σ- and π-effects counteract each other in the initial state, whereas in the transition state the σ-bond is stronger due to the lower energy level at Pt. The overall effect, as deduced from experimental data, is a decrease in activation energy when going from $X=NH_2$ to $X=CN$, which indicates that the changes in π-interactions in the initial state are probably the dominant factor. It is obvious that the above reasoning is very qualitative*, and that more quantitative information on the subject would be of great value.

The range of activation energies (7–10 kcal/mole) is not wide[12], so that we are dealing with relatively small effects, which is only natural in view of the large distance between the allene and *para*-substituent X.

The frequency factors are about 10^{10} sec^{-1}, which indicates that the transition state is more rigid than the initial state. In addition different solvation probably plays a role here.

In view of the catalytic activity of metal atoms in the polymerization of allenes[28–31], and because of the possible role of metal–π-allene compounds as intermediates in the formation of π-allyl–metal compounds[15,16], it would be of interest to obtain more information on possible relationships between structural data and lability of the above-described allene groups.

REFERENCES

1 T. G. Hewitt and J. J. de Boer, *Chem. Commun.*, (1968) 1413.
2 H. C. Volger and K. Vrieze, *J. Organometal. Chem.*, 9 (1967) 527.
3 K. Vrieze and H. C. Volger, *J. Organometal. Chem.*, 9 (1967) 537.
4 M. Orchin and P. J. Schmidt, *Coordin. Chem. Rev.*, 3 (1968) 345.
5 M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta*, (1968) 123.
6 R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, 89 (1967) 2231.
7 S. Otsuka, A. Nakamura and K. Tani, *J. Organometal. Chem.*, 14 (1968) P 30.
8 J. A. Osborn, *Chem. Commun.*, (1968) 1231.

---

* The crystal structure indicates that the hybridization of the central carbon deviates considerably from *sp*, which shows that the bonding is in fact more complicated.

9 R. CRAMER, *J. Amer. Chem. Soc.*, 86 (1964) 217.
10 R. CRAMER, *J. Amer. Chem. Soc.*, 89 (1967) 5377.
11 C. E. HOLLOWAY, G. HULLEY, B. F. G. JOHNSON AND J. LEWIS, *J. Chem. Soc., A*, (1969) 53.
12 K. VRIEZE, H. C. VOLGER, MISS M. GRONERT AND A. P. PRAAT, *J. Organometal. Chem.*, 16 (1969) P 19.
13 J. CHATT AND M. L. SEARLE, *Inorg. Synth.*, Vol. 5, McGraw-Hill, New York, 1957, p. 210.
14 M. S. KHARASCH, R. C. SEYLER AND FRANK R. MAYO, *J. Amer. Chem. Soc.*, 60 (1938) 882.
15 R. G. SCHULTZ, *Tetrahedron*, 20 (1964) 2809.
16 M. S. LUPIN AND B. L. SHAW, *Tetrahedron Lett.*, (1964) 883.
17 (a) P. D. KAPLAN, P. SCHMIDT AND M. ORCHIN, *J. Amer. Chem. Soc.*, 89 (1967) 4537; (b) J. S. ANDERSON, *J. Chem. Soc.*, (1934) 971.
18 T. G. HEWITT, K. ANZENHOFER AND J. J. DE BOER, *Chem. Commun.*, (1969) 312.
19 F. BONATI AND G. WILKINSON, *J. Chem. Soc.*, (1964) 3156.
20 A. ALLERHAND, H. S. GUTOWSKY, J. JONAS AND R. A. MEINZER, *J. Amer. Chem. Soc.*, 88 (1966) 3185.
21 E. L. ALLRED, D. M. GRANT AND W. GOODLETT, *J. Amer. Chem. Soc.*, 87 (1965) 673.
22 T. G. HEWITT AND J. J. DE BOER, to be published.
23 L. E. SUTTON, *Chem. Soc. Special Publ.*, No. 11 (1958) 353.
24 K. VRIEZE, P. COSSEE, A. P. PRAAT AND C. W. HILBERS, *J. Organometal. Chem.*, 11 (1968) 353.
25 K. VRIEZE, H. C. VOLGER AND A. P. PRAAT, *J. Organometal. Chem.*, 15 (1968) 447 and references mentioned therein.
26 S. S. ZUMDAHL AND R. S. DRAGO, *J. Amer. Chem. Soc.*, 90 (1968) 6669.
27 R. MCWEENY, R. MASON AND A. D. C. TOWL, *Trans. Faraday Soc.*, to be published.
28 S. OTSUKA AND A. NAKAMURA, *Polym. Lett.*, 5 (1967) 973.
29 H. GREENFIELD, I. WENDER AND J. H. WOTIZ, *J. Org. Chem.*, 21 (1956) 875.
30 T. J. KEALY AND R. E. BENSON, *J. Org. Chem.*, 26 (1961) 3126.
31 R. E. BENSON AND R. V. LINDSEY, JR., *J. Amer. Chem. Soc.*, 81 (1959) 4247.
32 T. KASHIWAGI, N. YASUOKA, N. KASAI AND M. KUKUDO, *Chem. Commun.*, (1969) 317.
33 P. RACANELLI, G. PANTINI, A. IMMIRZI, G. ALLEGRA AND L. PORRI, *Chem. Commun.*, (1969) 361.