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THE COORDINATION CHEMISTRY OF ALLENES

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A. INTRODUCTION

Compared with olefins and acetylenes, allenes(1,2-dienes) have attracted little attention as potential ligands in transition-metal complexes. This stems in part from the relative instability of allenes which tend to oligomerise or polymerise on storage. Furthermore, oligomerisation and polymerisation reactions of allenes are catalysed by many of the transition-metal complexes which would normally be considered suitable hosts for allene ligands. Labile complexes of monomeric allenes have been proposed as intermediates in these reactions and it is this proposal which has stimulated much of the recent interest in the coordination chemistry of allenes and other homocumulenes [1,2].

Allenes have cumulated C=C bonds, at right angles to each other, formed from alternate *sp*- and sp^2-hybridised carbon atoms. The allene moiety should be able to act as a simple monodentate olefinic-type ligand or as a bridging ligand between two or more metal atoms. More complex ligands may be formed via oligomerisation reactions.

This review also deals with the few examples of homocumulene complexes, and is comprehensive up to mid-1975.

B. PREPARATION OF ALLENE COMPLEXES

Complexes of unsubstituted allene monomer have only been obtained with rhodium, iridium, palladium and platinum. Iron, cobalt and nickel give complexes of allene oligomers. Substituted allenes are less prone to undergo oligomerisation and complexes of the monomeric ligands have been obtained for all the Group VIII metals. The well-established methods of olefin- and acetylene-coordination chemistry have been adapted to the preparation of complexes of monomeric allenes (eqns. 1—6). Cationic allene complexes have been obtained via the protonation of propargyl complexes (eqn. 7) and σ,π-allene complexes from displacement reactions of metal carbonylate ions with suitably substituted allenic bromides (eqn. 8)

$$\mathrm{CpMn(CO)_3} \xrightarrow[\mathrm{C_3Ph_4}]{h\nu} \mathrm{CpMn(CO)_2(C_3Ph_4)} \qquad (1)[3]$$

$$\mathrm{(Ph_3P)_3RhCl} \xrightarrow[\mathrm{C_3H_4}]{} \mathrm{(Ph_3P)_2Rh(Cl)(C_3H_4)} \qquad (2)[4]$$

$$\mathrm{[(C_2H_4)PtCl_2]_2} \xrightarrow[\mathrm{C_3Me_4}]{} \mathrm{[PtCl_2(C_3Me_4)]_2} \qquad (3)[5]$$

$$\mathrm{[PtMe(acetone)L]^+PF_6^-} \xrightarrow[\mathrm{C_3H_4}]{0^\circ\mathrm{C}} \mathrm{[PtMe(C_3H_4)L]^+PF_6^-}$$

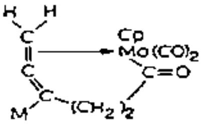
$$\text{where } \mathrm{L = PMe_2Ph,\ AsMe_3} \qquad (4)[6]$$

$$\mathrm{[Ir(diphos)_2]^+Cl^-} \xrightarrow[\mathrm{C_3H_4}]{} \mathrm{[Ir(diphos)C_3H_4]^+Cl^-} \qquad (5)[4]$$

$$cis\text{-}\mathrm{PtCl_2(PPh_3)_2} \xrightarrow[\mathrm{C_3H_4}]{\mathrm{N_2H_4,EtOH}} \mathrm{Pt(PPh_3)_2C_3H_4} \qquad (6)[7]$$

$$\mathrm{CpFe(CO)_2CH_2C{\equiv}CR} \xrightarrow[\mathrm{C_6H_6}]{\mathrm{HClO_4}} \mathrm{[CpFe(CO)_2(CH_2{=}C{=}CHR)]^+ClO_4^-} \qquad (7)[8]$$

$$\mathrm{CpMo(CO)_3^-Na^+} \xrightarrow[\mathrm{Br(CH_2)_2CH:C:CH_2}]{}$$



(8)[9,10]

(i) Groups IVA—VIIA

Allene complexes of the Group IVA and VA metals are unknown. This is similar to the situation for mono-olefinic ligands and reflects a combination of the poor acceptor and donor properties of the early transition metals in their lower oxidation states.

The substituted cumulenes, tetraphenylallene and tetraphenylbutatriene, displace carbon monoxide from $Cr(CO)_6$ but the organometallic complexes isolated in low yield are arenechromium tricarbonyls in which the allene moiety remains uncoordinated. In the presence of $Mo(CO)_6$, tetraphenylbutatriene is converted to 1-(diphenylmethylene)-3-phenlyindene [11].

Neither molybdenum nor tungsten form allene complexes by any of the substitution or addition reactions shown in equations 1—6). Reactions between the carbonylmetalate ions $MCp(CO)_3^-$ (M = Mo, W) and allenic bromides afford σ-allenic complexes; these eliminate carbon monoxide on being heated briefly at 30°C and form σ,π-allenic complexes (eqn. 8) [9]. On prolonged heating (50°C, 48 hr) the σ,π complexes rearrange to π-cyclopentenone complexes [10]. Tetraphenylallene displaced CO from $CpMn(CO)_3$ to give $MnCp(CO)_2(C_3Ph_4)$ but there was no evidence of π-complex formation between allene and either $CpMn(CO)_3$ or $Mn_2(CO)_{10}$ [12].

(ii) Group VIII

(a) Iron

The tendency here is for substituted allenes to afford mononuclear complexes whilst the parent allene dimerises or trimerises to form trimethylene or π-allyl ligands (Section F(i)). Tetramethyl- and tetraphenyl-allene yield the mononuclear complexes $Me_4C_3Fe(CO)_4$ [13] and $Ph_4C_3Fe(CO)_3$ [14,15] respectively. The former is soluble in CS_2 and exhibits fluxional behaviour in solution (Section D(ii)). The tetraphenylallene complex liberates 86% of the theoretical amount of carbon monoxide on pyrolysis and exhibits only three terminal carbonyl absorption bands in its IR spectrum. It is a diamagnetic monomer suggesting that the organic ligand acts as a four-electron donor but the details of the bonding are unknown.

A binuclear iron complex of tetraphenylbutatriene was first obtained from the triene and $Fe(CO)_5$ in refluxing ethylcyclohexane [14] and then from $Ph_2C{=}CBr_2$ and $Fe_3(CO)_{12}$ [16]. Its original formulation [14] as $(C_4Ph_4)Fe_2(CO)_5$ was altered to $(C_4Ph_4)Fe_2(CO)_6$ on the basis of mass spectrometric evidence [17,18] for the loss of six carbon monoxide groups. An X-ray crystallographic study [19] established it as an example of an olefin-iron tetracarbonyl complex with the iron atom coordinated exclusively to the central bond of the cumulated double-bond system.

Unsubstituted butatrienes and hexapentaenes are extremely unstable; iron complexes have been prepared by generation of the ligand in situ through dehalogenation of the appropriate 1,4-dibromobut-2-yne [18,20,21]

$$BrCH_2{-}C{\equiv}C{-}CH_2Br + Fe_3(CO)_{12} \xrightarrow[\text{iso-octane}]{\text{Zn},60°} (C_4H_4)Fe_2(CO)_6 \qquad (9)$$

(b) Cobalt, rhodium and iridium

Unsubstituted allenes undergo oligomerisation or polymerisation reactions in the presence of $Co_2(CO)_8$. $CpCo(CO)[C_3Ph_4]$ has been obtained [3] from $CpCo(CO)_2$ and $CpCo(PPh_3)[C_3Ph_4]$ from $CpCo(Ph_3P)I_2$ via the isopropyl Grignard route [22].

Rhodium has provided the greatest variety of complexes of monomeric allenes to date: $RhX(PPh_3)_2(all)$ (all = C_3H_4, X = Cl, Br, I [4]; all = $CF_3C_3H_3$, X = Cl, Br [23]) from $RhX(PPh_3)_3$; $Rh(acac)(all)_2$, (all = C_3H_4 [5], 1,1-DMA [24]) from $Rh(acac)(C_2H_4)_2$; and $Rh_2(acac)_2(CO)_2(all)$, (all = C_3H_4, TMA [24]) from $Rh(acac)(CO)C_2H_4$.

The structures of representatives of each type have been established by X-ray crystallography (see section C). Several of the complexes are sufficiently stable to undergo reactions which do not involve loss of the allene ligand [23] (Section E). Reversible addition of allene to *trans*-$IrCl(CO)(PPh_3)_2$ was indicated [4] by the appearance of an IR bond attributable to $\nu_{asym}(C{=}C{=}C)$ of the coordinated allene when allene was bubbled through a solution of Vaska's complex. The more nucleophilic $[Ir(diphos)_2]^+$ cation is reported [4] to give an isolable allene complex $[Ir(diphos)C_3H_4]^+Cl^-$ and the complexes $Ir(PPh_3)_2(CO)X(CF_3 \cdot C_3H_3)$, X = Cl, I) have also been isolated [25]. Both the cationic and the neutral chloro complexes slowly release the allene even in the solid state; dissociation is rapid in solution. The iodo complex, however, is stable in the solid state but this too releases the allene in solution, as does $IrCl(PPh_3)_2C_3H_4$ [26] formed from $[IrCl(PPh_3)_2]_n$ or $IrCl(Ph_3P)_2C_2H_4$ and allene. In view of this instability it is surprising that $IrCl(PPh_3)_2C_3H_4$ and SO_2 form a five-coordinate adduct apparently with the SO_2 and C_3H_4 ligands coordinated separately. (However, see Section E).

(c) Nickel, palladium and platinum

There is some uncertainty about the existence of a mononuclear nickel complex of unsubstituted allene. An air-sensitive, orange-red crystalline complex was isolated from the reaction of allene with "$(Ph_3P)_2Ni$" [27]. Its ^1H NMR spectrum is reported to display two vinylidene singlets (2H) at δ 2.8 and 3.04 ppm, and a pair of methylene doublets (2H) at δ 1.48 and 1.57 ppm, $J(P{-}H)$ = 10.5 Hz, along with an aromatic region δ 6.8—7.5 ppm, (30 H). The spectroscopic and analytical data are consistent with its formulation as $(Ph_3P)_2Ni(CH_2 : C : CH_2)$ but the molecular weights reported are very low (350, 290) compared with the calculated value of 623. To account for this, it has been suggested that one of the phosphine ligands dissociates from the complex in solution. However, there is no evidence of allene monomer complex formation in the ^1H NMR spectra of the systems $Ni(C_2H_4)(Ph_3P)_2$—allene and "$Ni(Ph_3P)_2$—allene" at −70°C [28]. Indeed, even at this temperature there are resonances attributable to the allene trimer complex $[Ni(C_9H_{12})Ph_3P]$ in both 1 : 1 and 3 : 1 mixtures of allene and the

"$Ni(Ph_3P)_2$" complex. Formation of the trimer complex is evident at ca. −10°C in the other system. NMR data have been given [28] for the complexes $(Ph_3P)_2Ni(all)$, (all = PhCH : C : CHPh, $Me_2C : C : CH_2$). Most reactions between palladium complexes and allenes lead to π-allyl complexes via insertion of the allene into Pd—C and/or Pd—Cl bonds (Section F). The only known palladium—allene complex is $Pd(Ph_3P)_2$ allene; its structure has been shown to be analogous to that of the corresponding platinum complex (Section C).

Unlike the other Group VIII metals, platinum shows no tendency to oligomerise or polymerise allenes. Several stable platinum—allene complexes have been obtained via replacement reactions (eqns. 3, 4 and 6) [4,5,7,28—30]. Structural and spectroscopic data are discussed in Sections C and D.

(iii) Group IB. Copper and silver

Apart from a few complexes of some cyclic allenes with silver(I) and copper(I), the allene chemistry of Group IB is relatively unexplored. Direct reaction of the allene with silver nitrate solution or reduction of copper(II) chloride with SO_2 in the presence of the allene leads to 1 : 1 or 1 : 2 complexes [31]. For the polynuclear chlorine-bridged complex $(CuCl)_2$(cyclodeca-1,2,6,7-tetraene) there are weak absorptions at 1660 cm^{-1} and 1840 cm^{-1} attributed to $\nu_{coord.}$(C=C=C) and $\nu_{uncoord.}$(C=C=C) respectively; the proposed structure has the tetraene acting as a bridging ligand through a pair of trans-annular double bonds. An alternative structure for the copper complex which does not appear to have been considered but which is consistent with the IR data has the cyclic ligand acting as a bridge through both C=C's of the same allene unit as in $[Rh_2(acac)_2(CO)_2(CH_2 : C : CMe_2)]$ (v).

C. STRUCTURES AND BONDING

Structural parameters of those allene complexes which have been subjected to single crystal X-ray diffraction are detailed in Table 1, and depicted in Fig. 1. In the mononuclear complexes, the allene molecule functions as a olefin-like ligand. As with olefin—metal complexes there is an increase in the C=C internuclear distance on complexation and two types of structure are evident. One of these has the coordinated C=C bond at approximately right

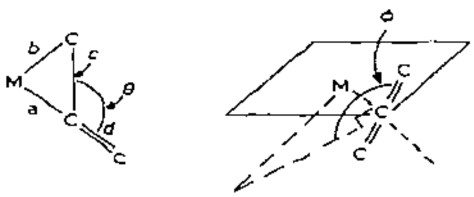


Fig. 1. Structural parameters of allene complexes determined by single-crystal X-ray diffraction; see Table 1 for data.

TABLE 1

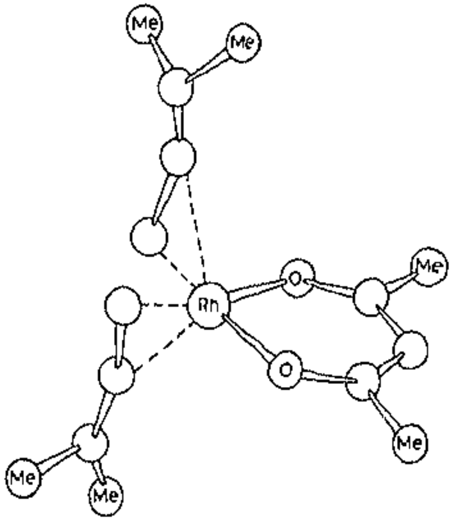
Internuclear distances (Å) and some angles in allene—transition-metal complexes

Complex	*a*	*b*	*c*	*d*	θ	ϕ	Ref.
Rh(acac)($Me_2C:C:CMe_2)_2$ (I)	2.03	2.18	1.38	1.32	148.9	97.9	32
	2.03	2.18	1.37	1.32	147.2	97.8	
Rh(acac)($Me_2C:C:CH_2$)	2.06	2.14	1.40	1.30	153.3	95.5	24
	2.05	2.12	1.41	1.29	152.6	85.6	
Rh($Ph_3P)_2$(I) $CH_2:C:CH_2$ (II)	2.04	2.17	1.35	1.34	158	—	33
Pd($Ph_3P)_2(CH_2:C:CH_2$) (III)	2.07	2.12	1.40	1.30	148.3	8.6	34
Pt($Ph_3P)_2(CH_2:C:CH_2$)	2.03	2.13	1.48	1.31	412	9	35
Pt($Ph_3P)(CH_2:C:CMe_2$)	2.05	2.11	1.43	1.32	140.8	7.8	36
($PtCl_2Me_2C:C:CMe_2)_2$ (IV)	2.07	2.25	1.37	1.36	151.4	95.4	32, 37
[Rh(acac)CO$]_2$-$CH_2:C:CH_2$ (V)	2.07	2.13	1.41	1.37	144.5	103.2	24
	2.06	2.13				102.5	
[CpFe(CO$)_2$-$Me_2C{=}C{=}CMe_2]^+BF_4^-$ (VI)	2.06	2.24	1.37	1.335	145.7	—	38

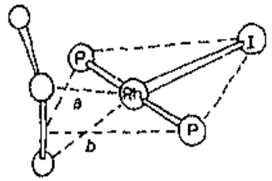
angles ($\phi \simeq 90°$) to the metal—ancillary ligand plane. In the other type the allene and the metal—ligand system are almost coplanar ($\phi \simeq 10°$). The allene ligand in these two situations formally occupies one and two coordination positions respectively.

Due to the structural similarities between olefin and allene complexes it is appropriate to describe the bonding in allene complexes with $\phi \simeq 90°$ in terms of the Dewar—Chatt—Duncanson (DCD) molecular orbital picture of the metal—olefin bond [39,40]. For the complexes of zerovalent metals with $\phi \simeq 10°$ the DCD model has been modified as described by Nelson et al. [41]. Ligand→metal ($\pi \rightarrow d$) and metal→ligand ($d \rightarrow \pi^*$) transfers of electron density both serve to lengthen the carbon—carbon bond and to bend substituents away from the metal atom. There has been much discussion of the relative merits of the so-called monodentate-π and bidentate-σ descriptions of bonding in metal—olefin and metal—acetylene complexes. These two types of bonding situation are illustrated for allene complexes by (VIIA) and (VIIB).

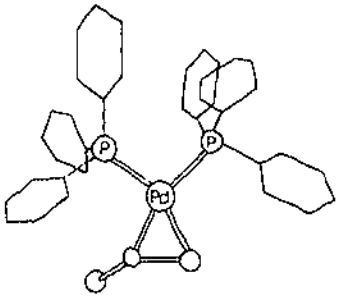
Maitlis [42] has proposed that the π- and σ-descriptions are extremes of a continuuum of bond types. Whether a complex lies closer to the π- or the σ-description will depend on the relative extents of ligand→metal and metal→ligand electron density transfer and this in turn will be determined by the nature and oxidation state of the metal, by the number and nature of the ancillary ligands and by the allene's substituents. The free allene molecule



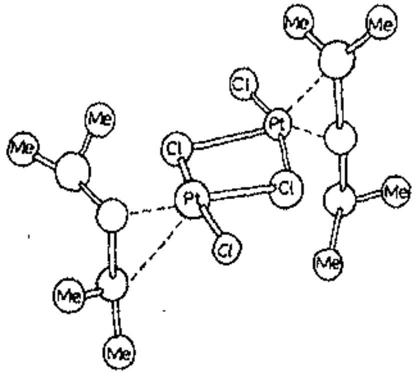
(I)



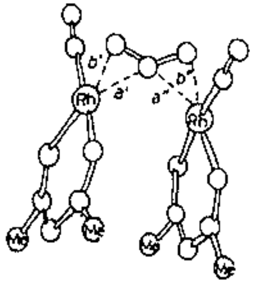
(II)



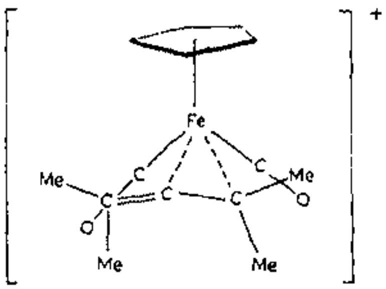
(III)



(IV)



(V)



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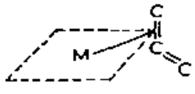
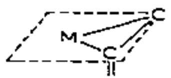


(VII A)



(VII B)

is linear but in allene complexes the three carbon system deviates from linearity by 22—39°. In this respect, the allene ligand resembles other three-atom ligand systems e.g. CS_2 [43]. A molecular orbital interpretation of this bending is based on a substantial contribution to the structure from the first excited state of the ligand molecule [44]; indeed the first excited state of allene is known to be bent [45]. In valence bond terms, the central and terminal coordinated carbons of the allene have assumed sp^2 and sp^3 coordination respectively. These differences in hybridisation may also account for differences in metal-to-carbon bond lengths (columns a and b, Table 1).An alternative explanation is that the central carbon atom with two orthogonal π^*-orbitals is able to participate in two modes of metal→ ligand back-bonding [32].

D. SPECTROSCOPIC PROPERTIES OF ALLENE COMPLEXES

(i) Infrared spectra

Infrared data on allene complexes are very limited. A lowering of the characteristic ν_{asym}(C=C=C) of the free allene is observed on coordination — values of $\Delta\nu$ are in the range 180—260 cm^{-1} (Table 2) compared with 60—150 cm^{-1} for olefin ligands. Square-planar platinum complexes exhibit the largest shifts; an absorption at 1680 cm^{-1} in the spectrum of $(Ph_3P)_2Pt(C_3H_4)$ has been compared [4] to ν(C=C) at 1700 cm^{-1} in methylene cyclopropane and has been suggested to indicate a substantial contribution from the bidentate σ-type structure. The formally bidentate nature of the allene ligand has been confirmed by X-ray crystallography (Table 1).

The IR spectra of some Ag^I and Cu^I complexes of some cyclic allenes

TABLE 2

ν_{asym}C=C=C (cm^{-1}) and $\Delta\nu$ [a] of coordinated allenes.

Complex	ν_{asym}C=C=C	$\Delta\nu$	Ref.
$Pt(Ph_3P)_2C_3H_4$	1680	260	7
$Rh(Ph_3P)_2(Cl)C_3H_4$	1730	210	4
$Ir(Ph_3P)_2(Cl)C_3H_4$	1719	221	26
$Ir(Ph_3P)_2(Cl)(O_2)C_3H_4$	1760	180	26

[a] ν_{asym}C : C : C in CH_2 : C : CH_2 = 1940 cm^{-1}.

shows two weak absorptions in the region 1650—1910 cm^{-1} attributed to free and coordinated C=C bonds of the allene [31]. This indicates a substantial degree of localised bonding. Coordinated allene exhibits strong IR absorption at 855 cm^{-1}; this is assigned to the out-of-plane deformation mode of the uncoordinated $=CH_2$ group; it is almost unchanged from the value of 850 cm^{-1} in the free allene.

(ii) NMR spectra

Platinum—allene complexes have been the major focus of NMR studies. The proton resonance of the coordinated CHR group is shifted to higher field by δ 2—3 ppm, compared with the free allene (Table 3); it exhibits the 1 : 4 : 1 splitting pattern characteristic of coupling with the ^{195}Pt nucleus ($I = \frac{1}{2}$, 33.3% natural abundance). The large $J(Pt—H_A)$ values (Table 3) are very

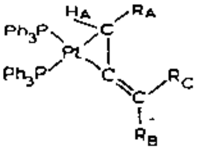


TABLE 3

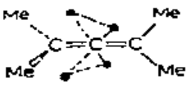
^1H NMR data [a] for allene complexes

Complex [b]	δH^A	δH^B	δH^C	Coupling constants, J	Ref.
$L_2PtC_3H_4$	2.46	5.07	6.47	P^AH^B, 11.6; P^BH^B, 3; P^AP^C, 23.5	28
	2.02	4.43	4.67	$Pt—H^A$, 62; $Pt—H^B$, 77; $Pt—H^C$, 110	4
L_2Pt-DMA	2.33	1.41 (Me)	2.31 (Me)	$Pt—H^A$, 55	
$L_2PtPhCH=C=CHPh$	4.13	6.30	—	P^AH^A, 6.3; P^BH^A, 8.7; P^AH^B, 10.7; P^AH^C, 23.5; $Pt—H^A$, 67.2; $Pt—H^B$, 60.8	28
$L_2PtCH_2=C=CHCF_3$	2.12	4.87	—		23
$L_2PdC_3H_4$	3.15	4.75	6.00	—	
$L_2PdPhCH : C : CHPh$	4.75	6.05	—	P^AH^B, 10.0; P^BH^B, 1	28
$L_2NiPhCH : C : CHPh$	4.17	6.12	—	P^AH^B, 8.9; P^BH^B, 2	28
DMA	2.5	1.63 (Me)	1.91 (Me)	—	
$L_2RhClC_3H_4$	0.53	4.08	4.35	—	4
$L_2RhClC_3H_4$	1.22	4.78	5.02		
$L_2RhClCH_2=C=CHCF_3$	1.46	5.50	—		

[a] Units: chemical shifts δ in p.p.m.; coupling constants J in Hz.
[b] Abbreviations: L = Ph_3P; DMA = 11,-dimethylallene.

similar to those found for methylplatinum complexes [46]; furthermore, the $J(\mathrm{Pt{-}H_B})$ values are typical of *cis*-Pt—H couplings in square-planar platinum—alkenyl complexes [47]. Both of these observations could be interpreted in terms of a σ-bonded or metallocyclopropane type structure. NMR data indicate that 1,1,1-trifluorobuta-2,3-diene is coordinated to platinum and rhodium via the unsubstituted double bond [23]; chemical evidence supports this conclusion (Section E).

Fluxional behaviour. Depending on the coordination symmetry, either three or four proton resonances are expected in the NMR spectra of complexes of allene or tetramethylallene. In several cases, the expected pattern is only obtained at low temperatures, coalescence to a singlet occurring as the temperature is raised. At —60°C the ^{1}H NMR spectrum of $\mathrm{Fe(CO)_4}$-$\mathrm{(Me_2C{=}C{=}CMe_2)}$ in $\mathrm{CS_2}$ consists of three signals at 2.03 (1H), 2.00 (1H) and 1.77 ppm (2H), indicating binding of the iron atom to only one double bond of the allene; at room temperature the spectrum collapses to a singlet at δ 1.84. This is consistent with rapid migration of the iron atom between all available coordination sites as in VIII [13]. ^{195}Pt—methyl coupling persists during the fluxional behaviour of $\mathrm{(PtCl_2Me_2C{=}C{=}CMe_2)_2}$ (IV) and the migration rate is independent of concentration indicating a monomolecular process [5,48]. A reduction in electron density at the metal atom decreases the activation energy as evidenced by the increasing rate of migration for $\mathrm{PtCl_2(Me_2C{=}C{=}CMe_2)L}$ ($\mathrm{L} = p\text{-}\mathrm{XC_5H_4N}$) in the series X = $\mathrm{NH_2}$, $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, H, Br, CN [5,48]. With pyridine N-oxides, rates are much lower than expected; they have been rationalised by assuming that $p_\pi \rightarrow d_\pi$ donation from



(VIII)

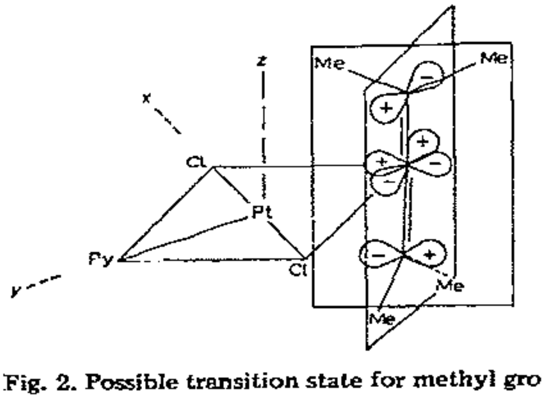


Fig. 2. Possible transition state for methyl group exchange in $\mathrm{[PtCl_2Me_2C:C:CMe_2]_2}$.

lone pairs of electrons on the oxygen enhanced the $d_\pi \rightarrow \pi^*$ component of the metal—allene bond [49]. A mechanism for the migration reaction has been suggested which involves an intermediate (or transition state) with bonding between the metal d_{xy}-orbital and the pair of empty orthogonal π^*-orbitals on the allene's central carbon atom (Fig. 2).

E. REACTIONS OF ALLENE COMPLEXES

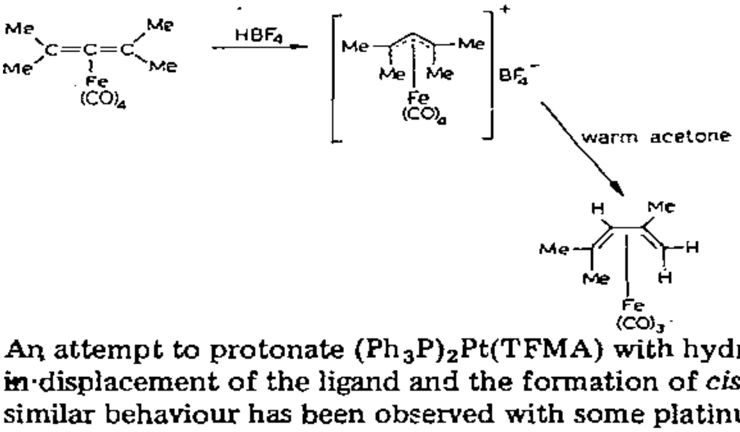
The lability of the allene ligand has given rise to a number of simple replacement reactions with molecules such as CS_2 [50], PPh_3 [3,4], CO [4], $CF_3C_2CF_3$ [23] and RNCS (R = Me, Ph) [51].

(i) Hydrogenation

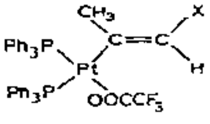
The allene complex $(Ph_3P)_2Rh(C_3H_4)Cl$ is reported to resemble $(Ph_3P)_2$-$Rh(C_2H_4)Cl$ in being resistant to hydrogenation at 1 atm H_2 pressure and 25°C in benzene [4]. Similar resistance is exhibited by the trifluoromethylallene (TFMA) complex $(Ph_3P)_2RhCl(CH_2 : C : CHCH_3)$ but at 80°C hydrogenation occurs affording 1,1,1-trifluorobut-2-ene [25]. It seems likely that under these more forcing conditions an equilibrium between free and coordinated allene is established followed by rhodium hydride formation, re-coordination of the allene and finally hydrogenation and release of the hydrogenated ligand.

(ii) Protonation

Reversible protonation reactions are involved in the acid-induced rearrangement of (tetramethylallene)$Fe(CO)_4$ to 2,4-dimethyl-1,3-pentadiene$Fe(CO)_3$.



An attempt to protonate $(Ph_3P)_2Pt(TFMA)$ with hydrogen chloride resulted in displacement of the ligand and the formation of *cis*-$(Ph_3P)_2PtCl_2$ [25]; similar behaviour has been observed with some platinum—acetylene and —fluoroolefin complexes [52] where intermediate alkenyl complexes undergo further addition of HCl. The use of CF_3COOH as the proton source provides an acid anion which stabilises alkenyl and alkyl complexes [47,53]. $(Ph_3P)_2Pt(all)$ (all = C_3H_4 or TMFA) underwent protonation with CF_3COOH affording the alkenyl complexes ((IX), X = H or CF_3). Complex ((IX), X = H) is identical to that obtained [47] from the protonation of $(Ph_3P)_2Pt(CH_3C \vdots CH)$. *cis*-



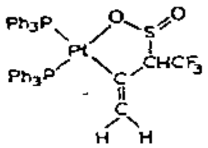
(IX)

$(Ph_3P)_2Pt(CF_3COO)[CCF_3{=}C(CF_3)H]$ readily isomerises to the *trans*-complex [54]; no such isomerisation could be effected with *cis*-$(Ph_3P)_2Pt(CF_3COO)$-$[CCH_3{=}C(CF_3)H]$ [23]. Alkenyl complexes have also been obtained [23] from $(Ph_3P)_2Rh(Cl)(all)$ (all = C_3H_4, TMFA) and hydrogen chloride; the propenyl complex slowly decomposed in solution affording 2-chloroprop-1-ene and $[(Ph_3P)_2RhCl]_2$. Either oxidative addition of HX(X = Cl, CF_3COO) to the allene complex followed by hydrogen transfer to the ligand or direct electrophilic attack at the terminal-CH_2 of the coordinated allene could account for the observed products.

(iii) Insertion reactions

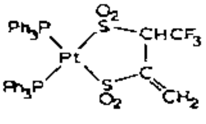
Sulphur dioxide. Reactions which lead to the formal insertion of SO_2 into metal—carbon σ-bonds are well documented [55]. Either O- or S-sulphinates may be formed. In one case, the O-sulphinate formed initially has been shown to rearrange to the more stable S-isomer. σ-Allyl and -propargyl complexes undergo SO_2 insertion with rearrangement [56]. This is explained by initial electrophilic attack of SO_2 at the carbon—carbon multiple bond, followed either by ring closure at the original α-carbon and formation of a new M—C_β bond or by nucleophilic displacement of a coordinated CHR=CH— fragment by $O{=}S^{+}{-}O^{-}$.

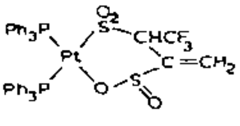
If one adopts the metallocyclopropane view of the structure of the allene complexes $L_2P(all)$ and $L_2Rh(Cl)(all)$ then it can be seen that there are two potential sites for attack by SO_2 namely the two metal—carbon σ-bonds and the uncoordinated double bond. A 1 : 1 adduct is formed from equimolar amounts of $(PH_3P)_2Pt(C_3H_3CF_3)$ and SO_2 [23]. The IR and NMR spectra of the adduct indicate the existence of two isomeric O-sulphinates and that rearrangement has occurred to produce the ring structure (X). A possible



(X)

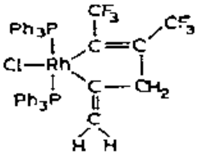
source of the isomerism is the non-planarity of the ring. The *exo*-methylene hydrogens will be in slightly different environments according to the relative dispositions of the S=O and CF_3 groups. Rearrangement accompanying SO_2 insertion implies that the uncoordinated double bond is the initial site of attack. The isolation of an O-sulphinate was somewhat surprising in view of the tendency to S-sulphinate formation shown by many organometallic complexes. Further reaction of the mono-O-sulphinate complex with an excess of SO_2 did produce a complex which contains at least one and probably two S-sulphinate groups on the basis of its IR spectrum [23], although an unequivocal distinction between the bis-S- and O—S-sulphinate structures (XIA) and XIB) cannot be made on spectroscopic evidence alone. The possibility


(XIA)


(XI B)

that complex (XI) contained one inserted and one coordinated SO_2 molecule was considered. Such an adduct would be five-coordinate. Complex (XI) did not have any spectroscopic properties which could be interpreted in terms of five-coordination. The intermediacy of the mono-O-sulphinate complex in the formation of the bis-SO_2 complex was established by monitoring the reaction by IR spectroscopy. A fairly rapid reaction (15 mins) occurred to give the mono-SO_2 complex as evidenced by the appearance of IR bands near to 800 cm^{-1} and 1000 cm^{-1}. These bands diminished in intensity over 24 h and a band at 1050 cm^{-1} due to the bis adduct grew in intensity over the same period. The first stage in the SO_2 insertion reaction could be the coordination of the SO_2 molecule either as a Lewis acid or as a base. The former is more likely for complexes containing low valent transition metals. There is one report of an iridium complex which, it is claimed, contains coordinated SO_2 and allene ligands. The IR data ($\nu_{sym}(SO_2) = 1040$, $\nu_{asym}(SO_2) = 1215$, 1190 cm^{-1}) are however also consistent with a structure resulting from SO_2 insertion into the iridium—allene bond, but the high field value δ 1.23 ppm, of the methylene resonance is not. Clearly further work is required on this interesting compound.

Hexafluorobut-2-yne. Hexafluorobut-2-yne and $(Ph_3P)_2Rh(Cl)(C_3H_4)$ form a 1 : 1 adduct $(Ph_3P)_2Rh(Cl)(C_7H_4F_6)$ as the major product along with a small amount of the known alkyne complex $(Ph_3P)_2Pt(C_4F_6)$. The adduct was assigned the structure (XII) on the basis of IR and ^1H and ^{19}F


(XII)

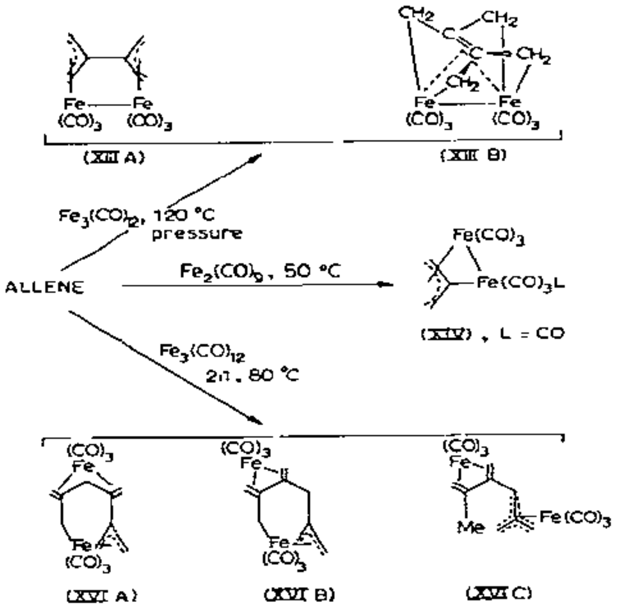
NMR spectroscopy. In the analogous product obtained from the 1,1,1-trifluoromethylallene complex $Ph_3PRhCl(C_4H_3F_3)$ the $=CHCF_3$ unit is retained [25]. Formation of the rhodocyclopentene complex can be envisaged as occurring through coordination of the alkyne followed by insertion into the Rh—C(terminal) bond of the metallocyclopropane structure.

F. π-ALLYL COMPLEXES FROM ALLENES

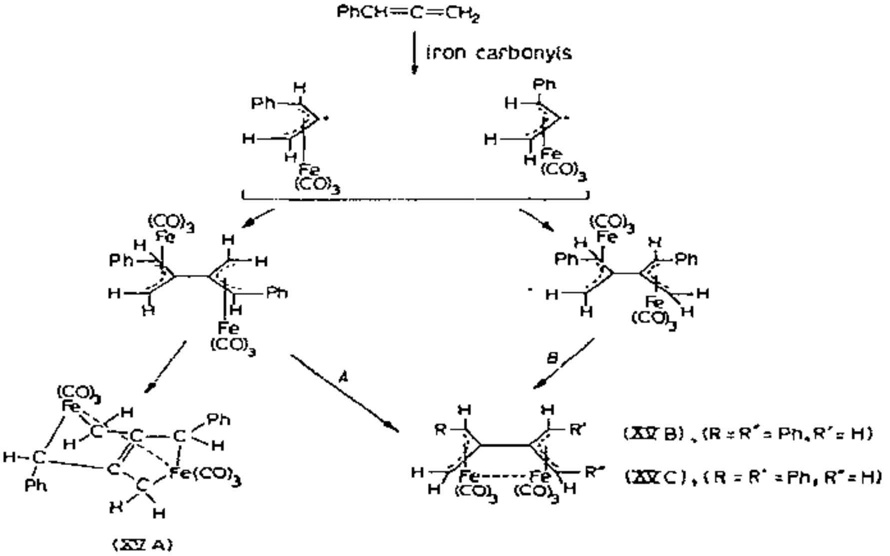
A number of dimerisation, oligomerisation and insertion reactions of allenes lead to π-allyl complexes. Coordination of the allene molecule is usually assumed to precede formation of the allyl complex but so far there are no examples of isolable π-allene-allyl intermediates.

(i) Iron

Allene reacts with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ to yield a variety of bi- and trinuclear π-allyl complexes. The major product of the reaction between equimolar amounts of $Fe_3(CO)_{12}$ and allene at 120°C under pressure is the 2,2′-bi-π-allylene complex $Fe_2(CO)_6(C_6H_8)$ (XIII) [3,12]. The ^{1}H NMR spectrum of (XIII) exhibits two singlets separated by only δ 0.07 ppm, at 35°C which coalesce at −10°C. This suggests fluxional behaviour involving rapid valence tautomerism between the two forms (XIIIA) and (XIIIB) [57]. X-ray diffraction studies [58] confirmed the presence of (XIIIA) in the solid state. Complex (XIII) is also formed when $Fe_2(CO)_9$ is used as the iron source [59] but the main product when $Fe_2(CO)_9$ is in excess is an oil $(C_3H_4)Fe_2(CO)_7$.



The structure of the crystalline mono triphenylphosphine derivative (XIV) L = Ph_3P determined by X-ray diffraction [60] has an allyl group π-bonded to one iron atom and σ-bonded to the other, both metal atoms thus attaining the 18-electron configuration. Three isomers (XVA—C) of the dinuclear complex $[(C_3H_3Ph_3)_2Fe_2(CO)_6]$ result from the reaction between $Fe_2(CO)_9$ and monophenylallene at 40—45° C [58]. A bi-π-allyl structure for isomer A

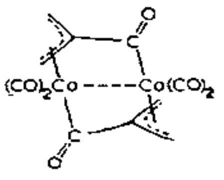


was excluded on the grounds of the similarity between the chemical shifts of its protons and those of tricarbonyl-1-phenylbutadieneiron, and the absence of splittings characteristic of hexacarbonylbi-π-allyldi-iron in the metal—carbonyl region of the IR spectrum. The simplicity of the ^{1}H NMR spectrum (δ 7.40 (Ph), 2.92 (b + b′), 1.77 (a + a′) and 0.80 (c + c′)) demands a symmetrical ligand structure such as that shown in (XVA). Similar arguments were used to arrive at structures (XVB) and (XVC) for the two remaining isomers. Complex (XVA) readily isomerises to (XVC) at ca. 135° C. Neither (XVB) nor (XVC) show any tendency to isomerise. In (XVB) and (XVC) both iron atoms have the 18-electron configuration whereas this is not the case in (XVA). The tendency of iron in its organometallic compounds to achieve the 18-electron configuration may be a possible driving force for the isomerisation which can be envisaged to proceed through an intermediate bi-allyl complex. Apart from a slight broadening of the peaks, the NMR spectrum of (XVC) does not change up to 135° C, thus there is no evidence of valence tautomerism in the monophenylallene complexes.

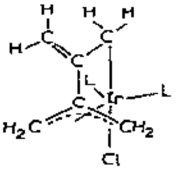
Trimerisation and dimerisation of allene occur when it is heated with $Fe_3(CO)_{12}$ in a 2 : 1 ratio [61]; the C_9H_{12} ligand appears in the form of two isomeric complexes (XVIA) and (XVIB). Complex (XVIA) isomerises to (XVIB) and eventually to (XVIC) on heating. The structures of these isomers which were suggested on the basis of spectroscopic data have been confirmed by X-ray diffraction [62]. The most remarkable structural feature is the trimethylene unit of (XVIC).

(ii) Cobalt, rhodium and iridium

The polymerisation of allenic compounds catalysed by dicobalt octacarbonyl yields polymers whose IR spectra show bands due to metal-carbonyl groups. This observation prompted a re-examination of the reactions between cobalt carbonyls and allenes. When allene is bubbled through a benzene solution of $Co_2(CO)_8$, there is an exothermic reaction and a change in colour to red-brown. Sublimation of the solid reaction residue afforded $Co_4(CO)_{12}$ and yellow crystals of composition $[(C_3H_4)Co(CO)_3]_2$. Formulation of this material as a π-allylacylcobalt complex (XVII) was based on its diamagnetism and spectroscopic properties (ν_{CO} 2050, 2010 cm^{-1}; $\nu_{C=O}$ 1620 cm^{-1}; δ 3.61, 2.28 ppm, (equal intensity)) [12]. The formal insertion of allene into the M—H bonds of $L_3Rh(CO)H$ and $L_2Ir(CO)_2H$ ($L = Ph_3P$) affords the allyl complexes $L_2M(CO)\pi$-allyl (M = Rh, Ir) [62]. Treatment of $IrCl(Ph_3P)_3$ or $IrCl(Ph_3P)_2(C_3H_4)$ with an excess of allene resulted in the formation of the white crystalline complex $IrCl(Ph_3P)_2(C_6H_8)$ (XVIII) [26]. X-ray investigation has shown the allene dimer to be in the form of a tridentate 2,2'-bi-σ,π-allyl ligand. This was the first demonstration of the primary insertion step proposed for the catalytic oligomerisation and polymerisation of allenes.



(XVII)

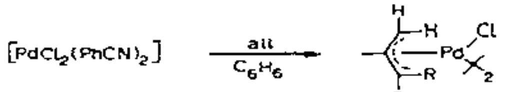


L = Ph_3P

(XVIII)

(iii) Nickel, palladium and platinum

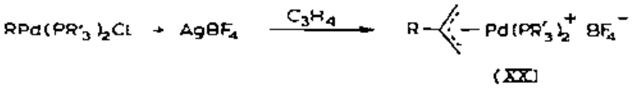
Nickel-allyl complexes are intermediates in the catalytic oligomerisation and polymerisation of allenes; they are discussed in Section G. Allenes undergo formal insertion into the Pd—Cl bonds of $(PhCN)_2PdCl_2$ or Na_2PdCl_4 [63—67]. The insertion reaction leading to (XIX) is reversible; triphenylphos-



(XIX)

all = C_3H_4 , R = R' = H
all = MeC_3H_3, R = H , R' = Me
all = $Me_2C_3H_3$, R = R' = Me

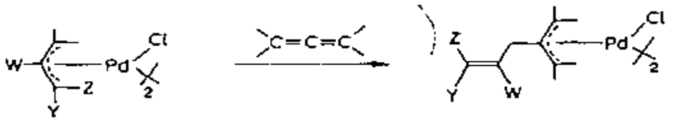
phine cleaves the chlorine bridges in (XIX) to give $(Ph_3P)PdCl(C_3H_4Cl)$ this subsequently eliminates allene leaving a residue of $(Ph_3P)_2PdCl_2$ [64]. Preliminary coordination of the allene is a common feature of the various mechanisms proposed for insertion into Pd—Cl or Pd—C bonds. Whereas $[PdCl\text{-}R(PEt_3)_2]$ fails to react with allene at room temperature, rapid reaction ensues in the presence of $AgBF_4$. This removes chloride as AgCl and provides a vacant coordination site on the palladium atom [68]. Other reactive palladium complexes have an available site for coordination of the allene or easily displaced ligands such as PhCN. Coordination of the allene is assumed to precede its insertion into the Pd—C bond which leads to the cationic complex (XX). Rapid *syn-anti* proton exchange occurs on addition of allenes



(XX)

R' = Me, Ph ; R = Me

to π-allylic palladium complexes. The rate of *syn-anti* proton signal collapse parallels the rate of insertion of a given allene and depends on the substituents on the π-allyl function, on the substituents on the allene and on the nature of the other palladium ligands. Allenes with one unsubstituted C=C bond react most rapidly and the reaction is first order with respect to both complex and allene. These observations have been interpreted in terms of a short lived σ-allyl intermediate whose formation provides a site on the palladium for the attacking allene [69—71]. Migration of the σ-allyl ligand to the central carbon atom of the coordinated allene is suggested as the rate determining step since the ^1H NMR signals due to the product (XXI) appear over a

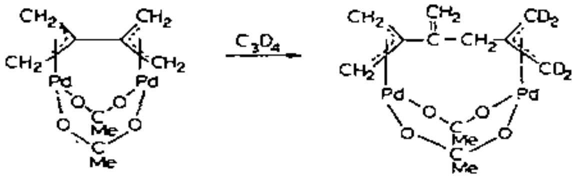


(XXI)

e.g., W = Y = Z = H ;
W = Me ; Y = Z = H
W = Z = H ; Y = Me

relatively long time interval compared with the collapse of the *syn-anti* proton signals. It has not been possible to distinguish between a multi-step or concerted process for the migration. Initial coordination of the allene has been proposed [72—74] as the rate determining step as a result of an independent kinetic investigation of allene insertion into π-allylpalladium complexes. Not only does the suggested displacement of bridging chlorine by allene seem less probable than the coordination of allene at a coordination site created by a π-allyl→σ-allyl rearrangement, but the kinetic results can be interpreted equally well on the basis of such a rearrangement. Some allene dimerisation occurs in the reaction with $Pd(acac)\pi\text{-}C_3H_5$, the 2,2'-di-π-allyl complex (XXII) (X = acac) is formed as a by-product [69—71]. An

(XXII)



(XXII)

(X = CH$_3$COO)

(XXIII)

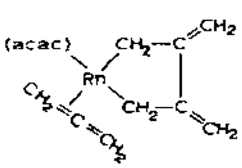
analogous complex (X = Cl) can be obtained directly by the reduction of $PdCl_4^{2-}$ in the presence of allylic halides [75]. Further insertion of allenes into the 2,2′-di-π-allyl complexes (XXII) (X = acac or Cl) cannot be effected but when X = acetate insertion into the palladium—allyl bond occurs as evidenced by the formation of complex (XXIII) [76]. The enhanced reactivity of the bridged acetate complex was attributed to a degree of strain which could be relieved by the increased distance between the two π-allyl ligands [77]. The ^1H analogue of complex (XXIII) has also been obtained directly from palladium acetate and allene [78].

π-Allylplatinum complexes, e.g. [π-allyl $Pt(PEt_3)_2]^+BPh_4$, are formed by the insertion of allene into the Pt—H bond of $(PEt_3)_2PtHX$ (X = hal, NO_3). The pronounced influence of the nature of X or the rate of allene insertion has been interpreted in terms of a cationic π-allene intermediate [79]; a few such cationic complexes have been isolated [6,80].

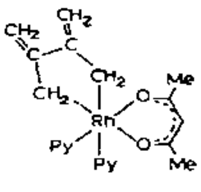
G. TRANSITION-METAL-CATALYSED OLIGOMERISATION AND POLYMERISATION REACTION OF ALLENES

As stated earlier, much of the impetus for the study of complexes derived from allenes and transition-metal compounds stems from observations that such complexes occur as intermediates in the catalytic oligomerisation and polymerisation reactions of allenes. The fate of the allene in such reactions is critically dependent on the precise nature of the catalyst and on the reaction conditions as shown in Table 4.

A sequence of coordination-insertion reactions seems the most probable course for the catalysed oligomerisation and polymerisation of allenes. This suggestion is strengthened by the results of two recent studies. The first concerns the reaction between allene and (acac)$Rh(C_2H_4)_2$ [81]. At —78°C there is a rapid reaction with the formation of a yellow crystalline complex



(XXIV)



(XXV)

TABLE 4

Allene oligomerisations

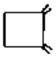
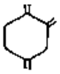
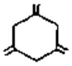
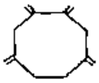
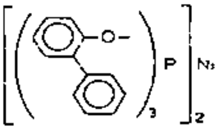
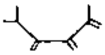
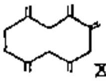
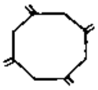
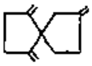
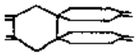
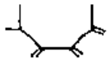
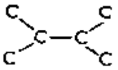
Catalyst	Allene oligomer	Ref.
$[(C_6H_5)_2PC_6H_4P(C_6H_5)Ni(CO)_2]_n$ 200 °C vapour phase		96
		96
	 XXIX A	96
$[(PhO)_3P]_2Ni(CO)_2$, THF, 110°	XXIX A	97
$[(PhO)_3P]_3Ni(CO)$	 XXIX B	97
$[(PhO)_3P]Ni(CO)_3$	 * XXX	97
$(Ph_3P)_2Ni(CO)_2$		97
	XXIX A	98
	 from dimethyl allene	99
$Ni(1,5\text{-}COD)_2 + R_3P$ (R = alkyl, aryl)	XXX  XXXI	100,105
$+(RO)_3P$	XXIX B	104,105
$Ni(1,5\text{-}COD)_2$	XXXI	104,105
* incorrectly assigned the structure	 in ref. 97	
$(Ph_3P)_3RhCl$, $CHCl_3$ solution, 80°	 + pentamer ?	101
$(Ph_3P)_2Rh(CO)Cl$		

TABLE 4 (continued)

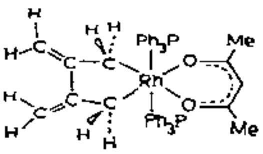
Catalyst	Allene oligomer	Ref.
$Rh_2Cl_2(C_2H_4)_4$ + 1-2 Ph_3P, EtOH, 60°	XXXI	102
$[Rh(CO)_2Cl_2]_2$ + 2 Ph_3P, EtOH, 40°	(XXX) + XXXI +  	103

[a] 1,5-COD = 1,5-cyclo-octadiene.

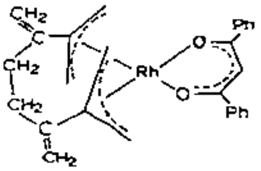
with the stoichiometry (acac)Rh$(C_3H_4)_3$ (XXIV). This readily loses allene in solution or on being treated with pyridine or triphenylphosphine; the latter reactions afford complexes with the stoichiometry L_2Rh(acac)$(C_3H_4)_2$ (L = py (XXV); L = Ph_3P (XXVI)). Both these complexes and (XXIV) liberate tetrabromoethylethylene on reaction with bromine indicating that they contain an allene dimer unit with the skeleton:



This was confirmed by an X-ray crystallographic examination of (XXV) [82]. The *trans* structure was proposed for (XXVI) on the basis of its ^1H NMR spectrum which shows the presence of four equivalent methylene protons and two pairs of equivalent olefinic protons. That the third C_3H_4 unit in (XXIV) is present as an allene ligand is supported by the ease with which it is eliminated and by IR absorption bands at 1670 and 860 cm^{-1} attributable to coordinated allene. Reaction of LRh$(C_3H_4)_3$ (L = dibenzoylmethane) with allene at −35°C produces the bis-π-allylic complex (XXVII) the implication being that the

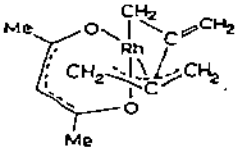


(XXVI)



(XXVII)

allene tetramer ligand is formed by sequential coordination-insertion reactions [81]. Analogues of (XXVII) can also be obtained directly from dikRh$(C_2H_4)_2$, (dik = acac(acetylacetone), Hfac (hexafluoro-acac) or dbm (dibenzoylmethane)), and allene at −35°C. These produced 2,3,6,7-tetramethyloctane on hydrogenolysis and 1,2,5,6-tetramethylenecyclooctane on treatment with CO. The inference that a ligand based on the 2,3,6,7-tetramethyleneoctane skeleton had been formed was confirmed by an X-ray crystallographic study of the dbm complex (XXVII) which showed the ligand to be bound to the Rh atom by two π-allylic bonds. Complex (XXVII) reacted with allene in hydrocarbon solutions at 60—70°C to give highly crystalline polymers with the regular repeating unit $[-CH_2-C(=CH_2)-]_n$ along with a mixture of oligomers. At some stage during the build up of the oligomeric allene ligands, π-allyl units must be formed. It is possible that this occurs as early as the dimer stage affording structure (XXVIII) as an alternative to (XXIV). An analogous σ,π-allyl structure has been determined by X-ray diffraction for $IrCl(Ph_3P)_2$-(C_6H_8). Subsequent coordination of allene and its insertion into the rhodium—carbon σ-bond could then lead through a trimer complex to the observed tetramer complex. The second study [83] of catalysed oligomerisation concerned the selective oligomerisation of allene to cyclotrimer (XXIXA), cyclotetramer (XXX) and cyclopentamer (XXXI) — a series of nickel complexes, Table 4. Organometallic nickel complexes which contain allene trimer and tetramer ligands have been isolated; they provide convincing evidence of a multi-step pathway for catalysed oligomerisation. Reactions of $Ni(1,5\text{-}COD)_2$ with allene are summarised in Figure 3. Bis(π-allyl) coordination of the C_9H_{12} ligand in complex (XXXII) is assumed by analogy with the structure of $[NiC_9H_{12}\{P(C_6H_{11})_3\}]$ [84] (XXXIII) which has been determined by X-ray diffraction [85]. Both the ^1H NMR parameters [83] of (XXXII) and its liberation of 2,3,5-trimethylenecyclopentane on being treated with CO



(XXVIII)

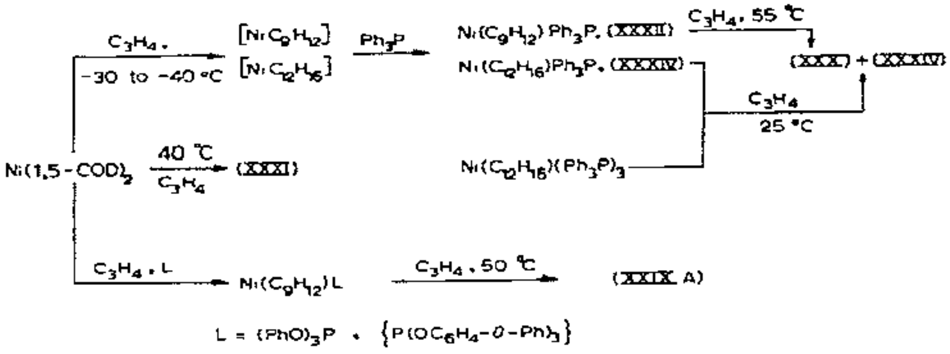
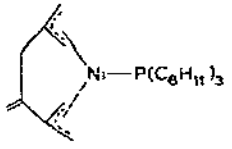
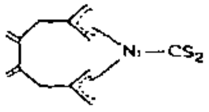


Fig. 3. The reactions of allene with Ni 1,5-$(COD)_2$.

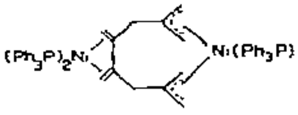


(XXXIII)

are in accord with the bis(π-allyl) structure. Displacement of the phosphine ligand of (XXXIV) by CS_2 at −40°C was accompanied by the disappearance of phosphorus coupling with the *anti*-protons of the π-allyl group. At higher temperatures displacement of both the phosphine and $C_{12}H_{16}$ tetramer occurred. The ^1H NMR spectrum of the CS_2 adduct (XXXV) at −20°C indicates the presence of a symmetrical bis(π-allyl) ligand. This same ligand appears to be present in the binuclear complex (XXXVI) although here the



(XXXV)



(XXXVI)

exo-methylene groups are coordinated according to both IR and ^1H NMR data. All the available evidence on the catalytic oligomerisation of allene is accommodated by Fig. 3. Mono allene complexes can be obtained when substituted allenes are employed. There are no structural data on the dimer complex; it could have either the tridentate σ-, π-allyl ligand structure of the iridium complex $(Ph_3P)_2IrCl(C_6H_8)$ (XVIII) or the metallocyclopentane structure suggested for the rhodium complex $Rh(C_3H_4)(C_6H_8)(acac)$, (XXIV). Any or all of the bis(π-allyl) complexes of Fig. 3 may exist in η^1-σ, η^2-π or η^3-π equilibrium with, for example, electron withdrawing phosphite ligands

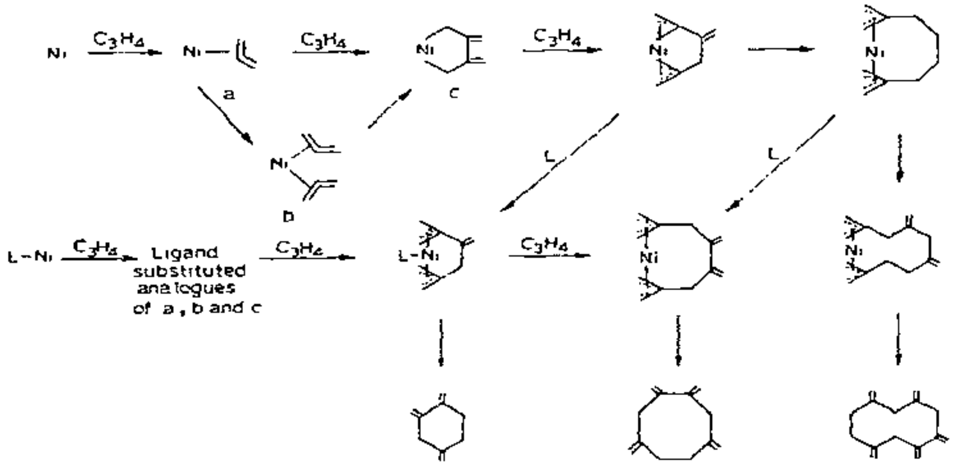
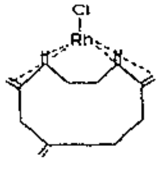


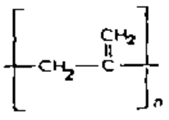
Fig. 4. Stages in the nickel-catalysed oligomerisation of allene.

favouring the first and electron donating phosphines the last. Electrophilic attack of allene should therefore be enhanced by phosphine ligands and retarded by phosphites. Indeed, phosphite liganded catalysts give higher yields of trimer (XXXB) and phosphine catalysts higher yields of tetramer (XXXX). However, the coordinative unsaturation of intermediates that do not have phosphine or phosphite ligands is expected to favour further coordination and hence the formation of higher oligomers. This is supported by the high reactivity of Ni(1,5-COD)$_2$ compared to phosphine and phosphite substituted nickel complexes, and by the preferential formation of pentamer and higher oligomers with this catalyst.

There is one example of a complex of an allene pentamer [$RhCl(C_{15}H_{20})$] (XXXVII). This was obtained from allene and either [$Rh_2Cl_2(C_2H_4)_4$] or [$Rh_2Cl_2(C_3H_5)_4$] [86—88]. Diphos displaces free allene pentamer from (XXXVII).



(XXXVII)

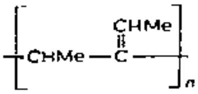


(XXXVIII)

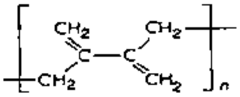
Polymerisation. Amorphous irregular polymers are the usual products of the thermal, photochemical or free-radical initiated polymerisation of allenes. In contrast, regular crystalline polymers can be obtained from polymerisations catalysed by transition-metal complexes.

A regular vinylidene sequence (XXXVIII) forms the major part of the polymers derived from Ni(0) and Ni(I) catalysts [89]. The IR spectra of the polymers also indicated the presence of some conjugated diene units [90]. The regular vinylidene polymer, 1,2-polyallene, is characterised by IR absorption bands at 2900—3100 [ν(C—H)], 1636 [ν(C=C)], 1426 [δ(CH_2)] and 897 cm^{-1} [δ(=CH_2)] and equal intensity ^{1}H NMR signals at δ 2.69 (CH_2) and δ 4.95 (=CH_2) [89,91,92]. Its structure has been confirmed by X-ray crystallography which shows the vinylidene units to be in a helical arrangement [92,93].

Homogeneous 1,2-polyallene has been prepared using a Ni(acac)$_2$-, triisobutylaluminium catalyst [94]. Propagation appears to occur preferentially at the unsubstituted double bond of monomethylallene and 1,1-dimethylallene [91]. A similar steric control is exerted in the insertion of allene into palladium—allyl complexes, here the inserted molecule becomes attached to the least substituted carbon atom of the original π-allyl moiety [69]. Optical activity is retained in the polymer formed from 1,3-dimethylallene with (π-allyl NiI)$_2$ as catalyst, regular head-to-tail addition giving the repeating unit (XXXIX). Head-to-head addition occurs with allene in the



(XXXIX)



(XL)

presence of a palladium nitrate—PPh$_3$ (1 : 1) catalyst in glacial acetic acid; the conjugated double bond system of the polymer (XL) is indicated by a strong absorption at 1596 cm^{-1}. In the absence of triphenylphosphine, products such as allyl acetate, 2,3-dimethylbuta-1,3-diene, 3-methyl-2-acetoxymethylbuta-1,3-diene and 2,3-diacetoxymethylbuta-1,3-diene are formed [95]. The addition of ligands is clearly a crucial if little understood factor in controlling allene oligomerisation or polymerisation; whereas the addition of triphenylphosphine to [RhCl(C$_2$H$_4$)$_2$]$_2$ favours the formation of allene tetramer, triphenylphosphite or alkyl isonitrites promote polymerisation.

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