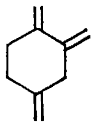
Reaction Paths and Mechanisms in the Catalytic Cycloaddition of Allene over Nickel(0) Template Systems

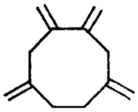
By **Sei Otsuka,* Kazuhide Tani,** and **Tsuneaki Yamagata,** Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

Catalytic cycloadditions of allene, $CH_2=C=CH_2$, have been effected with a variety of nickel(0)–phosphorus ligand systems. The selective catalytic reaction path leading to the cyclotrimer, cyclotetramer, or cyclopentamer depends primarily on the nature of the ligands. Intermediate nickel(0) complexes containing the linear trimer (C_9H_{12}) or tetramer ($C_{12}H_{16}$) have been detected spectroscopically or isolated by stabilisation with phosphorus ligands. On the basis of the structures of the isolated complexes and kinetics, multistep reaction paths are described and the roles of the phosphorous ligands in these catalysts discussed.

THERMAL reactions of allene, $CH_2=C=CH_2$, in particular cyclodimerisation, have recently received considerable attention.[1] Two orthogonal $2p$ orbitals of the central carbon atom are considered to assist the [2 + 2] cycloaddition reaction.[2] However, whether the reaction proceeds through a concerted or stepwise mechanism is still in dispute.[3] In metal-catalysed reactions allene is known to cyclise to methylene-substituted compounds ranging from four- to twelve-membered rings.[4-9] Mango and Schachtschneider have presented a theoretical argument to show that formally forbidden cycloadditions may be realised in the presence of a transition-metal catalyst.[10] However, experimental evidence is accumulating in support of the fact that catalysed cycloadditions of olefins[11] and acetylene[12,13] proceed by multistep processes. In view of the electronic structure of allene, mechanistic aspects of catalysed cycloaddition seem to merit further investigation.

We have found nickel(0) complexes which catalyse cyclo-oligomerisation[6,7] producing selectively cyclotrimer (I), cyclotetramer (II), or cyclopentamer (III) among possible isomers, *i.e.* two trimethylenecyclohexanes, four tetramethylenecyclo-octanes, and four pentamethylenecyclodecanes. Our primary object here is to present unequivocal evidence supporting the multistep reaction path involved in these metal-assisted cycloadditions.


(I)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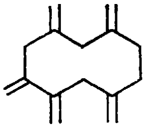
(III)

RESULTS

Stoicheiometric Reactions.—Treatment of the complex $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene) with an excess of allene at −30 to −40 °C, either with or without toluene or tetrahydrofuran, yielded an air-sensitive, thermally unstable, red oily solid. In one experiment red needles were observed[14] when $[Ni(cod)_2]$ was treated with liquid allene below −30 °C, but this crystalline product could not be isolated. Generally the reaction between the complex $[Ni(cod)_2]$ and an excess of allene yielded a red oily solid even at −70 °C. The ^1H n.m.r. spectrum of this crude product in C_7D_8 at −30 °C showed complicated signals due to cyclo-octa-1,5-diene. Catalytic hydrogenation (PtO_2) of the product gave a mixture of 2,3,5-trimethylhexane and 2,3,5-trimethylhex-2-ene, together with a C_{12} hydrocarbon mixture containing 2,4,5,7-tetramethyloctane, suggesting that two complexes are present, one containing a linear allene trimer and the other a tetramer as the ligand. Since the oligomerisation proceeded, even at −70 °C, to the trimer or tetramer stage on a reaction mixture containing an excess of allene, attempts were made to stabilise the initial stage by using phosphine ligands and/or by limiting the amount of added allene.

The ethylene complex $[Ni(C_2H_4)(PPh_3)_2]$ appears to be a good starting material for preparation of the allene monomer complex since relative π-acidities of allene and ethylene indicate that replacement of ethylene by allene should occur. In fact, allene monomer complexes of formula $[Ni(substituted\ allene)(PPh_3)_2]$ were obtained from 1,3-diphenyl- and 1,1-dimethyl-allene (Table 1). An equimolar mixture of allene and the complex $[Ni(C_2H_4)(PPh_3)_2]$ (0·07 mmol each) was prepared in C_7D_8 (0·5 cm³) at −70 °C. The ^1H n.m.r. spectrum, as measured at −70 °C, showed very broad signals (Δ 50 Hz, where Δ = width at half peak height) at δ 3·1 p.p.m. due to the ethylene protons and a broad weak signal centred around δ 4·7 p.p.m. Since the ethylene protons in $[Ni(C_2H_4)(PPh_3)_2]$ gave rise to a singlet at δ 2·48 p.p.m., and the protons in free ethylene dissolved in toluene showed a

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[1] W. R. Dolbier, jun., and Sheng-Hong Dai, *J. Amer. Chem. Soc.*, 1970, **92**, 1774; for a review see J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, 1970, **15**, 289.

[2] R. Hoffmann, *21st Org. Chem. Symp. Abs.*, Amer. Chem. Soc., Salt Lake City, Utah, June, 1969, pp. 110—129; J. M. Brown, *Ann. Rep.*, 1969, **66**, *B*, 367.

[3] W. C. Herndon, *Chem. Rev.*, 1972, **72**, 157.

[4] R. E. Benson and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 4247.

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[9] J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.*, 1962, **84**, 1257.

[10] E. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484.

[11] B. Barnett, B. Bussemeier, P. Heimbach, R. W. Jolly, C. Krüger, I. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972, 1457.

[12] H. Dietl, H. Reinheimer, J. Moffat, and M. Maitlis, *J. Amer. Chem. Soc.*, 1970, **92**, 2276.

[13] G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 1969, **91**, 3800 and references therein.

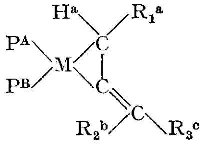
[14] S. Otsuka, K. Mori, and F. Imaizumi, *J. Amer. Chem. Soc.*, 1965, **87**, 3017.

sharp singlet at δ 4·70 p.p.m., the broad signal at δ 3·1 p.p.m. is considered to be due to exchange between free and co-ordinated ethylene molecules. The sharp singlet at δ 4·48 p.p.m. was absent indicating consumption of all the allene molecules. Evidently substitution of the ethylene ligand in the complex $[Ni(C_2H_4)(PPh_3)_2]$ with allene is incomplete despite the disappearance of all the free allene.

The presence of unreacted ethylene complex complicated the ^1H n.m.r. spectrum at −70 °C. However, on raising the temperature above −10 °C, the spectrum gradually became clearer. Now signals were recognised at δ 5·1 (m), 4·65 (m), 3·2(s), 3·05(s), and 1·75—1·55(m) p.p.m., which can be assigned to the allene trimer complex, $[Ni(C_9H_{12})PPh_3]$, (V) (*vide infra*). In addition to these signals a slightly broad singlet (Δ 7 Hz) due to the ethylenic hydrogen atoms was observed at δ 2·70, indicating rapid exchange between complexed and free ethylene molecules. The above observation precludes the claim by Pasquale[8] that the monomer complex $[Ni(C_3H_4)(PPh_3)_2]$, (IV), is isolable. At least it is improbable that complex (IV) is stable enough to exist above −10 °C in the system $[Ni(C_2H_4)(PPh_3)_2]$–C_3H_4.

TABLE 1

^1H N.m.r. data for complexes $[M(allene)(PPh_3)_2]$ in C_7D_8

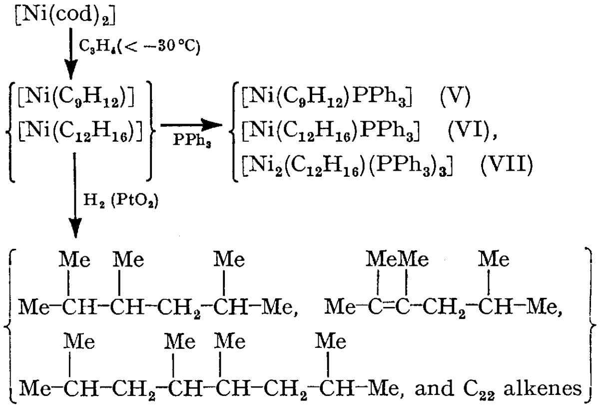


M	Allene	Chemical shift (p.p.m.) δH [a]	δH [b]	δH [c]	$J_{P^AH^a}$	$J_{P^BH^a}$	$J_{P^AH^b}$	$J_{P^BH^b}$	$J_{P^AH^c}$	$J_{P^BH^c}$	$J_{H^aH^b}$
Pt	$CH_2=C=CH_2$ [a,b]	2·46	5·07	6·47			11·6	3	23·5	3	3
	PhCH=C=CHPh [a,c]	4·13	6·30		6·3	8·7	10·7	1·4			3·0
	$CH_2=C=CMe_2$ [a,d]	2·33 [e]	1·41(s) [f]	2·31(s) [f]							
Pd	$CH_2=C=CH_2$ [g]	3·15(br)	4·75(br)	6·00(br)							
	PhCH=C=CHPh [h]	4·75	6·05				10·0	1			2·2
Ni	$(CH_2=C=CH_2)$	(2·51) [i]	(4·84) [i]	(6·3) [i]							
	PhCH=C=CHPh [j]	4·17	6·12				8·9	2			2·7
	$CH_2=C=CMe_2$ [a,d]	2·5(br)	1·63(s) [f]	1·91(s) [f]							

[a] Measured at 22·5 °C. [b] J_{PtH^a} *ca.* 62, J_{PtH^b} *ca.* 77, J_{PtH^c} *ca.* 110 Hz. [c] J_{PtH^a} 67·2, J_{PtH^b} 60·8 Hz. [d] Measured in C_6D_6. [e] J_{PtH^a} 55 Hz. [f] Signal of methyl protons. [g] Measured at −74 °C. [h] Measured at −36 °C. [i] Estimated from the data for allene and 1,3-diphenylallene complexes in this Table. [j] Measured at −15 °C.

The reported preparation[8] of complex (IV) involves treatment of ' bistriphenylphosphinenickel(0) '[15] with allene. As the complex contains only triphenylphosphine ligands it was convenient to follow the initial step of the reaction with allene by ^1H n.m.r. spectroscopy. A mixture of *ca.* 3 mol of allene and ' $[Ni(PPh_3)_2]$ ' in C_7D_8 at −70 °C again showed signals due to complex (V) and a singlet at δ 4·48 p.p.m. due to free allene; no other signal was observed except those due to aromatic protons. On raising the temperature to 22·5 °C the signal at δ 4·48 p.p.m. almost disappeared leaving only signals due to (V). A mixture of ' $[Ni(PPh_3)_2]$ ' with 1 mol of allene was then prepared at −70 °C in an n.m.r. tube. Signals were hardly recognisable over noise levels in the region δ 0·08—8·0 p.p.m., except those due to the aromatic protons of PPh_3. The free allene signal was absent, indicating that even at −70 °C allene is consumed completely to form complexes. When the temperature was raised to 22·5 °C, signals emerged, albeit at low intensity, at δ 3·20(s) and 3·0(s) p.p.m. These can be readily assigned to *syn*-protons of the π-allylic group of complex (V). Again there was no evidence for the existence of (IV). If the reaction system did contain complex (IV), the allene ligand should have given rise to three signals of intensity ratio 2 : 1 : 1 in a region which may be predicted from data of the Pd^0 and Pt^0 congeners (see Table 1). However, all spectra for the systems $[Ni(C_2H_4)(PPh_3)_2]$–C_3H_4 and $[Ni(PPh_3)_2]$–C_3H_4 lacked these characteristic signals, in particular a signal around δ 5·3 p.p.m., indicating the absence of (IV).

Addition of 1 mol of PPh_3 to the above red viscous nickel complex, obtained from $[Ni(cod)_2]$ and an excess of allene in n-hexane at −30 °C, immediately caused precipitation of an allene tetramer complex, $[Ni(C_{12}H_{16})PPh_3]$, (VI), as an orange-yellow powder (m.p. 103—106 °C decomp., 20% yield). Treatment of the orange-red filtrate with Al_2O_3 and subsequent crystallisation from n-hexane at −40 °C gave complex (V) as orange-red crystals (m.p. 97—98 °C decomp., 19%). When a solution of PPh_3 was added to the red oily solid material in toluene, followed by a small amount of n-hexane, an orange crystalline tetramer complex, $[Ni_2(C_{12}H_{16})(PPh_3)_3]$ (VII) (m.p. 115—118 °C decomp.), was slowly precipitated (30%



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[15] G. Wilke, E. W. Müller, M. Kröner, P. Heimbach, and H. Breil, B.P., 935,716/1963 (*Chem. Abs.*, 1963, **59**, 14026C).

yield). The mother liquid contained complex (V), as detected by ^1H n.m.r. spectroscopy. The relative amounts of the isolated phosphine-stabilised complexes (V)—(VII) indicate that the red product initially formed from $[Ni(cod)_2]$ and C_3H_4 at −30 °C contains $[Ni(C_9H_{12})]$ and $[Ni(C_{12}H_{16})]$ in roughly equal amounts.

In contrast to rapid formation of the allene tetramer complex $[Ni(C_{12}H_{16})]$ from $[Ni(cod)_2]$, complex (V) reacted with allene slowly, allowing the reaction to be monitored using ^1H n.m.r. spectroscopy. A mixture of (V) (0·1 mmol) and allene (0·2 mmol) in C_6D (0·5 cm^3) showed no significant change in spectrum during 24 h at room temperature. On heating at 50 °C, new signals appeared at δ 5·0 (d, *J* 3 Hz), 4·8(s), 4·75(m), 3·0(s), and 2·2 p.p.m. (s) at the expense of the free allene signal, consistent with the formation of tetramer (II) [equation (1)]. About 92% free allene was consumed after 20 h, the intensity of signals due to complex (V) remaining almost constant, a fact

$$[Ni(C_9H_{12})PPh_3]\ (V) + 4C_3H_4 \xrightarrow{50°\ C} (II) + (V) \quad (1)$$

which confirms the intermediacy of (V) in the cyclotetramerisation (see Discussion section). Both complexes (VI) and (VII) are more reactive than (V); they readily reacted with allene, even at room temperature, in benzene to give (V) and tetramer (II) [equation (2)]. It is noteworthy that the reaction does not produce pentamer (III), in accordance with the observed selectivity in catalysis.

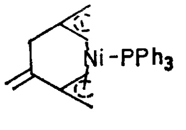
$$[Ni(C_{12}H_{16})PPh_3]\ (VI)\ \text{or}\ [Ni_2(C_{12}H_{16})(PPh_3)_3]\ (VII) + 3C_3H_4 \xrightarrow[20\text{—}25\ °C]{} (II) + (V) \quad (2)$$

The reaction of the complex $[Ni(cod)_2]$ with allene in the presence of 1 mol of a phosphite ligand L produced an analogous complex $[Ni(C_9H_{12})L]$ as an orange viscous oil $[L = P(OPh)_3]$ or orange crystals $[L = P(OC_6H_4\text{-}o\text{-}Ph)_3]$. These complexes are much more inert than (V) with respect to attack by allene or carbon monoxide. A mixture of the complex $[Ni(C_9H_{12})\{P(OC_6H_4\text{-}o\text{-}Ph)_3\}]$ (0·1 mmol) and allene (0·15 mmol) dissolved in C_6D_6 (0·5 cm^3) showed no appreciable change in ^1H n.m.r. spectrum during 24 h at room temperature. When warmed to 50 °C, the solution showed new signals at δ 5·0(m), 4·65(m), 2·86(s), and 2·31(s) p.p.m. at the expense of the free allene signal indicating formation of allene trimer (I) [equation (3)]. During 20 h free allene was completely consumed. The formation of allene tetramer (II) was totally prevented,

$$[Ni(C_9H_{12})L] + 3C_3H_4 \longrightarrow (I) + [Ni(C_9H_{12})L] \quad [L = P(OPh)_3\ \text{or}\ P(OC_6H_4\text{-}o\text{-}Ph)_3] \quad (3)$$

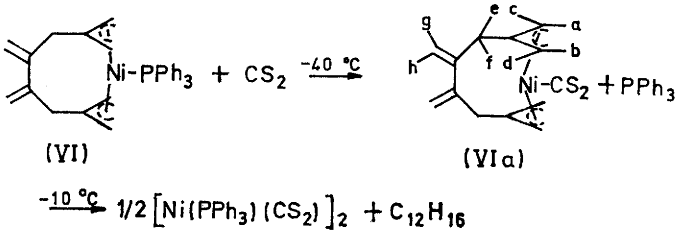
in accordance with the catalytic selectivity. However, formation of a small amount of solid polyallene seems to be unavoidable (Table 2).

Allene Trimer–Phosphine Complex, (V).—The stable trimer complex (V) was characterised by elemental analyses, molecular-weight determination (cryoscopic in benzene), i.r. and n.m.r. spectra.[7b] An *X*-ray structure analysis of an analogous complex $[Ni(C_9H_{12})\{P(C_6H_{11})_3\}]$ established bis(π-allyl) co-ordination for the C_9 ligand.[16] Treatment of complex (V) with CS_2 at room temperature gave (I) and the known complex $[Ni(CS_2)(PPh_3)]_2$,[17] and treatment of (V) with atmospheric carbon monoxide at room temperature in benzene produced 2,3,5-trimethylenecycloheptanone (as a readily polymerisable liquid) and (I) in 7 : 1 mol ratio, together with some $[Ni(CO)_3PPh_3]$. Catalytic hydrogenation of complex (V) yielded the same acyclic C_9 hydrocarbon mixture as that produced from the phosphine-free red oily product (*vide supra*), indicating that stabilisation by phosphorous ligands is not accompanied by cyclisation of the linear oligo-allene ligands.



(V)

Mononuclear Allene Tetramer–Phosphine Complex, (VI).—The extremely air-sensitive orange-yellow complex (VI) was characterised by elemental analyses, i.r. [$\nu_{max.}$ 897 cm^{-1}, δ(=CH_2)] and ^1H n.m.r. spectra.[7a] Carbon disulphide replaced the phosphine ligand in (VI) at <−40 °C, as detected by the disappearance of phosphorus coupling with *anti*-protons of the π-allyl group. At higher temperatures (above −10 °C) displacement of $C_{12}H_{16}$ with PPh_3 occurred giving $[Ni(PPh_3)(CS_2)]_2$ and the cyclic tetramer (II). Since this substitution rate is quite slow at −10 °C, a ^1H n.m.r. study could be carried out in this temperature range. The signals which appeared below −20 °C at δ 5·29 (2H, d, *J* 2 Hz, H^g), 4·69 (2H, m, H^h), 2·76 (2H, br, s, H^c or H^d), 2·63 (2H, br, s, H^d or H^c), 2·46 (4H, s, $H^e + H^f$), 1·20 (2H, s, H^a or H^b), and 0·88 (2H, s, H^b or H^a) p.p.m. conform to the C_{12} bis (π-allyl) structure of (VIa). Above −10 °C averaging between pairs of signals (H^a–H^b, H^c H^d, *etc.*) simplified the spectrum; at 24 °C signals occurred at δ 5·30 (d, 2H, *J* 2 Hz, H^g), 4·68 (m, 2H, H^h), 2·71 (s, 4H, $H^c + H^d$), 2·49 (s, 4H, $H^e + H^f$), and 1·07 (s, 4H, $H^a + H^b$) p.p.m. There were also signals of low intensity [δ 4·88 (d, *J* 6 Hz), 4·73(s), 2·99(s), and 2·26(s) p.p.m.] due to the allene tetramer (II); these intensities increased slowly at the expense of the signals of complex (VIa). The formation of complexes $[Ni(PPh_3)(CS_2)]_2$ and (II) was complete within 1 h at 24 °C. The structure of the C_{12} ligand in (VI) relates to that of the oligomer (II).



Binuclear Allene Tetramer–Phosphine Complex (VIII).—The air-sensitive orange binuclear complex (VII) was characterised by elemental analyses and the n.m.r. spectrum. Although the poor solubility in organic solvents prevented cryoscopic molecular-weight measurements, the binuclear structure could be inferred from the following data. The n.m.r. spectrum showed that complex (VII)

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[16] M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1971, **10**, 77; B. L. Barnett, C. Krüger, and Yi-Hung Tsay, *ibid.*, 1972, **11**, 137.

[17] M. C. Baird, G. Hartwell, jun., R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Comm.*, 1967, 92; M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.

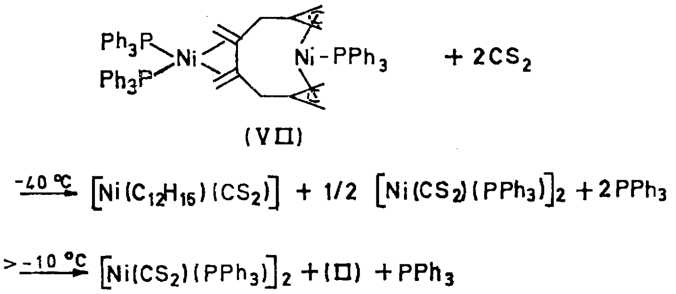
TABLE 2

Cyclo-oligomerisation of allene with nickel(0) catalysts in benzene [a]

Catalyst	Added ligand [b]	Concentration [c] (mol %)	Reaction conditions (t/°C, time/h)	Conversion (%)	Selectivity (%) Trimer [d] (I)	Tetramer (II)	Pentamer (III)	Higher oligomers and polymer
e		0·20	40, 40	100	Trace	Trace	52	48
e	$4PPh_3$	2·5	70, 20	93	28	66	6	Trace
e	PBu^n_3	2·5	50, 72	100	13	60	18	10
e	$2P(OPh)_3$	0·25	70, 20	15	48	21	Trace	31
e	P(O-*o*-tolyl)$_3$	2·5	70, 24	100	38	9	20	33
e	P(O-*o*-biphenylyl)$_3$	2·5	70, 24	96	39	11	5	44
$[Ni(C_2H_4)(PPh_3)_2]$		2·5	70, 26	100	20	53	10	17
$[Ni(cod)(PBu^n_3)_2]$		2·5	60, 48	100	17	83	Trace	Trace
$[Ni\{P(OPh)_3\}_4]$		2·5	70, 20	81	72	25	3	Trace

[a] Allene (2·1 g, 52·5 mmol); benzene (10 cm^3). [b] Added *in situ* to the reaction mixture at −78 °C (see Experimental section). [c] Mol % of Ni^0 complexes based on allene. [d] About 5% 1,3,5-trimethylenecyclohexane was present. [e] $[Ni(cod)_2]$; cod = cycloocta-1,5-diene.

reacted with carbon disulphide to give (II) and $[Ni(CS_2)(PPh_3)]_2$ *via* a phosphine-free intermediate (VIa). In the open-chain $C_{12}H_{16}$ ligand in complex (VII) free *exo*-methylene group is absent, as the i.r. spectrum lacked absorption in the region 880—900 cm^{-1} and the ^1H n.m.r. spectrum (in C_6D_6) showed no signals in the olefinic region, while two π-allyl systems are involved in the co-ordination, as in (VIa). These data can best be accommodated by formulating the structure (VII) as shown above. The nickel atom co-ordinated to the 1,3-diene part requires two triphenylphosphine ligands to satisfy an inert-gas configuration and the other nickel atom carrying the two π-allyl ligands also aquires such a configuration by additional bonding to one PPh_3 molecule. Polymeric structures can probably be excluded.



Catalytic Cycloadditions.—Results for several preparative runs effected at 40—70 °C are shown in Table 2. In the absence of added phosphorus ligands the complex $[Ni(cod)_2]$ led to selective formation of pentamer (III), other isomeric pentamers and lower oligomers being virtually absent (g.l.c.). Electron-donating phosphine ligands, *e.g.* PBu^n_3, led predominantly to the tetramerisation product (II), while reaction with electron-accepting triaryl phosphites proceeds with trimerisation to (I) (95%) and the 1,3,5-isomer (5%). The selectivity could be improved by decreasing the allene : nickel mol ratio and by lowering the reaction temperature. Polymer formation was not appreciable during the initial stages of the reaction.

A brief kinetic study was carried out to determine the rate dependence on allene concentration. Only initial rates were measured and low allene : nickel mol ratios (10—21 : 1) were used so that a selectivity of at least 70% was maintained in each case. The rate of reaction increased in the order $Ni^0–P(OPh)_3 < Ni^0 – PPh_3 < Ni^0$. Rates for both pentamerisation and tetramerisation were first order with respect to the allene concentration, whereas the trimerisation rate was nearly zero order. These results can be accommodated by the reaction sequences (4)—(6) (7)—(9), and (10), (11). In these schemes, rapid steps

Pentamerisation

$$Ni^* + 4C_3H_4 \xrightarrow{\text{fast}} [Ni(C_{12}H_{16})] \quad (4)$$

$$[Ni(C_{12}H_{16})] + C_3H_4 \xrightarrow{\text{slow}} [Ni(C_{15}H_{20})] \quad (5)$$

$$[Ni(C_{15}H_{20})] \xrightarrow{\text{fast}} Ni^* + C_{15}H_{20} \quad (6)$$

* labile ligands, *e.g.* cod, are not shown.

Tetramerisation

$$Ni–PR_3 + 3C_3H_4 \xrightarrow{\text{fast}} [Ni(C_9H_{12})PR_3] \quad (7)$$

$$[Ni(C_9H_{12})PR_3] + C_3H_4 \xrightarrow{\text{slow}} [Ni(C_{12}H_{16})PR_3] \quad (8)$$

$$[Ni(C_{12}H_{16})PR_3] \xrightarrow{\text{fast}} Ni–PR_3 + C_{12}H_{16} \quad (9)$$

Trimerisation

$$Ni–P(OAr)_3 + 3C_3H_4 \longrightarrow [Ni(C_9H_{12})P(OAr)_3] \quad (10)$$

$$[Ni(C_9H_{12})P(OAr)_3] \longrightarrow Ni–P(OAr)_3 + C_9H_{12} \quad (11)$$

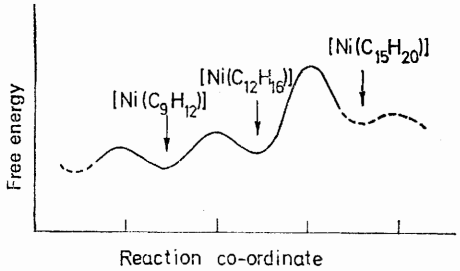
leading to trimer complexes $[Ni(C_9H_{12})]$ and $[Ni(C_9H_{12})PR_3]$ are abbreviated (see Discussion section).

DISCUSSION

The reaction of the complex $[Ni(cod)_2]$ with a few mol to a large excess of allene produces below −30 °C complexes containing allene trimer and tetramer. At higher temperature the Ni^0 complex catalyses the pentamerisation reaction. In the presence of 1 to 2 mol of a phosphorus ligand such as PPh_3, $P(OPh)_3$, or $P(OC_6H_4$-*o*-$Ph)_3$ the reaction produces only the trimer complex (V) in contrast to Pasquale's report.[8] Evidently the potential barriers are quite low up to the trimer and to the tetramer stages in the absence of a phosphorus ligand (see Figure), and even in the presence of such a ligand they are low up to the trimer stage.

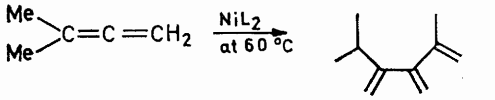
Appropriate substituents on allene are effective in retarding the first few steps and the monomer complex $[Ni(allene)L_2]$ can then be isolated using both 1,3-diphenylallene and 1,1-dimethylallene (Table 1).

Recently Wilke and his co-workers[18] observed catalytic linear dimerisation of 1,1-dimethylallene with NiL_2 [$L = P(OC_6H_4\text{-}o\text{-}Ph)_3$] leading to a triene [equation (12)] and also isolated a sparingly soluble (apparently polymeric) intermediate complex of unknown structure.



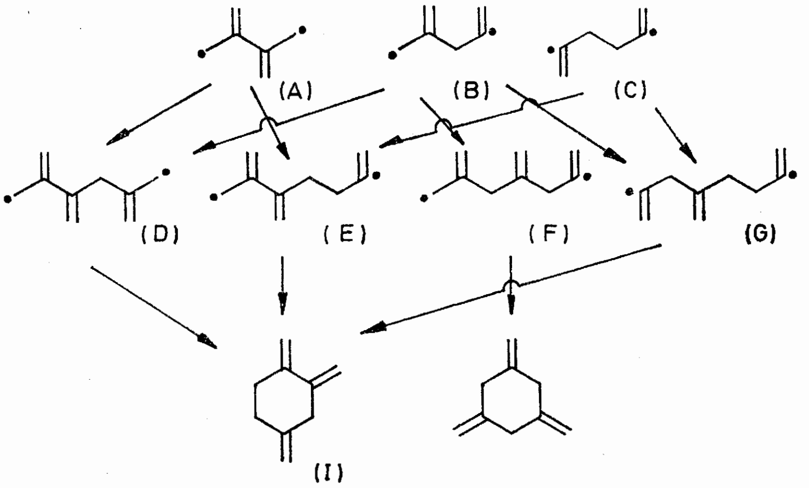
Partial reaction potential profile for the cyclopentamerisation reactions

As this dimerisation reaction involves hydrogen migration, it will not be discussed further here. Assuming no hydrogen migration there are three possible skeletal



(12)

structures (A, B, and C) for the intermediate dimer. Since trimer (D) is the one corresponding to the ligand in complex (V), dimer (C) can be excluded. Both dimers (A) and (B) can be the precursors for (D). However, since 1,3,5-trimethylenecyclohexane constitutes only *ca.* 5% of the trimer, dimer (A) should be predominant. Indeed, as far as we are aware, all reported allene dimer complexes, *e.g.* μ-[1—3:1′-3′-η-(2,2′-biallyl)]-hexacarbonyldi-iron(*Fe–Fe*),[19] hexacarbonyl-μ-[1—3:1′—3′-η-(1,1′-diphenyl-2,2′-biallyl)]-di-iron(*Fe–Fe*),[20] and di-μ-acetato-μ-[1—3:1′—3′-η-(2,2′-biallyl)]-dipalladium,[21] involve the dimer with carbon skeleton (A). It is to be noted that structure (A) is inadequate for formation of a mononuclear complex.



Plausible paths leading to (I), (II), and (III) are shown in the Scheme. There are two sites available in intermediates (VIII) and (V) for allene insertion. A cyclic tetramer formed from (V) would be either (II) or 1,2,4,6-tetramethylenecyclo-octane depending on the insertion site. Exclusive formation of complexes (IX) and (VI) from (VIII) and (V) respectively indicates that there is a preferential site for insertion, namely at the more readily polarisable π-allyl moiety adjacent to the *exo*-methylene group. The linear allene tetramer ligand in complex (IX) has two equivalent allylic groups. Therefore, if a cyclic pentamer is to be formed from (IX), the pentamer should be (III) and not 1,2,4,6,8-pentamethylenecyclodecane as suggested elsewhere.[5,8]

The remarkable effect of the phosphorus ligands in controlling the catalytic reaction paths deserves comment. The observed zero-order reaction for the cyclotrimerisation is accounted for by the enhanced kinetic inertness of the complex $[Ni^0(C_9H_{12})L]$, in accordance with the well known propensity of phosphites to stabilise zero-valent nickel.[22] The complexes $[Ni(C_9H_{12})$-(triaryl phosphite)] undergo unimolecular thermal decomposition, liberating the cyclised trimer C_9H_{12}, rather than allene insertion. This is reasonable since the C_9H_{12} ligand in these phosphite complexes would be reluctant to undergo valence isomerisation to σ-allyl co-ordination, which requires oxidation of the Ni^0 atom. The important role of the phosphite ligand here

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[18] M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem.*, 1972, **84**, 120.

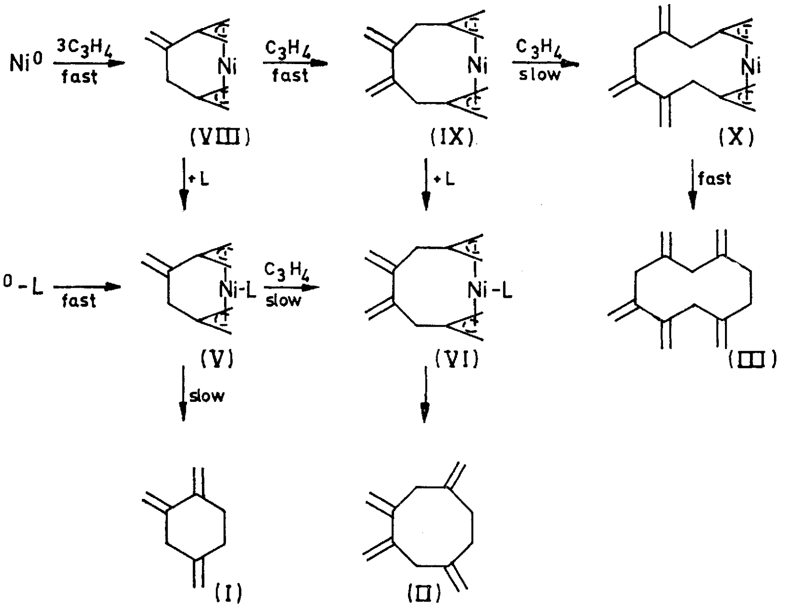
[19] A. Nakamura, Pu-Jun Kim, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1964, **37**, 292; *J. Organometallic Chem.*, 1965, **3**, 7.

[20] S. Otsuka, A. Nakamura, and K. Tani, *J. Chem. Soc.* (*A*), **1968**, 2248.

[21] T. Okamoto, *Chem. Comm.*, 1970, 1126; R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1969, **20**, 17.

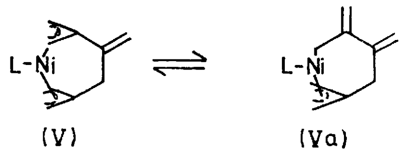
[22] W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, 1970, **9**, 2354.

is to shift the π–σ-allyl co-ordination equilibrium (13) [23] towards the π-form (V).



Scheme

Here it is assumed that monomer insertion takes place at the σ-allyl–metal bond rather than at the π-allyl end. Although it was not possible to experimentally demonstrate the existence of the σ-allyl form, to which electrophilic attack of allene should take place, there are some indications in support of this postulate. For example one indication, supported by the established structure of the tetramer complexes (VI) and (IX), is preferential allene insertion at the carbon end of an extended p_π system in complexes (V) and (VIII), where negative-charge localisation may be enhanced compared to that in the isolated allyl system. Another indication is the ligand effect of tertiary phosphine ligands (*vide infra*), which may be reasonably interpreted assuming that insertion occurs preferentially at the partially anionic end of the allyl group.



(13)

The oxidation state of the nickel atom in complex (Va) may be regarded as formally I or higher (which would be stabilised by electron-donating ligands). Thus the role of a tertiary phosphine ligand in complex (V) is, contrary to that of the electron-withdrawing phosphite, to shift the π–σ equilibrium towards the σ-form (Va). Electrophilic attack of allene is then facilitated, unimolecular thermal decomposition to give (I) being prevented. A similar argument has been put forth by Buchholz *et al.*[23d] for the role of phosphorus ligands in selective oligomerisation of butadiene.

The π–σ allyl equilibrium should also exist with both complexes (VI) and (IX). Predominant formation of (II) from (VI) and (III) from (IX) suggests that blockage of a co-ordination site by a ligand L in (VI) (see Scheme) is effective in raising the potential barrier for allene co-ordination (hence, the insertion). In addition the free energy of activation for thermal decomposition of (VI) should be low [perhaps it may be lower than that of (V)], since further insertion of allene to produce pentamer (III) is a minor reaction path (Table 2). The phosphine-free complexes (VIII) and (IX) are co-ordinatively unsaturated species posing lower potential barriers for allene insertion. The largest reaction rate, together with polymer formation, in the [Ni(cod)$_2$]-catalysed reaction appears to be in accord with the above interpretation.

Concerted cyclo-trimerisation and -pentamerisation of allene should be symmetry-allowed processes. Nevertheless, as we have seen, the catalytic reactions leading to these cyclo-oligomers certainly proceed *via* a number of paths.

EXPERIMENTAL

Reactions involving organometallic complexes were carried out under an atmosphere of nitrogen. Allene (Matheson Co., purity *ca.* 98·7%) was dried, by bubbling it through a solution of triethylaluminium in liquid paraffin (10%), and distilled before use. The complex [Ni(cod)(PBu$^n_3$)$_2$] was obtained from [Ni(cod)$_2$] and an excess of

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[23] (*a*) J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 583, and references therein; (*b*) M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *Angew. Chem.*, 1969, **81**, 453; (*c*) P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1968, **8**, 29; (*d*) H. Buchholz, P. Heimbach, H. J. Hey, H. Selbeck, and W. Wiese, *Co-ordination Chem. Rev.*, 1972, **8**, 129.

PBu_3^n as yellow crystals (m.p. 95—100 °C), for which the molecular weight and analytical data conformed reasonably with calculated values.

Kinetic Measurements.—Using a Warburg apparatus of total volume 20 cm^3, equipped with a side neck through which reactants could be introduced by syringe under an inert-gas atmosphere, the rate dependences on allene pressure (270—900 mmHg)were measured at 50 or 70 °C. Toluene solutions containing [Ni(cod)$_2$] (0·03 or 0·04M), with or without phosphorous ligands (Ni : P = 1 or 0·5 : 1), were used.

Catalytic Oligomerisation.—Using a glass ampoule (40 cm^3), the reaction of allene (2·1 g) in the presence of a given nickel complex was carried out generally in benzene at 40—70 °C. Volatile products were analysed by g.l.c. using naphthalene as internal standard. The non-volatile residue was regarded as a polymer, correction being made for the metal and the non-volatile phosphorus ligand involved. The C_9, C_{12}, and C_{15} cyclo-oligomers were isolated by preparative g.l.c. [Apiezon GL and poly(phenylether) columns]. Results are summarised in Table 1.

Reaction of [Ni(cod)$_2$] *with Allene at Low Temperature.*—The complex [Ni(cod)$_2$] (2·7 g, 10 mmol) and liquid allene (10 cm^3, 150 mmol) were placed in a flask and stirred at −35 °C for 3 h. Unreacted allene was removed below −30 °C to leave a viscous red air-sensitive material [$\nu_{max.}$ 890 (=CH_2) cm^{-1}]; the n.m.r. spectrum (C_7D_8) measured at low temperature showed only broad unassignable complicated signals. The resulting red material was dissolved in n-pentane (*ca.* 30 cm^3) and treated with hydrogen in the presence of PtO_2 catalyst (0·1 g) at −10 to +20 °C to give a pale yellow mixture. G.l.c. analysis showed essentially two peaks (1 : 2) in the C_9 region and four peaks (1 : 0·5 : 1 : 0·5) in the C_{12} region, apart from peaks due to cyclo-octa-1,5-diene and cyclo-octane. The ratio of the C_9 to C_{12} fractions was *ca.* 1 : 1. The two C_9 isomers were 2,3,5-trimethylhexane and 2,3,5-trimethylhex-2-ene, and the first peak of the C_{12} fraction was assigned as 2,4,5,7-tetramethyloctane. Authentic 2,4,5,7-tetramethyloctane was prepared by Wurtz's synthesis from 2-chloro-4-methylpentane.

Allene Trimer Complexes.—(*a*) 1,2,4-*Trimethylenecyclohexane*(*triphenylphosphine*)*nickel*(0), (V). Gaseous allene (600 cm^3) was introduced into a toluene (70 cm^3) solution of the complex [Ni(cod)$_2$] (2·0 g, 7·3 mmol) and PPh_3 (1·95 g, 7·4 mmol) at −35 °C to give a red solution from which was isolated, after alumina chromatography, orange-red crystals (1·8 g, 56%), m.p. 97—98 °C (decomp.) [Found: C, 73·8; H, 6·35. *M* 441 (cryoscopic in benzene). Calc. for $C_{27}H_{27}NiP$: C, 73·5; H, 6·15%. *M* 448]. I.r. spectrum (KBr disc) 1 638 (C=C) and 888 (=CH_2) cm^{-1}. δ (C_6D_6) 1·70 (2H, d, J_{PH} 11·0 Hz), 1·72 (2H, d, J_{PH} 11·0 Hz), 2·87 (2H, broad d, J_{PH} 4·1 Hz), 3·11 (2H, s), 3·27 (2H, s), 4·65 (1H, broad s), 5·04 (1H, broad s), and 6·9—7·7 (15H, m, aromatic protons) p.p.m.

(b) 1,2,4-*Trimethylenecyclohexane*[*tris*(*biphenyl-2-yl*) *phosphite*]*nickel*(0). This complex was similarly obtained, by treating with allene a benzene solution of [Ni(cod)$_2$] and $P(OC_6H_4$-*o*-$Ph)_3$, as orange crystals (1·0 g, 52%), m.p. 96—99 °C (decomp.) (Found: C, 75·4; H, 5·40. Calc. for $C_{45}H_{39}NiO_3P$: C, 75·35; H, 5·50). δ (C_6D_6) 7·50—6·75 (27H, m), 4·92 (1H, m), 4·49 (1H, m), 2·59 (2H, d, J_{PH} 1·5 Hz), 2·44 (2H, d, J_{PH} 1·5 Hz), 2·38 (2H, br, d, J_{PH} 7 Hz), 1·38 (2H, d, J_{PH} 16·0 Hz), and 1·33 (2H, d, J_{PH} 16·0 Hz) p.p.m.

(c) 1,2,4-*Trimethylenecyclohexane*(*triphenyl phosphite*)-*nickel*(0). This complex was obtained as an orange-red oil. $\nu_{max.}$ 1 630 cm^{-1} (unco-ordinated C=C). δ (C_6D_6) 1·87 (2H, d, J_{PH} 15·5 Hz), 1·95 (2H, d, J_{PH} 15·5 Hz), 2·58 (2H, br, d, J_{PH} 6·5 Hz), 2·81 (2H, d, J_{PH} 1·5 Hz), 2·95 (2H, d, J_{PH} 1·5 Hz), 4·48 (1H, m), 4·88 (1H, m), and 6·75—7·35 (20H, m, aromatic protons) p.p.m.

Allene Tetramer Complexes.—(a) 1,2,4,7-*Tetramethylene-cyclo-octane*(*triphenylphosphine*)*nickel*(0), (VI). Solid [Ni(cod)$_2$] (2·0 g, 7·3 mmol) was dissolved in liquid allene (7 cm^3) at −30 to −40 °C. After 2 h the unreacted allene was removed *in vacuo* below −30 °C to leave a viscous red residue. The residue was dissolved in n-hexane (50 cm^3) and treated with an n-hexane solution (50 cm^3) of triphenylphosphine (1·0 g, 7·3 mmol) at −30 °C to precipitate an orange-yellow solid, which was washed with n-hexane and dried *in vacuo* (1·0 g., 20%), m.p. 103—106 °C (decomp.). Attempted recrystallisation of the product (VI) was unsuccessful because of its conversion to complex (VII) (Found: C, 74·45; H, 6·35; Ni, 12·2. Calc. for $C_{30}H_{31}NiP$: C, 74·85; H, 6·50; Ni, 12·2%).

(b) 1,2,4,7-*Tetramethylenecyclo-octanetris*(*triphenylphosphine*)*dinickel*(0), (VII). A red viscous material obtained from [Ni(cod)$_2$] (2·0 g, 7·3 mmol) and liquid allene (7 cm^3, 105 mmol) (*vide supra*) was dissolved in toluene (5 cm^3) at −30 °C. To the stirred solution was added at −30 °C a toluene solution (10 cm^3) of PPh_3 (1·9 g, 7·3 mmol). After stirring for 2 h, n-hexane (15 cm^3) was added to precipitate orange crystals (1·2 g), m.p. 115—118 °C (decomp.) (Found: C, 75·05; H, 6·01; Ni, 10·65. Calc. for $C_{60}H_{61}Ni_2P_3$: C, 74·55; H, 5·80; Ni, 10·95%). There was no strong band at 890 cm^{-1}.

Reaction of [Ni(C_9H_{12})(PPh_3)] *with* CO.—On treating a benzene solution (2 cm^3) of complex (V) (0·5 g, 1·1 mmol) with gaseous CO at room temperature a pale yellow solution was obtained which contained (I) and 3,4,6-trimethylenecycloheptanone in a mol ratio of 1 : 6·7 (g.l.c.). *m/e* 148. I.r. spectrum (neat) 1 708 (C=O), 1 635 (C=C), 1 600 (C=C), and 896 (=CH_2) cm^{-1}. δ (CCl_4) 2·17 (s, 2H, $-CH_2-$), 3·19 (m, 4H, $-CH_2-$), and 4·80—5·25 (m, 6H, =CH_2) p.p.m.

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