Oligomerisation and Telomerisation of Buta-1,3-diene catalysed by Bis-(η-cyclo-octa-1,5-diene)-palladium and -platinum

By **Michael Green, Gary Scholes, and F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The $[Pd(cod)_2]$-catalysed reaction of buta-1,3-diene with secondary amines (morpholine, piperidine, diethylamine, or dimethylamine) affords octa-2,7-dienylamines, the highest yields being obtained with the cyclic amines. However, treatment of buta-1,3-diene with acetic acid–diethylamine in the presence of $[Pd(cod)_2]$ (cod = cyclo-octa-1,5-diene) affords an improved yield of the diethylamine C_8 adduct. The addition of 1 mol of PPh_3 per mol of Pd has only a small effect on the above reactions. The addition of acetic acid to buta-1,3-diene is catalysed by $[Pd(cod)_2]$ to give octa-2,7-dienyl acetate and 1-vinylhex-5-enyl acetate in the ratio of 4 : 1. The $[Pd(cod)_2]$-catalysed reaction of isoprene with morpholine affords as the major product the tail-to-tail amine adduct. The specificity of this reaction is improved by the addition of 1 mol of PPh_3. The system $[Pd(cod)_2]$–PPh_3 catalyses the addition of acetaldehyde to buta-1,3-diene to form 2-methyl-3,6-divinyltetrahydropyran. With phenyl isocyanate, piperidones are formed. Reaction of buta-1,3-diene with morpholine in the presence of $[Pt(cod)_2]$ gives only octa-1,3,6-triene; however, addition of the co-catalyst $Al(OPr^i)_3$ or $Al(OBu^t)_3$ leads to the formation of the octadienylamine adducts. Telomerisation of buta-1,3-diene with acetic acid catalysed by $[Pt(cod)_2]$ gives selectively octa-2,7-dienyl acetate. Possible mechanisms for these reactions are discussed.

MANY transition-metal complexes catalyse the oligomerisation of buta-1,3-diene to either cyclic or linear products. Cobalt,[1-3] iron,[4] or rhodium[5] complexes promote dimerisation to octa-1,3,6-triene and 3-methylhepta-1,4,6-triene. Wilke and his co-workers[6] have extensively studied the dimerisation and oligomerisation of buta-1,3-diene by nickel(0) complexes. In these reactions ' ligand-free ' nickel complexes afforded cyclo-octa-1,5-diene, divinylcyclobutane, and 4-vinylcyclohexene, while ' nickel–ligand ' systems yield linear oligomers. Several research groups[6-13] have studied oligomerisations catalysed by complexes of sub-group 8 metals in the presence of an organic compound containing active hydrogen. Telomerisation with the co-catalyst often becomes the principal reaction, affording octa-2,7-dienyl derivatives. (Tertiary phosphine)palladium complexes[14] are particularly effective in promoting incorporation of the co-catalyst into the oligomers.

The recent availability of the ' ligand-free ' palladium and platinum complexes $[M(cod)_2]$ (M = Pd or Pt; cod = cyclo-octa-1,5-diene)[15] has enabled us to study[16] their ability as catalysts for the oligomerisation of buta-1,3-diene, both in the presence and in the absence of co-catalysts. We have previously reported stoicheiometric reactions between $[Pt(cod)_2]$ or $[Pt(C_2H_4)_2(Me_3P)]$ and buta-1,3-diene which yield stable organoplatinum compounds in which the metal is incorporated into a ring system.[17]

The results described herein show that the complexes $[M(cod)_2]$ catalyse the dimerisation and telomerisation of buta-1,3-diene at lower temperatures and are more selective than the catalysts previously employed.

---

[1] S. Otsuka, T. Taketomi, and T. Kikuchi, *Kogyo Kagaku Zasshi*, 1963, **66**, 1094.

[2] D. Wittenberg, *Angew. Chem.*, 1963, **75**, 1124.

[3] S. Tanaka, K. Mabuchi, and N. Shimazaki, *J. Org. Chem.*, 1964, **29**, 1626.

[4] H. Takahashi, S. Tai, and M. Yamagushi, *J. Org Chem.*, 1965, **30**, 1661.

[5] T. Alderson, E. L. Jenner, and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1965, **87**, 5638.

[6] P. W. Jolly and G. Wilke, ' The Organic Chemistry of Nickel,' Academic Press, 1975, vol. 2 and refs. therein.

[7] S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Letters*, 1967, 2451; *Bull. Chem. Soc. Japan*, 1968, **41**, 454.

[8] E. J. Smutny, *J. Amer. Chem. Soc.*, 1968, **89**, 6793; *Ann. New York Acad. Sci.*, 1973, **214**, 125.

[9] K. E. Atkins, W. E. Walker, and R. M. Manyik, *Chem. Comm.*, 1971, 330.

[10] K. Takahashi, A. Miyake, and G. Hata, *Bull. Chem. Soc. Japan*, 1972, **45**, 1183.

[11] W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Letters*, 1970, 3817.

[12] G. Hata, G. Takahashi, and A. Miyake, *J. Org. Chem.*, 1971, **36**, 2116.

[13] (*a*) R. Baker, D. E. Halliday, and J. N. Smith, *Chem. Comm.*, 1971, 1583; (*b*) R. Baker, D. E. Halliday, A. H. Cook, and T. N. Smith, *J.C.S. Perkin II*, 1974, 1511; (*c*) R. Baker, A. H. Cook, and T. N. Smith, *ibid.*, p. 1517; (*d*) R. Baker, A. Onions, R. J. Popplestone, and T. N. Smith, *ibid.*, 1975, 1133; R. Baker, D. E. Halliday, and T. N. Smith, *J. Organometallic Chem.*, 1972, **85**, C61.

[14] J. Tsuji, *Accounts Chem. Res.*, 1973, **6**, 8.

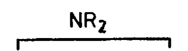
[15] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

[16] M. Green, G. Scholes, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *Abs. 8th Internat. Conf. Organometallic Chem.*, Kyoto, 1977.

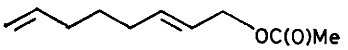
[17] G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1976, **98**, 3373.

RESULTS AND DISCUSSION

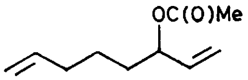
Treatment of buta-1,3-diene with [Pd(cod)$_2$] in the presence of secondary amines at 60 °C affords octa-2,7-dienylamines (1a)—(1d).[13] Except for dimethylamine, where gas chromatography–mass spectrometry (g.c.–m.s.) indicated the presence of some of the branched-chain species, the amine products were pure isomers, conversions being essentially quantitative for morpholine, 80% for piperidine, and 20% for diethyl- and dimethyl-amine. No reaction was observed with di-isopropylamine. Trace amounts of vinylcyclohexene, octa-1,3,7-triene, and cyclo-octa-1,5-diene were observed as products in some reactions. It was of interest that no butenylamines corresponding to 1 : 1 additions were formed. The stereochemistry of the double bonds of (1) was assigned as *trans* on the basis of strong absorptions in the 970 cm^{-1} region of the i.r., and the lack of bands between 650 and 700 cm^{-1}. Addition of 1 mol of triphenylphosphine per mol of [Pd(cod)$_2$] catalyst produced only a small increase in conversion of the amines.



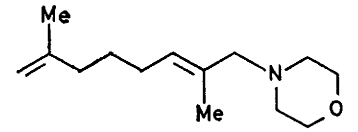
	NR$_2$
(1a)	$NCH_2CH_2OCH_2CH_2$
(1b)	$NCH_2CH_2CH_2CH_2CH_2$
(1c)	NEt_2
(1d)	NMe_2



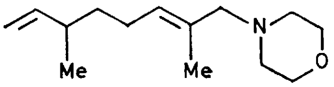
(2)



(3)



(4)



(5)

It has been observed previously [7,11,18] that the acetate adducts octa-2,7-dienyl acetate (2) and 1-vinylhex-5-enyl acetate (3) are formed as major and minor products, respectively, in reactions of buta-1,3-diene with acetic acid and palladium catalysts. Moreover, these reactions proceed more efficiently when the palladium is bound to PPh$_3$.[7] The reaction of acetic acid with buta-1,3-diene, using [Pd(cod)$_2$] as catalyst at 60 °C, gave a mixture of (2) (80%) and (3) (20%) in *ca.* 40% yield in the absence of solvent or added tertiary phosphine. When phosphine–palladium (P : Pd ratio = 2 : 1) catalysts are used reaction temperatures of 90—120 °C are required to obtain comparable yields.[7,11,18]

When equimolar quantities of diethylamine and acetic acid were treated with buta-1,3-diene in the presence of [Pd(cod)$_2$] the octa-2,7-dienylamine (1c) was formed in improved yield (45%). The transfer of allylic groups has been previously observed with phosphine–palladium catalysts,[19] and it is likely that (1c) is produced from a rapid reaction of diethylamine with (2), rather than by direct telomerisation.

Although (tertiary phosphine)palladium complexes catalyse the reaction of alcohols with butadiene to form octa-2,7-dienyl ethers as major products, accompanied by 1-vinyl-1-alkoxyhex-5-ene,[20] no such reaction occurred in the presence of [Pd(cod)$_2$]. Telomerisation of water with buta-1,3-diene also does not occur with [Pd(cod)$_2$], even in the presence of carbon dioxide under varying reaction conditions. Carbon dioxide has been shown [9] to promote telomerisation with water using a triphenylphosphine–palladium catalyst.

Reactions with isoprene have also been studied. In the presence of morpholine and [Pd(cod)$_2$], under similar conditions to those which gave (1a), there was an 85% conversion of the morpholine into a mixture of (4) (67%), (5) (23%), and a third unidentified isomer (6) (10%). Addition of 1 mol of PPh$_3$ per mol of palladium to this system caused an increase in specificity of product formation [*viz.* (4) : (5) : (6) = 75 : 17 : 8] but a decrease in the overall yield of adducts to *ca.* 50%. Again no 1 : 1 adducts of morpholine and the diene were observed.

The tail-to-tail dimerisation of the major product (4) was deduced from the ^{1}H n.m.r. spectrum. In addition to two singlets at τ 8.3 and 8.35 for CH$_3$ groups, there is a singlet at τ 7.2 assigned to the allylic protons adjacent to the nitrogen atom. Moreover, multiplets due to three olefinic protons are observed at τ 4.75 (1 H) and 5.35 (2 H), the latter showing only small couplings to other protons. The n.m.r. spectrum of (5) shows a singlet at τ 8.4 assigned to the CH$_3$ attached to the double bond and a doublet (J 7 Hz) at τ 9.0 assigned to the CH_3CH group. A singlet at τ 7.2 is assigned to the allylic protons adjacent to the nitrogen atom, and a complex multiplet at τ 4.4—5.4 corresponds to four olefinic protons. The complexity of this multiplet is in agreement with the larger number of couplings expected for the olefinic protons in this isomer.

A novel reaction of buta-1,3-diene catalysed by palladium complexes is the co-cyclisation of 2 mol of the diene with compounds containing heteropolar

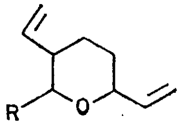
---

[18] T. Arakawa and H. Miyake, *Koygo Kagaku Zasshi*, 1971, **74**, 1143.

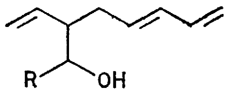
[19] K. E. Atkins, W. E. Walker, and R. M. Manyik, *Tetrahedron Letters*, 1970, 3821.

[20] S. Takahashi, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 254.

double bonds to form a six-membered heterocyclic compound.[14] The first example of co-cyclisation [21–23] involved buta-1,3-diene and aldehydes to give 2-substituted 3,6-divinyltetrahydropyrans (7) and 1-substituted 2-vinyl-4,6-heptadien-1-ols (8). Various (tertiary phosphine)palladium complexes have been used as catalysts, especially triphenylphosphine-containing species. The ratio of (7) : (8) formed depends on the molar proportion of PPh_3 to palladium, the unsaturated alcohol being the main product when the ratio was near unity whereas when the ratio was above two the pyran formed essentially selectively. With these results in mind, an attempt was made to use [Pd(cod)$_2$] to catalyse the reaction of buta-1,3-diene with acetaldehyde but decomposition of the palladium complex occurred and no organic products were isolated. Addition of 1 mol equiv. of PPh_3 to [Pd(cod)$_2$], however, produced a catalyst for the selective formation of 2-methyl-3,6-divinyltetrahydropyran (7; R = Me) in 33% yield. G.l.c. indicated the presence of four isomers which could only be separated in pairs. The ^{1}H n.m.r. spectrum of each pair showed a pair of doublets between τ 8.8 and 9.0 signifying the existence of conformational isomers undergoing rapid inversion. No reaction occurred between buta-1,3-diene and common ketones, such as acetone, in the presence of [Pd(cod)$_2$].

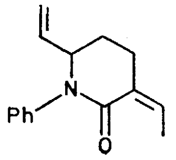


(7)

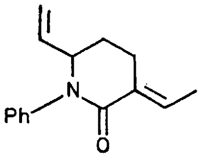


(8)

In the presence of [Pd(cod)$_2$], phenyl isocyanate and buta-1,3-diene are converted quantitatively into an isomeric mixture of the piperidones (9) and (10).

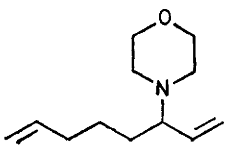


(9)



(10)

A very different reactivity pattern is observed in some of the above reactions when [Pt(cod)$_2$] is used as the catalyst. Thus buta-1,3-diene and morpholine in the presence of [Pt(cod)$_2$] afford octa-1,3,6-triene as the only product in *ca.* 40% yield. Other secondary amines, such as piperidine or diethylamine, give only trace amounts of C_8 hydrocarbon. However, it is interesting that addition of 1 mol equiv. of the Lewis acids $Al(OPr^i)_3$ or $Al(OBu^t)_3$ to the morpholine–buta-1,3-diene reaction system afforded a mixture of (1a) (80%) and (11) (20%) in 75% yield. Addition of the aluminium alkoxides to either piperidine or diethylamine and buta-1,3-diene in the presence of [Pt(cod)$_2$] gave only low conversions (*ca.* 10%) to amine adducts. A similar change in product from hydrocarbon to amine has been observed [13d] on addition of $Al(OPr^i)_3$ to a cobalt catalyst.



(11)

The complex [Pt(cod)$_2$] does not catalyse the co-cyclisation of buta-1,3-diene with acetaldehyde, nor promote addition of alcohols. However, it is a very effective catalyst for the telomerisation of buta-1,3-diene with acetic acid giving a 100% conversion into (2). This is interesting, since as mentioned above with [Pd(cod)$_2$] as catalyst a mixture of (2) and (3) is formed in 40% yield. Addition of diethylamine to the reaction of buta-1,3-diene with acetic acid in the presence of [Pt(cod)$_2$] gave only a 7% yield of (1c).

In contrast to the reaction of isoprene with morpholine in the presence of [Pd(cod)$_2$] which gave (4)—(6), reaction in the presence of [Pt(cod)$_2$] afforded only a low conversion (*ca.* 3%) into a mixture of four isomeric hydrocarbons of molecular weight 136. The structures of these dimers have not been established.

Although there seem to be no apparent trends in these catalytic processes some discussion of probable mechanisms is appropriate. The favoured mechanism for the cyclic dimerisation and oligomerisation of butadiene catalysed by metals of the nickel triad includes the intermediates (12)—(14) (Scheme 1).[6,17,24] The intervention of a co-catalyst (YH), containing active hydrogen, could afford an intermediate (15), from which linear telomers can be formed by protonation of the M–C^6 bond and nucleophilic attack at C^1. The observation [20] that 3-deuterio-8-methoxyocta-1,6-diene is formed by treating buta-1,3-diene with MeOD supports this mechanism. Formation of a linear dimer from the same intermediate (15) is possible if protonation at C^6 is followed by elimination of the proton at C^4. The preferred mode of breakdown of (15) will depend on the metal and on the nature of the nucleophilic co-catalyst.

The telomerisation of secondary amines with buta-1,3-diene using [Pd(cod)$_2$] as catalyst can be readily explained by this mechanism. The formation of the single isomer (1) is consistent with the nucleophile Y: attacking the least substituted end of the allyl chain. It is interesting that, in the absence of a secondary amine, [Pd(cod)$_2$] fails to catalyse the oligomerisation of buta-1,3-diene, even in the presence of added tertiary phosphine. This implies that formation of (12) is

---

[21] K. Ohno, T. Mitsuyasu, and J. Tsuji, *Tetrahedron Letters*, 1971, 67; *Tetrahedron*, 1972, **28**, 3705; K. Ohno and J. Tsuji, *Chem. Comm.*, 1971, 247.

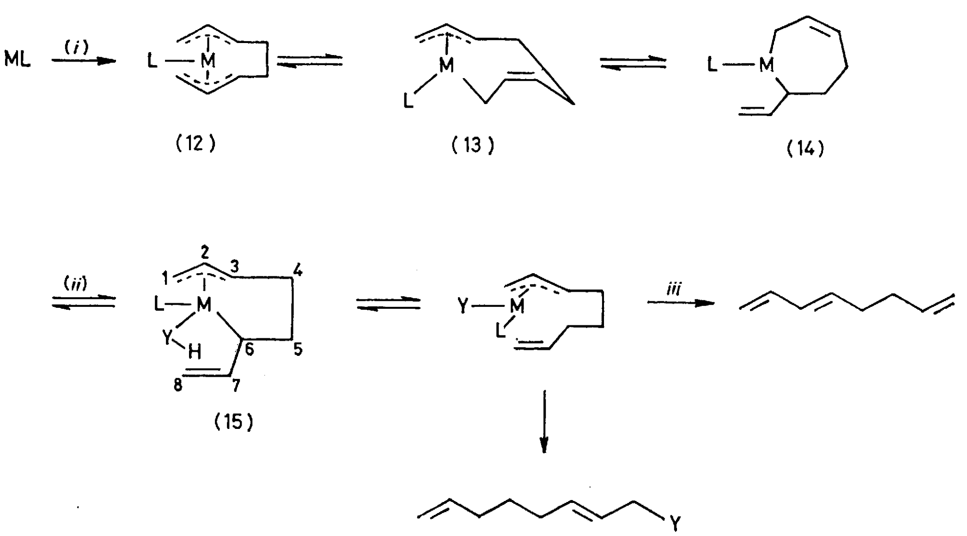
[22] R. M. Manyik, W. E. Walker, K. E. Atkins, and E. S. Hammack, *Tetrahedron Letters*, 1970, 3813.

[23] P. Haynes, *Tetrahedron Letters*, 1970, 3687.

[24] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, 1971, vol. 2.

readily reversed, and only in the presence of a compound containing an active hydrogen is this equilibrium forced over to the product side. Alternatively another mechanism may be involved (see below).

For nickel, evidence for bis(η-allyl) intermediates comes from the isolation of [13; M = Ni, L = $(C_6H_{11})_3P$].[6] However, reaction of such an intermediate with amines should afford octa-2,6-dienyl adducts and not octa-2,7-dienyl products as has been observed.[13] It could be that in cyclodimerisation this complex is an important intermediate, but in telomerisation reactions either (13) is not important or an alternative mechanism is operative.



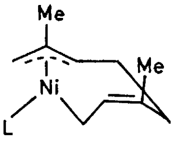
SCHEME 1 (*i*) Buta-1,3-diene; (*ii*) YH; (*iii*) —YH

The possibility of an alternative mechanism for telomerisation and linear oligomerisation is suggested by the results obtained using $[Pt(cod)_2]$ as catalyst. Thus when dimerisation occurs in the presence of morpholine the product is octa-1,3,6-triene, whereas when telomerisation is observed, on adding a Lewis acid, the major product is the octa-2,7-dienylamine (1a).

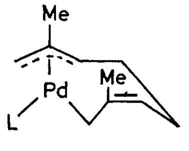
Reaction of buta-1,3-diene with $[Pt(C_2H_4)_2(Me_3P)]$ gives (13; M = Pt, L = Me_3P),[17] but we have found that reaction of this complex with butadiene and morpholine fails to give any amine adduct. The *cis* configuration of the double bond in (13; M = Pt, L = Me_3P) is revealed by an *X*-ray crystallographic study, but only *trans* double bonds have been observed in the products of catalytic reactions of $[Pt(cod)_2]$. This could be interpreted as evidence that intermediates such as (13), and hence (12), are not involved; however, there is some uncertainty here in view of the possibility of *cis* to *trans* isomerisation.

The use of substituted 1,3-dienes in these catalytic processes could be mechanistically informative because the stereochemistry of the products gives an insight into the intermediates involved. Thus the 3,7-dimethyl-substituted cyclic compound (16), corresponding to head-to-tail coupling of isoprene, has been isolated from reactions of nickel complexes with isoprene.[6] In contrast to the results with nickel, telomerisation of isoprene with morpholine using $[Pd(cod)_2]$ as catalyst affords (4) as major product, with tail-to-tail linkage of isoprene units. Again this suggests that either a different mechanism is operative or that intermediates (17) and (18) [corresponding to (13) and (15), Scheme 1] are involved.

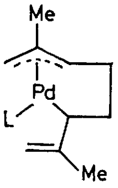
Other palladium complexes have been used to catalyse the dimerisation of isoprene. Thus five linear dimers have been identified from the oligomerisation of isoprene catalysed[25] by $[PdBr_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and sodium phenoxide. The isomer distribution varied remarkably with the amount of phenol co-catalyst present. This complex was also used[10] to telomerise isoprene with active methylene compounds such as pentane-2,4-dione. In these experiments 1 : 1 adducts were isolated, again highlighting the probable differences in mechanisms between oligomerisation and telomerisation reactions.



(16)



(17)



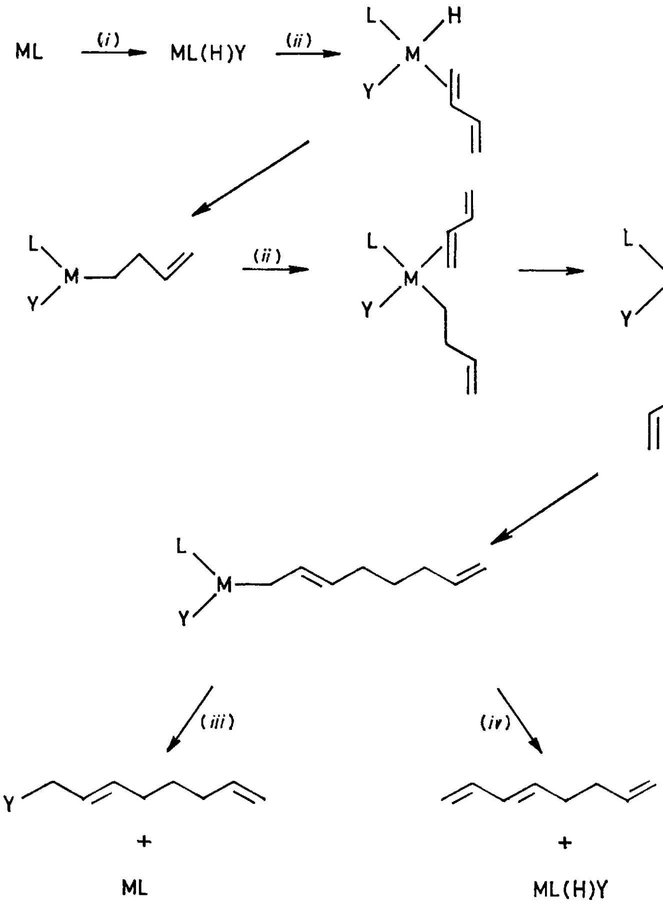
(18)

An alternative mechanism to account for the formation of the telomerisation and oligomerisation products described in this paper could involve oxidative addition of the active hydrogen-containing substrate in the first step (Scheme 2).[24] Various observations lend support to this mechanism. Thus formation of the octadienylamines (1) could involve oxidative insertion of Pd^0 into N–H bonds. That this is possible is indicated by the

---

[25] K. Takahashi, G. Hata, and A. Miyake, *Bull. Chem. Soc. Japan*, 1973, **46**, 600.

recent report[26] of the oxidative addition of NH bonds of pyrrole and pentafluoroaniline to Pt^0, and the earlier report[27] of nickel-hydride formation from pyrrole and bis(tricyclohexylphosphine)nickel. Oxidative formation of metal–hydride bonds in this manner would increase down the sub-group Ni < Pd < Pt. Apparently a delicate balance may be reached with palladium which selectively yields octadienylamines, whereas the nickel catalyst affords mixtures of butadienyl- and octadienylamine adducts and octa-1,3,7-triene. Formation of the latter might be favoured by the lower tendency of nickel to undergo the initial oxidative-addition step so that the amine, following initial co-ordination to the metal, promotes oligomerisation in an alternative reaction path. The synthesis of octa-1,3,6-triene from buta-1,3-diene in the presence of morpholine and $[Pt(cod)_2]$ could be explicable in terms of Scheme 2, with, in the case of platinum, preferred elimination of a $[PtH(R_2N)]$-type species in the final step, due to the higher stability of PtH compared with PdH. The reason why addition of aluminium alkoxides facilitates telomerisation with the platinum system is unclear. It could be that Lewis acids activate the NH bond in one of the intermediates by complexation with the nitrogen atom of the amine. The particular effectiveness of morpholine in the telomerisation reactions seems unrelated to its basicity (pK_a 8.3), since diethylamine (pK_a 11.1) affords (1c) with only *ca.* 20% conversion, and di-isopropylamine (pK_a 11.1) does not add to butadiene in the presence of $[Pd(cod)_2]$. It is possible that morpholine derives its activity from a stretching and weakening of the NH bond *via* intramolecular hydrogen bonding to the oxygen in the boat configuration.



SCHEME 2 (*i*) HY; (*ii*) buta-1,3-diene; (*iii*) —ML; (*iv*) —ML(H)Y

EXPERIMENTAL

A Perkin-Elmer F11 chromatograph was used for analytical g.l.c. work (nitrogen carrier gas, 6 ft × 0.125 in stainless-steel column, 10% SE-30), and a Pye 104 chromatograph for all the preparative g.l.c. studies (nitrogen carrier gas, 6 ft × 0.375 in glass column, 25% SE-30). Heights multiplied by widths at half-heights were used to measure peak areas, and yields are in terms of percentage conversion of amine. N.m.r. spectra were recorded on Varian T-60 and HA-100 spectrometers with $CDCl_3$ as solvent. Infrared spectra were obtained with a Perkin-Elmer 457 spectrometer, and mass spectra with an A.E.I. MS902 instrument operating at 70 eV.*

The amines used were dried over KOH and distilled

---

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} *J*; 1 Torr = (101 325/760) Pa.

[26] J. Fornies, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1006.

[27] K. Jonas and G. Wilke, *Angew. Chem. Internat. Edn.*, 1969, **8**, 519.

under nitrogen. Buta-1,3-diene, isoprene, acetaldehyde, and phenyl isocyanate were purified by distillation prior to use, and were distilled directly into the reaction vessel which was attached to a high-vacuum system *via* a ground-glass joint. The reaction vessels consisted of thick-walled glass tubes (capacity, *ca.* 150 cm^3) fitted with Westef greaseless high-vacuum stopcocks. Because of the low thermal stability of [Pd(cod)$_2$] it was introduced under nitrogen into the reaction tube while maintaining the latter at below −30 °C.

4-Vinylcyclohexene, octa-1,3,6- and -1,3,7-triene, and cyclo-octa-1,5-diene were identified by comparison of their g.c. retention times with those of pure samples, and by their mass-spectral cracking patterns. Compounds (1)—(3), (7; R = Me), and (9)—(11) have all been previously well characterised and were identified in this work by their i.r.[7,8,11,21–23] and ^{1}H n.m.r.[7,8,11,13,21] spectra.

Telomerisations of Buta-1,3-*diene in the Presence of Bis*(η-*cyclo-octa*-1,5-*diene*)*palladium*.—(*a*) *With morpholine*. A mixture of [Pd(cod)$_2$] (32 mg, 0.1 mmol), morpholine (4.3 g, 50 mmol), and buta-1,3-diene (8.1 g, 150 mmol) warmed to 60 °C for 17 h gave 96% conversion into (1a) (9.3 g), together with small amounts of octa-1,3,7-triene and 4-vinylcyclohexene. Addition of triphenylphosphine (26 mg, 0.1 mmol) in a repeat experiment gave 100% conversion into (1a) (9.7 g).

(*b*) *With piperidine*. Reaction of piperidine (4.2 g, 50 mmol) with buta-1,3-diene (8.1 g, 150 mmol) in the presence of [Pd(cod)$_2$] (32 mg, 0.1 mmol) at 60 °C (17 h) gave 80% conversion into (1b) (7.6 g). The conversion increased to 85% in experiments to which PPh$_3$ (26 mg, 0.1 mmol) had been added.

(*c*) *With diethylamine*. A mixture of [Pd(cod)$_2$] (32 mg, 0.1 mmol), diethylamine (1.3 g, 18 mmol), and buta-1,3-diene (3.0 g, 54 mmol) at 60 °C for 17 h gave 20% conversion into (1c) (0.6 g). Addition of PPh$_3$ did not improve the yield. Infrared spectrum: $\nu_{\max.}$ (neat liquid) at 1 630m, 1 440m, 1 430m, 1 370m, 1 360m, 1 190m, 1 160w, 980w, 960s, and 900s cm^{-1}. Hydrogen-1 n.m.r. spectrum: τ 4.0—4.6(m, 3 H), 4.8—5.2(m, 2 H), 6.8—7.0(d, *J* 4 Hz, 2 H), 7.4(q, *J* 7 Hz, 4 H), 7.7—8.2(m, 4 H), 8.2—8.7(m, 2 H), and 8.9(t, *J* 7 Hz, 6 H).

(*d*) *With dimethylamine*. Similarly, [Pd(cod)$_2$] (32 mg, 0.1 mmol), dimethylamine (2.0 g, 44 mmol), and buta-1,3-diene (7.0 g, 132 mmol) gave 20% conversion into (1d) (1.3 g). Infrared spectrum; $\nu_{\max.}$ (neat liquid) at 1 630m, 1 440m, 1 425m, 995s, 960s, and 895m cm^{-1}. Mass spectrum: *m/e* 153, 110, 98, 84, 58, 55, 45, 44, and 42.

(*e*) *With acetic acid*. Buta-1,3-diene (8.1 g, 150 mmol), acetic acid (3.5 g, 58 mmol), and [Pd(cod)$_2$] (32 mg, 0.1 mmol) for 17 h at 60 °C afforded a mixture which was fractionated to give 3.7 g (38%) of (2) (80%) and (3) (20%).

(*f*) *With acetic acid and diethylamine*. A mixture of acetic acid (6.0 g, 100 mmol), diethylamine (7.0 g, 97 mmol), buta-1,3-diene (11.5 g, 215 mmol), and [Pd(cod)$_2$] (32 mg, 0.1 mmol) at 60 °C (17 h) gave, after removal of excess of buta-1,3-diene, a mixture. The latter was poured into water and made alkaline with NaHCO$_3$. Extraction with diethyl ether (three times), washing the combined extracts with water, and drying (K$_2$CO$_3$) afforded a pale yellow liquid. Distillation gave (1c) (7.9 g, 46%).

(*g*) *With acetaldehyde*. Similarly, acetaldehyde (1.95 g, 44 mmol), buta-1,3-diene (8.1 g, 150 mmol), PPh$_3$ (26 mg, 0.1 mmol), and [Pd(cod)$_2$] (32 mg, 0.1 mmol) after 20 h (60 °C) gave a mixture (2.2 g, 33%) of isomers of (7; R = Me), partial separation of which could be achieved on a 6 ft column of 25% SE-30 at 150 °C. A higher-boiling fraction (300 mg) was not examined further.

(*h*) *With phenyl isocyanate*. A mixture of phenyl isocyanate (3.2 g, 27 mmol), buta-1,3-diene (20 g, 373 mmol), PPh$_3$ (40 mg, 0.15 mmol), and [Pd(cod)$_2$] (48 mg, 0.15 mmol) was heated at 60 °C for 48 h. Distillation gave 6.2 g (100%) of an equimolar mixture of (9) and (10) (b.p. 150—155 °C, 1 Torr; lit.,[21] 153—158 °C, 3 Torr).

Telomerisation of Isoprene with Morpholine in the Presence of [Pd(cod)$_2$].—Isoprene (3.4 g, 50 mmol), morpholine (1 g, 11.5 mmol), and [Pd(cod)$_2$] (32 mg, 0.1 mmol) at 60 °C (18 h) gave a mixture (2.1 g) of three C$_{10}$ amines in the ratio 67 : 23 : 10. Preparative g.l.c. gave (4) and (5) in 85% yield. Experiments in which PPh$_3$ (26 mg, 0.1 mmol) was added gave (4), (5), and (6) in the ratio 75 : 17 : 8. Infrared spectrum of (4): $\nu_{\max.}$ (neat liquid) at 3 060w, 2 920s, 2 840s, 2 790s, 1 640w, 1 450w, 1 115s, 1 005m, 910m, 885m, and 870m cm^{-1}. N.m.r. spectrum: τ 4.5—5.0(m, 1 H), 5.35(br s, 2 H), 6.40(m, 4 H), 7.2(s, 2 H), 7.65(m, 4 H), 7.8—8.8(m, 6 H), 8.30(s, 3 H), and 8.35(s, 3 H). Mass spectrum: *m/e* 223, 166, 140, 100, 87, 86, 81, 57, 56, 55, and 41. Infrared spectrum of (5): $\nu_{\max.}$ (neat liquid) at 3 060w, 2 920s, 2 840s, 2 790s, 1 630w, 1 450s, 1 120s, 1 010w, 910w, and 870w cm^{-1}. N.m.r. spectrum: τ 4.4(m, 4 H), 6.3(m, 4 H), 7.2(s, 2 H), 7.7(m, 4 H), 7.8—8.8(m, 5 H), 8.4(s, 3 H), and 9.0(d, *J* 7 Hz, 3 H). Mass spectrum: *m/e* 223, 140, 100, 87, 86, 81, 56, 55, 44, and 41.

Reactions Catalysed by Bis(η-*cyclo-octa*-1,5-*diene*)*platinum*.—(*a*) Morpholine (2 g, 23 mmol), buta-1,3-diene (8.1 g, 150 mmol), and [Pt(cod)$_2$] (41 mg, 0.1 mmol) were heated at 60 °C for 17 h. Removal of excess of buta-1,3-diene and distillation of the residue gave pure octa-1,3,6-triene (38% yield) (b.p. 120—122 °C, lit.,[4] 129 °C). Infrared spectrum: $\nu_{\max.}$ (neat liquid) at 1 640w, 1 595w, 1 430m, 1 000s, 965s, and 900s cm^{-1}.

Reaction of morpholine (3.5 g, 40 mmol), buta-1,3-diene (16.2 g, 300 mmol), Al(OPr^i)$_3$ (25 mg, 0.125 mmol), and [Pt(cod)$_2$] (50 mg, 0.125 mmol) for 48 h gave 75% conversion of morpholine into (1a) and (11).

(*b*) Morpholine (3.5 g, 40 mmol), isoprene (13.6 g, 200 mmol), and [Pt(cod)$_2$] (50 mg, 0.125 mmol) when allowed to react for 36 h (60 °C) gave only 3% conversion into four isomeric dimers. G.c.–m.s. showed that all four isomers had molecular ions at *m/e* 136.

(*c*) Buta-1,3-diene (8.1 g, 150 mmol), acetic acid (2.6 g, 43 mmol), and [Pt(cod)$_2$] (41 mg, 0.1 mmol) were heated at 60 °C for 17 h. Distillation of the products gave (2) (7.3 g, 100%). In another experiment buta-1,3-diene (8.1 g, 150 mmol), acetic acid (3 g, 50 mmol), and diethylamine (3.5 g, 4.8 mmol) were heated at 60 °C for 17 h but afforded only 0.7 g (7%) of (1c).

We thank Air Products and Chemicals Inc. for support, and Dr. J. L. Spencer for helpful discussions.

[7/1328 *Received*, 25*th July*, 1977]