

The Reaction of $\alpha\omega$ -Dodecatrienediylnickel with Allene and Reactions of the Resulting Bis- π -allylnickel Intermediates with Carbon Monoxide and Alkyl Isocyanides

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A series of C_{15} , C_{18} , C_{21} , and C_{24} bis- π -allylnickel complexes has been formed by the sequential addition of up to 4 mole equivalents of allene to $\alpha\omega$ -dodecatrienediylnickel. Treatment of these complexes with carbon monoxide afforded cyclic hydrocarbons from a coupling reaction. Mixtures of two dimethylenecyclohexadecatrienes and trimethylenecyclo-octadecatrienes were obtained from the C_{18} and C_{21} complexes, respectively. Analogous products were also obtained from the C_{24} complex but could not be fully characterised. In contrast, addition of *n*-butyl isocyanide, followed by acid hydrolysis, gave 1 : 1 mixtures of ketones and hydrocarbons. After hydrogenation mixtures of two dimethylcycloheptadecanones and two trimethylcyclononadecanones were formed from the C_{18} and C_{21} complex, respectively. Experiments showed little selectivity in the formation of the C_{18} complex.

THE reaction of carbon monoxide with bis- π -allylnickel complexes has been demonstrated to result in either insertion, with formation of ketones, or a coupling process to yield hydrocarbons.^{1,2} Thus carbonylation of bis- π -allylnickel³ and $\alpha\omega$ -octadienediylnickel above -40°C ⁴ yields exclusively hydrocarbon products while at -60°C a similar reaction of $\alpha\omega$ -dodecatrienediylnickel afforded cyclic ketone in good yield.⁵ The unpredictable nature of these reactions was confirmed by the carbonylation of a bis- π -allylnickel complex obtained by the reaction of allene with $\alpha\omega$ -dodecatrienediylnickel; only a small amount of ketone was obtained at 10°C .⁶ In contrast, good yields of cyclic ketones have been obtained by the hydrolysis of imines produced by the insertion of alkyl isocyanides into this same nickel complex⁷ and dodecatrienediylnickel.⁸

In a previous communication we reported the insertion of 2 mole equivalents of allene into the dodecatrienediylnickel complex (1) and the formation of two large ring hydrocarbons by carbonylation.⁶ We have now shown that a series of bis- π -allylnickel intermediates can be formed by the successive insertion of up to 4 mole equivalents of allene into (1). The reactions of these intermediates with carbon monoxide afforded hydrocarbon from coupling reactions, while addition of *n*-butyl isocyanide, followed by hydrolysis with dilute acid, yielded 1 : 1 mixtures of ketones and hydrocarbons.

REACTIONS AND DISCUSSION

In a typical reaction, bis(cyclo-octadiene)nickel, $[\text{Ni}(\text{cod})_2]$, prepared from nickel acetylacetonate, was dissolved in an excess of butadiene to give a dark red solution containing dodecatrienediylnickel (1). Residual butadiene was removed under reduced pressure and the red oil dissolved in diethyl ether. The solution, cooled

to -80°C and filtered to remove traces of $\text{Ni}(\text{cod})_2$, was used as a starting point for all reactions.

Reactions with Carbon Monoxide.—Dried allene was distilled into the solution of (1) and the mixture stirred for 3 h at a temperature which gradually increased to 13°C . The mixture was cooled to -78°C and carbon monoxide passed through it overnight. Gas chromatography-mass spectroscopy indicated the presence of cyclododecatriene, a C_{13} ketone, and C_{15} , C_{18} , C_{21} , and C_{24} hydrocarbons. No other ketones could be detected and the C_{13} ketone was separated by column chromatography and shown to be 2-vinylcycloundeca-5,9-dienone.⁹ The hydrocarbons were separated by column chromatography and the overall ratio of products was estimated by g.l.c. to be $C_{12} + C_{13} : C_{15} : C_{18} : C_{21} : C_{24} = 1.0 : 0.61 : 0.52 : 0.69 : 0.52$.

The C_{15} hydrocarbon has previously been shown to be a mixture of 1-methylenecyclotetradeca-3,7,11-triene (3) and 1-methylene-11-vinylcyclododeca-3,7-diene (4).⁶ These products would arise from the bis- π -allylnickel intermediate (2) formed by insertion of 1 mole equivalent of allene into (1).

G.l.c. analysis of the C_{18} hydrocarbons showed them to be a 4 : 1 mixture of two isomers, which were assigned the structures (7) and (8) on the basis of the n.m.r. spectrum; $\delta(\text{CCl}_4)$ 5.3—5.53 (6 H, complex m, $\text{CH}=\text{CH}-$), 4.76 (4 H, bs, $\text{C}=\text{CH}_2$), 2.69—2.81 (4 H, bm, $=\text{C}-\text{CH}_2-\text{C}=\text{C}$), and 2.04—2.20 (12 H, m, $-\text{CH}_2-\text{C}=\text{C}$). The C_{21} hydrocarbon was shown to be a 1 : 1 mixture of isomers by a similar analysis and was assigned the structures (11) and (12); $\delta(\text{CCl}_4)$ 5.36 (6 H, bs, $-\text{CH}=\text{CH}-$), 4.72—4.82 (6 H, bm, $-\text{C}=\text{CH}_2$), 2.70 (6 H, bs, $=\text{C}-\text{CH}_2-\text{C}=\text{C}$), and 2.10 (12 H, m, $-\text{CH}_2-\text{C}=\text{C}$). Separation of the isomers was not possible in either case. The involatility of the C_{24} hydrocarbon made determination

¹ P. Heimbach, P. W. Jolly, and G. Wilke, *Adv. Organometallic Chem.*, 1970, **8**, 29.

² R. Baker, *Chem. Rev.*, 1973, **73**, 487.

³ G. Wilke and B. Bogdanovic, *Angew. Chem.*, 1961, **73**, 756.

⁴ P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel', Academic Press, London, 1974, vol II, ch. 3.

⁵ B. Bogdanovic, P. Heimbach, M. Kroner, and G. Wilke, *Annalen*, 1966, **727**, 143.

⁶ R. Baker, B. N. Blackett, and R. C. Cookson, *J.C.S. Chem. Comm.*, 1972, 802.

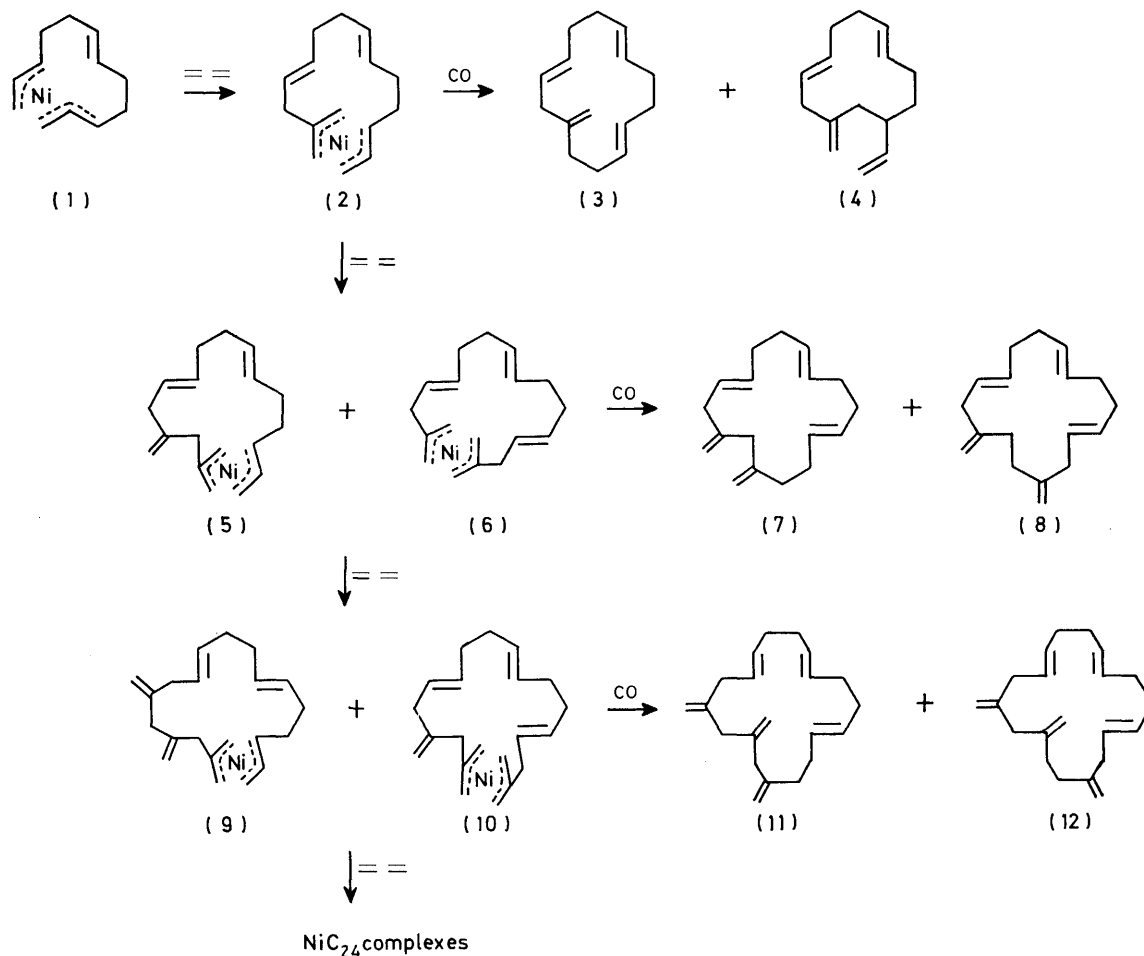
⁷ R. Baker, R. C. Cookson, and J. R. Vinson, *J.C.S. Chem. Comm.*, 1974, 515.

⁸ H. Breil and G. Wilke, *Angew. Chem. Internat. Edn.*, 1970, **9**, 367.

⁹ G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 105.

of its isomer distribution difficult. However, the formation of products similar to those of the C_{18} and C_{21} hydrocarbons is suggested by the similarity of the n.m.r. spectrum; $\delta(CCl_4)$ 5.34 (6 H, bs, $-CH=CH-$), 4.74—4.84 (8 H, bm, $-C=CH_2$), 2.66 (8 H, bm, $=C-CH_2-C=$), and 2.06 (12 H, bm, $-CH_2-C=$). In all cases the predominance of the all-*trans*-stereochemistry was suggested by a strong absorption at 960 cm^{-1} and the absence of an absorption below 850 cm^{-1} in the i.r. spectrum.

in the presence of carbon monoxide, undergo coupling of the allyl fragments to form the cyclic hydrocarbons assigned as (11) and (12). Again the presence of the third possible small ring isomer (14) was not detected. Further insertion of allene into (9) and (10) can lead to the formation of bis-allyl NiC_{24} intermediates and these, on treatment with carbon monoxide, afford C_{24} hydrocarbon from the coupling reaction. There is also evidence to suggest that further insertion of allene takes



SCHEME 1

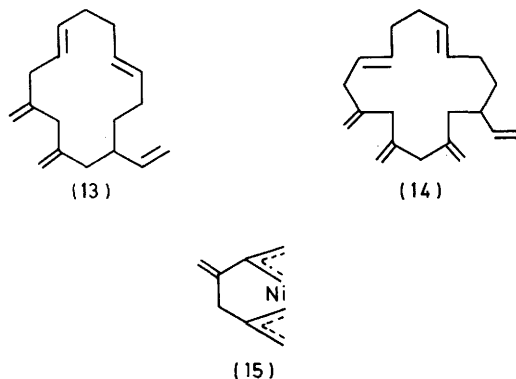
The reaction is considered to proceed according to Scheme 1. Formation of the bis- π -allyl intermediate (2) has been postulated to occur by insertion of 1 molar equivalent of allene into (1).⁶ In the presence of an excess of allene insertion of a second equivalent into (2) can occur with formation of the new bis-allyl intermediates (5) and (6). When (5) and (6) are treated with carbon monoxide, the allyl fragments couple and the two cyclic hydrocarbons assigned as (7) and (8) are formed. Formation of a third possible isomer (13) was not detected. The isolation of hydrocarbon derived from the addition of 3 equivalents of allene to (1) suggests that allene can also insert into (5) and (6). The bis-allyl intermediates (9) and (10) are probably formed and these,

place; C_{27} hydrocarbon ($M = 362$) was identified by mass spectroscopy as an impurity in a sample of C_{24} hydrocarbon that was isolated.

Thus, at least 4 equivalents of allene have been inserted into (1) and there are indications that further insertion took place. Once the second equivalent of allene has been inserted with formation of the NiC_{18} complex, there is apparently no energy barrier to prevent further insertion and a reaction leading ultimately to the formation of polymer can be envisaged. Carbonylation of the NiC_{18} , NiC_{21} , and NiC_{24} complexes, formed by the insertion of 2, 3, and 4 molar equivalents of allene into (1), has resulted in coupling of the allyl fragments to give large ring cyclic hydrocarbons. No ketone pro-

ducts derived from an insertion reaction were detected when carbon monoxide was passed into the solutions at either room temperature or at -78°C .

When the NiC_{15} complex (2), formed by insertion of 1 equivalent of allene into (1) was treated with carbon monoxide at 0 – 10°C , a 5 : 2 mixture of 1-methylene-cyclodeca-3,7,11-triene and 1-methylene-11-vinyl-cyclodeca-3,7-diene ring hydrocarbons was reported to be formed.⁶ A small amount (*ca.* 5%) of a carbonyl



insertion product was also isolated and shown to be the 15- rather than the 13-membered ring adduct by at least 15 : 1. Carbonylation of the complex at -70°C again produced small quantities of the insertion product but the isolated hydrocarbon was found to be almost exclusively the large ring isomer.¹⁰

Carbonylation at room temperature of (1) afforded cyclododeca-1,4,7-triene, no smaller ring hydrocarbons or ketone insertion products were detected. In marked contrast however, carbonylation of (1) at -60°C favoured the insertion reaction and a good yield of a 10 : 1 mixture of 11- and 13-membered ring ketones was obtained.^{9,11}

Coupling of the allyl groups or insertion of carbon monoxide does not appear to be determined by the substitution of the allyl group. In contrast to the carbonylation of (1), a similar reaction with bis- π -allylnickel at -40°C or room temperature afforded only hydrocarbon.¹ Carbon monoxide has also been observed to produce ketone in good yield with the bis- π -allylnickel complex (15) obtained from allene.^{12,13} Carbonylation of bis- π -3,3'-dimethylallylnickel was reported to afford coupled product 2,7-dimethyloctadiene.^{14,15} It is possible that there are steric and conformational effects which determine the course of these reactions but no general predictions appear possible at this time.

Selectivity of Hydrocarbon Formation.—The formation of the bis- π -allyl C_{15} nickel complex (2) occurred selectively when (1) was treated with a slight excess of allene at temperatures between -10 and -20°C .⁷ When (1) is treated with a 12-fold excess of allene, it is now

¹⁰ R. Baker, R. C. Cookson, and J. R. Vinson, unpublished results.

¹¹ B. Bogdanovic, P. Heimbach, M. Kröner, G. Wilke, E. G. Hoffmann, and J. Brandt., *Annalen.*, 1969, **727**, 143.

¹² R. Baker and A. H. Copeland, *Tetrahedron Letters*, 1976, 4535.

apparent that a number of new bis-allyl intermediates, can be formed. A more selective formation of the NiC_{18} complexes was attempted by reduction of the quantity of allene added to a 5-fold excess and by holding the reaction temperature constant at *ca.* 0°C .

Dried allene (3 ml, 45 mmol) was distilled into an ethereal solution of (1) [from nickel acetylacetonate (4 g, 15.5 mmol)] held at 0°C . Small portions of the solution were withdrawn at regular intervals and carbon monoxide passed in at room temperature. G.l.c. analysis of the mixtures enabled estimation of the relative amounts of products formed (Table). No account has been taken of the higher, involatile oligomers which are almost certainly formed but not detected by g.l.c.

At the outset of the reaction, rapid insertion of the first equivalent of allene into (1) occurred. This is indicated by the sharp fall in the concentration of C_{12} , together with a corresponding increase in that of C_{15} hydrocarbons. As the concentration of C_{12} continued to decrease, the concentration of C_{15} rose to a maximum of *ca.* 34% after 3 h, at which point insertion of a second equivalent of allene into the NiC_{15} complex began to occur. This second insertion of allene does not appear to be a ready reaction since after 3 h at 0°C the concentration of C_{18} was still too small to be estimated. In contrast, insertion of a third equivalent of allene into the NiC_{18} complex does appear to be favoured; the concentration of C_{18} did not rise above 13% before the concentration of C_{21} became measurable and, indeed, overtook that of the C_{18} . Insertion of allene into the

Change of hydrocarbon with time for reaction of (1) with allene *

Time (h)	C_{12}	C_{15}	C_{18}	C_{21}	C_{24}
1	79	21			
2	72	28			
3	66	34			
4	56	33	11		
7	37	26	13	16	9
17	24	21	15	22	18
28	16	23	19	26	17

* 5-Fold excess of allene, 0°C .

NiC_{21} complex also appears ready and the concentration of C_{24} rose steadily.

In the light of these results, the reported selective formation of the NiC_{15} complex by treatment of (1) with a slight excess of allene at -10 to -20°C is not surprising.⁷ In the current experiments after stirring with a 5-fold excess of allene at 0°C for 3 h, the concentration of C_{18} was too small to be estimated. Thus, cooling the reaction by a further 10 or 20°C might be anticipated to favour selective NiC_{15} formation. The results also suggest that selective formation of the NiC_{18} complex and also any of the other new bis-allyl complexes is almost impossible. The NiC_{18} complex appears to be particularly susceptible to attack by allene, since the

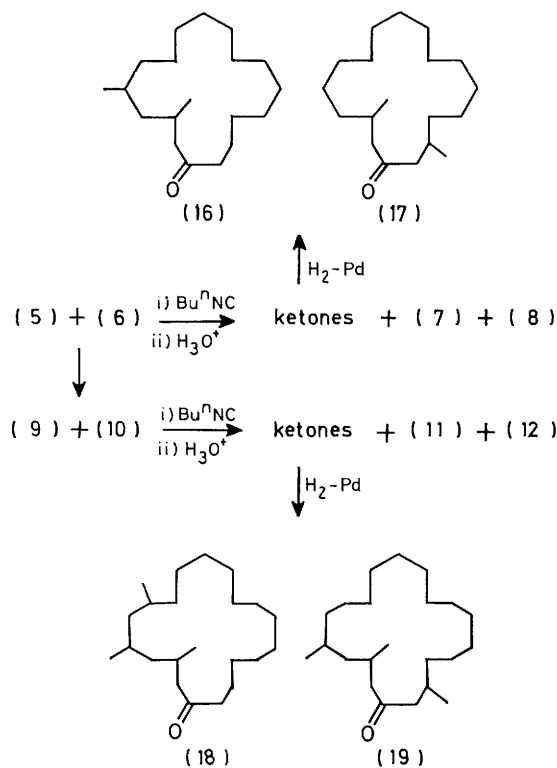
¹³ S. Otsuka, K. Tani, and T. Yamagata, *J.C.S. Dalton*, 1973, 2491.

¹⁴ E. J. Corey, L. S. Hegedus, and M. F. Semmelhack, *J. Amer. Chem. Soc.*, 1968, **90**, 2417.

¹⁵ M. F. Semmelhack, *Org. Reactions*, 1972, **19**, 117.

concentration of C_{21} rapidly overtook that of the C_{18} . At the longer time the percentage of each component in the volatile portion of the mixture appears to become reasonably constant and the absolute yield of each of the components will probably fall as the higher oligomers are formed. This multiple insertion of allene can be envisaged to occur indefinitely giving a distribution of oligomers with an ever increasing average molecular weight.

Reaction with Isocyanides.—The insertion of alkyl isocyanides into $\alpha\omega$ -bis- π -allylnickel complexes is reported to be strongly influenced by reaction conditions.⁷ Isocyanide insertion has been shown to be promoted by performing the reaction at low temperatures and in the presence of electron-donor ligands such as pyridine. The use of an isocyanide possessing a small alkyl group was also found to have a beneficial effect. In the experiments described below the conditions chosen were based



SCHEME 2

on this report and were anticipated to favour high yields of ketone.

Dried allene (7.5 ml, 112 mmol) was distilled into an ethereal solution of (1) [from nickel acetylacetonate (4 g, 15.5 mmol)] and the mixture allowed to reach equilibrium with room temperature. After being stirred for $3\frac{1}{4}$ h, the mixture was cooled to $-80^\circ C$ and n-butyl isocyanide (8 ml, 97 mmol) was added. The mixture was allowed to warm slowly overnight. The product mixture, after hydrolysis with dilute acid at $0^\circ C$, was shown by i.r. spectral analysis to contain a mixture of conjugated and non-conjugated ketones (1680 and 1710 cm^{-1}). The

ketones were separated by column chromatography and g.l.c.-mass spectral analysis of the mixture indicated the presence of C_{19} cyclic ketone ($M = 270$), C_{22} ketone ($M = 310$), and a small amount of C_{25} ketone ($M = 350$), together with products derived from the insertion of isocyanide into (1) and the NiC_{15} complex (2). The ketone mixture was hydrogenated (10% Pd-charcoal catalyst) and pure samples of C_{19} and C_{21} ketones isolated by preparative g.l.c. The C_{25} ketone was present in an amount too small to be isolated.

The sample of saturated C_{19} ketone ($M = 280$) was assigned to be a mixture of the isomeric structures (16) and (17) on the basis of the n.m.r. spectrum; $\delta(CCl_4)$ 1.3–2.3 (30 H, bm and bs, 4 $CH_2-C=O$, 2 methine, 24 CH_2), 0.90 and 0.85 (6 H, $2 \times d$, $J_{CH,CH}$ 6 Hz, $-CH-CH_3$). In the two overlapping doublets observed, the signal centred at δ 0.9 was assigned as a methyl group β to the carbonyl group and the doublet centred at 0.85 was assigned as the methyl group δ to the carbonyl group. This observation of methyl groups in different environments indicates the presence of (16), while the presence of (17) was suggested by the greater intensity of the doublet at lower field. The sample of saturated C_{21} ketone isolated was assigned to be a mixture of the isomeric structures (18) and (19); $\delta(CCl_4)$ 1.3–2.6 (33 H, bm and bs, 4 $CH_2-C=O$, 3 methine, 26 CH_2), and 0.86–0.98 (9 H, m, $-CH-CH_3$).

A comparison of the g.l.c. trace of the product mixture with that of the ketone mixture obtained after separation by column chromatography, enabled an estimate of the insertion:coupling ratio of the isocyanide into the complexes to be made. The ratios for both the NiC_{18} and NiC_{21} complexes were estimated to be approximately 1:1.

The insertion of n-butyl isocyanide into the NiC_{18} and NiC_{21} complexes is suggested to proceed according to Scheme 2. The intermediate NiC_{18} complexes (5) and (6) have previously been postulated to be formed when the NiC_{15} complex (2) is treated with an excess of allene. Addition of isocyanide to (5) and (6) can either promote ring closure to give the cyclic hydrocarbons (7) and (8) or insertion of isocyanide can occur to yield, after hydrolysis and hydrogenation, the ketones (16) and (17). Reaction of the NiC_{21} complexes (9) and (10) with isocyanide can be considered to proceed in a manner entirely analogous to that of (5) and (6); the ketones (18) and (19) can be formed together with the hydrocarbons (11) and (12).

The present results can be compared with the addition of n-butyl isocyanide to other bis- π -allylnickel complexes. Addition of n-butyl isocyanide to a solution of (2) at $-78^\circ C$ resulted in the formation of a 15-membered ring ketone; insertion was favoured over coupling by 27:1.⁷ A smaller ring ketone was not detected and variation of the alkyl group of the isocyanide, although found to alter the amount of insertion, had no effect on the preference for formation of the larger ring isomer. An insertion reaction was also favoured when isocyanides were added to (1); mixtures of 11- and 13-membered

ring ketones were isolated and the distribution of isomers was found to be dependent on the nature of the alkyl group of the isocyanide. For large, bulky groups, e.g. *t*-butyl, the large-ring isomer was favoured by 97 : 3, while the small-ring isomer was favoured by 83 : 17 when cyclohexyl isocyanide was employed.⁸

The results of reactions of carbon monoxide and isocyanides can be summarised as follows. (i) Treatment of (1) with both carbon monoxide and isocyanide afforded ketone insertion products in high yield. In each reaction the ketones isolated were a mixture of small- and large-ring isomers. (ii) Treatment of the NiC₁₅ complex with carbon monoxide afforded a small amount of insertion product, but with isocyanides the insertion reaction was highly favoured. No small-ring ketones were isolated from either reaction. (iii) Carbon monoxide insertion into the NiC₁₈ and NiC₂₁ complexes was not detected. Large-ring ketone products were isolated when the complexes were treated with isocyanide, but the insertion reaction was not highly favoured.

Clearly, the insertion of alkyl isocyanides into bis- π -allylnickel complexes is more efficient than that of carbon monoxide. Isocyanides, when acting as ligands, are reported to be stronger σ -donors but weaker π -acceptors of electron density than carbon monoxide.^{16,17} This difference in the ability of isocyanides to donate and accept electron density could be reflected in the higher insertion : coupling ratios exhibited by isocyanides.

EXPERIMENTAL

General Reaction Procedure and Preparation of Reagents.—All the reactions were performed in a two-necked flask fitted with a pressure equalising funnel and dry-ice condenser. The reactions were carried out in an atmosphere of high purity argon and all solvents were dried over sodium wire and purged with inert gas before use. Anhydrous nickel acetylacetonate was obtained by heating the dihydrate at 80 °C and 1 mmHg for 10 h. *cis,cis*-Cyclo-octa-1,5-diene was distilled, b.p. 150 °C, from calcium hydride and stored over molecular sieve. Butadiene and allene were both dried by passage over potassium hydroxide pellets before use and, when required, were distilled into the reaction vessel. Tris(isobutyl)aluminium was used as supplied. *n*-Butyl isocyanide was prepared according to the method of Ugi *et al.*;¹⁸ traces of pyridine were removed from the sample by washing with a 5% solution of hydrochloric acid.

All g.l.c. analyses were carried out using a 1.5 m, 10% E301 column and all preparative g.l.c. was performed on a 4m, 10% E301 column.

Preparation of Dodecatrienediylnickel (1).—A sample of Ni(cod)₂ was prepared as previously described.¹⁹ Buta-1,3-diene (30 ml) was distilled into the reaction flask and the mixture left to stir at butadiene reflux temperature (*ca.* -4 °C). The yellow solid gradually dissolved to give a clear, dark red solution of (1). After the Ni(cod)₂ had dissolved, the solution was stirred for a further 30 min before being cooled to -78 °C for 30 min to precipitate any residual Ni(cod)₂. The solution, while still at -78 °C, was

decanted through a glass-wool plug into a cooled three-necked flask previously flushed with argon and transferred to a Drikold-carbon tetrachloride bath at -25 °C. Diethyl ether (30 ml) was added dropwise before the apparatus was evacuated to remove excess of butadiene. The inert argon atmosphere was readmitted and the solution used as the starting point for all reactions.

Reaction of (1) with Allene and Carbon Monoxide.—(i) Dried allene (10 ml, 150 mmol) was distilled into a solution of (1) [from nickel acetylacetonate (4 g, 15.4 mmol)] contained in a three-necked flask equipped with a Drikold-acetone condenser. The mixture was allowed to reach equilibrium with room temperature and, after being stirred at 0 °C for 2 h, the solution, still dark red, was cooled to -30 °C and carbon monoxide bubbled through it overnight. The colour of the solution faded and a small quantity of yellow precipitate formed. Residual tetracarbonylnickel was removed from the reaction and destroyed by addition of bromine. Analysis of the product mixture by g.l.c.-mass spectroscopy indicated the presence of three major products: cyclododecatriene (*M* = 162) representing 25% of the mixture, C₁₃ ketone (*M* = 190) 37%, and C₁₅ hydrocarbon (*M* = 202) 38%. No products of higher molecular weight were detected.

(ii) The reaction was repeated and a similar procedure employed. Allene (7.5 ml, 112 mmol) was distilled into a solution of (1) [from nickel acetylacetonate (4 g, 15.4 mmol)] and the mixture stirred at an equilibrium temperature which rose from 4 to 13 °C over 3¼ h. The mixture was cooled to -78 °C and carbon monoxide bubbled through it for 16 h as before. G.l.c. analysis of the crude product mixture (5.8 g) indicated the presence of three new compounds in addition to those previously observed. Pure samples of each of these compounds were isolated by preparative g.l.c. and identified as the C₁₈ hydrocarbons (7) and (8), C₂₁ hydrocarbons (11) and (12), and C₂₄ hydrocarbons (*M* = 322). For compounds (7) and (8) (Found: C, 88.2; H, 10.7. C₁₈H₂₆ requires C, 89.2, H, 10.8%) *m/e* 242(2%), 227(4), 133(27), 105(39), 91(83), and 79(100); ν_{\max} 3 070, 3 010, 2 980, 2 920, 2 845, 1 645, 1 435, 960, and 895 cm⁻¹; (11) and (12) (Found: C, 89.3; H, 10.7. C₂₁H₃₀ requires C, 89.3%; H, 10.7%) *m/e* 282 (2%, *M*), 267(3), 227(4), 133(14), 105(33), 91(78), and 79(100); ν_{\max} 3 070, 3 010, 2 920, 2 845, 1 645, 1 435, 970, and 900 cm⁻¹. Analysis of the samples on 1.5 m, 5% Carbowax 20M showed the sample of C₁₈ hydrocarbon to be a 4 : 1 mixture of isomers, while the C₂₁ hydrocarbon was a 1 : 1 mixture of isomers. The overall ratio of the products C₁₂ + C₁₃ : C₁₅ : C₁₈ : C₂₁ : C₂₄ = 1 : 0.61 : 0.52 : 0.69 : 0.52.

C₁₈ Formation.—Dried allene (3 ml, 45 mmol) was distilled into an ethereal solution of (1) [from nickel acetylacetonate (4 g, 15.4 mmol)] contained in a three-necked flask equipped with a Drikold-acetone condenser. The mixture was stirred at 0 °C and small portions of the solution withdrawn at regular intervals by use of a syringe flushed with argon. The samples were carbonylated at room temperature for 1 h, during which period the solutions turned colourless and small amounts of yellow precipitate appeared. Each sample was analysed by g.l.c. and the relative amounts of the products in each mixture estimated by g.l.c.

*Reaction of (1) with Allene and *n*-Butyl Isocyanide.*—*n*-

¹⁶ Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, 1972, **8**, 225.

¹⁷ G. F. Van Hecke and W. D. Horrocks, *Inorg. Chem.*, 1966, **5**, 1960.

¹⁸ I. K. Ugi, R. Meyer, M. Lipinski, F. Bodesheim, and F. Rosendahl, *Org. Synth.*, 1961, **41**, 13.

¹⁹ 'Inorganic Synthesis,' ed. G. W. Parschall, McGraw-Hill, New York 1974, vol. xv, p. 5.

Butyl isocyanide (8 ml, 97 mol) in *ca.* 30 ml dry ether was added dropwise to an ethereal solution of the NiC₁₈, NiC₂₁, and NiC₂₄ complexes at -80 °C. The complexes were prepared by stirring (1) [from nickel acetylacetonate (5 g, 19.3 mmol)] with dried allene (10 ml, 150 mmol) for 3¼ h at a temperature in equilibrium with room temperature. The mixture was left to stir at -80 °C for 2½ h before being allowed to warm to room temperature over 14 h. The product mixture was cooled to 0 °C and 11 ml of a 30% solution of a mixture of glacial acetic and concentrated sulphuric acids (9 : 1, v/v) added dropwise. The solution immediately turned dark red. The mixture was left to stir at 0 °C for 1 h, after which the organic layer was separated and the aqueous phase extracted with 3 × 25 ml portions of ether. The combined organic extracts were washed with saturated sodium hydrogencarbonate solution and distilled water, and then dried (MgSO₄). The dark red ethereal solution was filtered and stirred with *ca.* 10 g activated charcoal for 30 min at room temperature. The mixture was filtered and the filtrate stirred with activated charcoal twice more. A pale yellow solution was obtained which afforded a yellow oil on evaporation of the solvent. I.r. analysis of the yellow oil showed ν 3 060, 2 900, 1 710m, 1 680m, 1 640, 1 620, 1 430, 970, and 895 cm⁻¹, suggesting the presence of both conjugated and non-conjugated ketones. The ketones were separated by column chromatography and, since none of the ketones was isolated pure from the column, the ketone fractions were combined. G.l.c.-mass spectral analysis indicated the presence of C₁₉ ketones ($M = 270$), C₂₂ ketones ($M = 310$), and a small amount of C₂₅ ketone, together with ketone products derived from the insertion of isocyanide into (1) and the 1 : 1 allene : (1) complex (2).

The ketone mixture was hydrogenated by stirring an ethanolic solution of the ketones (*ca.* 500 mg) containing 10% Pd-charcoal catalyst (50 mg) under hydrogen at room temperature until uptake of the gas ceased. The mixture was filtered through Kieselguhr, distilled water (25 ml) was added, and the solution extracted with 3 × 30 ml portions of ether. The combined organic extracts were dried

(MgSO₄) and then the mixture was filtered and the solvent evaporated to afford a colourless oil. Samples of the C₁₉ ketones (16) and (17) and C₂₂ ketones (18) and (19) were isolated by preparative g.l.c. The C₂₅ ketones, present in only small amounts, could only be identified by mass spectroscopy ($M = 364$). For compounds (16) and (17) (Found: M , 280.277 0. C₁₉H₃₆O requires M , 280.276 6), m/e 280 (25%, M), 265(8), 262(10), 251(15), 222(14), 111(23), 85(100), and 55(59); ν_{\max} 2 930, 2 860, 1 715, and 1 460 cm⁻¹. For compounds (18) and (19) (Found: C, 82.25; H, 13.0; O, 4.75. C₂₂H₄₂O requires C, 82.0; H, 13.05; O, 4.95%), m/e 322 (24%, M), 307(5), 304(12), 264(12), 111(25), 97(14), 95(12), 85(100), and 55(56); ν_{\max} 2 930, 2 860, 1 715, and 1 460 cm⁻¹.

A comparison of the g.l.c. trace of the product mixture with that of the ketone mixture, obtained after separation by column chromatography, enabled an estimate of the insertion : coupling ratio of the isocyanide into the complexes to be made. The ratios for both the NiC₁₈ and NiC₂₁ complexes were estimated to be approximately 1 : 1. In the experiment, the conditions used for forming the complexes were identical to those employed in the initial reaction. The ratios of the complexes in that reaction mixture after being stirred with allene for 3¼ h were estimated by g.l.c. to be C₁₂ : C₁₅ : C₁₈ : C₂₁ : C₂₄ = 1 : 0.61 : 0.52 : 0.69 : 0.52. These figures were based on the peak areas of the volatile products after carbonylation. The C₁₈ can be calculated to represent 16% and the C₂₁ 21% of these volatile products. This, therefore, sets an upper limit on the yields of C₁₉ and C₂₂ ketones isolated in the isocyanide insertion reaction at 8% and 11% respectively. Since no account has been taken of the higher, involatile oligomers probably formed in the reaction but not detected by g.l.c., these yields are probably higher than their true values.

An S.R.C. studentship (A. H. C.) is gratefully acknowledged. A gift of butadiene for the duration of this work from the International Synthetic Rubber Company, Southampton is also acknowledged.

[7/723 Received, 29th April, 1977]