

## TRANSITION METAL ALLYLS

### III \*. THE ( $\eta^3$ -ALLYL)<sub>2</sub>M COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM: STRUCTURAL CONSIDERATIONS

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#### Summary

The structures of a series of ( $\eta^3$ -allyl)<sub>2</sub>M complexes of nickel, palladium and platinum have been investigated with the help of <sup>13</sup>C NMR, <sup>1</sup>H NMR and Raman spectroscopy. The crystal structure of ( $\eta^3$ -cyclooctatrienyl)<sub>2</sub>Ni has been determined by X-ray methods; the two nickel-bonded  $\eta^3$ -allyl groups are mutually *trans*.

#### Introduction

Although bis( $\eta^3$ -allyl)metal complexes of nickel, palladium and platinum were isolated in the early sixties and have since been shown to be formed as intermediates in a variety of metal-catalyzed cyclooligomerization and cyclooligomerization reactions involving 1,3-dienes [1], detailed information on their structure and reactivity is surprisingly limited.

The ease with which insight can be obtained into the structure of organometallic species and the mechanism of their rearrangements has been greatly increased with the advent of Fourier-transform NMR spectroscopy [2] and laser Raman spectroscopy, and this has prompted us to reinvestigate the bis( $\eta^3$ -allyl)nickel complexes and the related complexes of palladium and platinum. In the accompanying paper we discuss the 1 : 1 adducts formed by these complexes with tertiary phosphines.

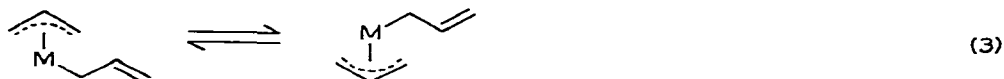
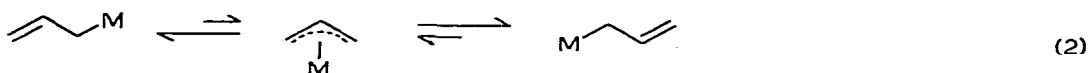
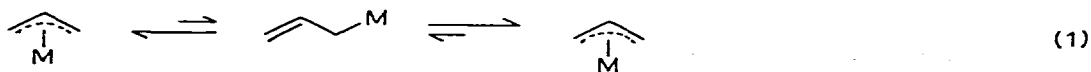
In a previous publication [3], we discussed the correlation between the ther-

\* Ref. 15 can be regarded as Part I and ref. 3 as Part II of the series.

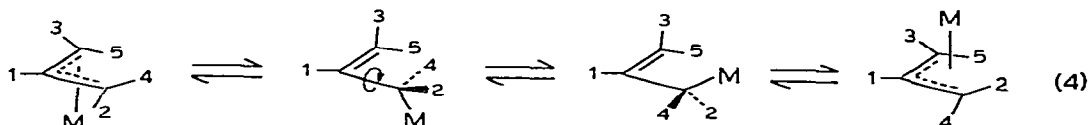
\*\* NMR and Raman spectroscopy investigations.

\*\*\* X-ray structural investigations.

modynamic and kinetic parameters of allyl-metal complexes on the one hand and the expected  $^1\text{H}$  NMR and IR spectra on the other. Three fluxional processes can be distinguished \*: 1) dynamic  $\eta^3$ -allyl (eq. 1), 2) dynamic  $\eta^1$ -allyl (eq. 2), 3) dynamic  $\eta^3$ -allyl,  $\eta^1$ -allyl (eq. 3). The last possibility is, of course, restricted to complexes containing at least two allyl groups.

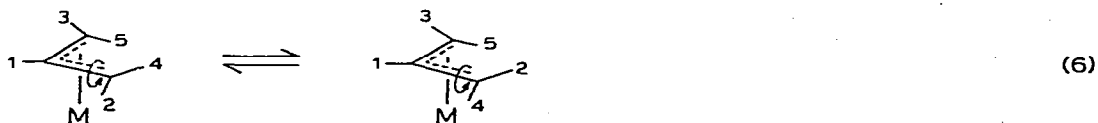
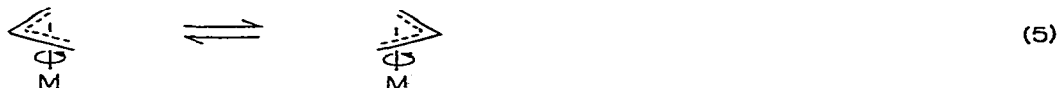


If the rate of exchange for these three processes is faster than the NMR time scale, then spectra derived from the simple  $\text{AX}_4$  spin system will be observed in the  $^1\text{H}$  NMR as the result of equilibration of the *syn*- and *anti*-protons due to rotation about the C—C single bond in the  $\eta^1$ -allyl form (eq. 4).



The vibrational frequencies are, in contrast, much higher than the exchange frequency, and the various intermediates shown in eqs. 1–3 will be detectable as long as they are present in significant concentrations. In the case of the allyl-metal complexes an absorption at ca.  $1600\text{ cm}^{-1}$  is attributed to a  $\eta^1$ -allyl group and one at ca.  $1520\text{ cm}^{-1}$  to a  $\eta^3$ -allyl group. The species shown in eqs. 1–3 would thus give rise in the IR/R spectra to absorptions at ca.  $1520\text{ cm}^{-1}$  (eq. 1), ca.  $1600\text{ cm}^{-1}$  (eq. 2) and at both ca.  $1520\text{ cm}^{-1}$  and ca.  $1600\text{ cm}^{-1}$  (eq. 3), respectively. On the other hand, if the rate of exchange of the processes shown in eqs. 1–3 is slower than the NMR time scale, then the spectra corresponding to the so-called static  $\eta^3$ -allyl or  $\eta^1$ -allyl- or  $\eta^1$ -allyl,  $\eta^3$ -allyl-metal complexes, respectively, will be observed.

Additional intramolecular fluxional processes which may be considered include rotation of the  $\eta^3$ -allyl group about the metal—allyl axis (eq. 5) and rotation about a C—C bond within the  $\eta^3$ -allyl system (eq. 6).



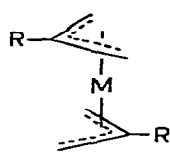
\* For simplicity the discussion is limited to the  $\text{C}_3\text{H}_5$  group.

Rotation about the metal-allyl axis (eq. 5) was first confirmed with the help of spin saturation transfer experiments for complexes of Fe, Mo and W [4] while an intramolecular twist mechanism has been proposed to account for the observed equivalence of the allyl groups in  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ru}(\text{CO})_2$  [5]. For  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  (I), however, a qualitative MO treatment indicates that simple rotation about the allyl-metal axis is symmetry forbidden and hence a high energy process [25]. Although rotation about a C-C bond (eq. 6) may occur in ionic allyl-metal complexes [6], the barrier for  $\eta^3$ -allyl complexes of the transition metals having filled *d*-orbitals can be expected to be prohibitively high; an MO calculation indicates that for  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  the barrier to rotation is ca. 90 kcal/mol [7].

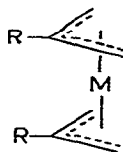
In addition to these various possibilities, many examples of fluxional behaviour in allyl-metal complexes which involve ligand exchange have been studied. A recent general discussion of the factors involved is to be found in ref. [6].

$(\eta^3\text{-allyl})_2M$ ,  $M = \text{Ni}, \text{Pd}, \text{Pt}$

The symmetrical  $(\eta^3\text{-allyl})_2M$  complexes can be adopt at least two configurations. The presence of two isomers in solutions of the unsubstituted  $(\eta^3\text{-C}_3\text{H}_5)_2M$  complexes was first reported in 1962 for nickel [8,9,11a] and in 1963 for palladium [10,11a-c]. The platinum complex [10,11a] was shown to be analogous in 1970 [12,13]. Similar behaviour has been reported for the  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2M$  complexes. The suggestion that in one isomer the  $\eta^3$ -allyl groups are mutually *trans* (e.g. Ia) was confirmed by X-ray crystallography for  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$  (II) [14], and this arrangement has also been found in  $(\eta^3\text{-pinenyl})_2\text{Ni}$  [15].

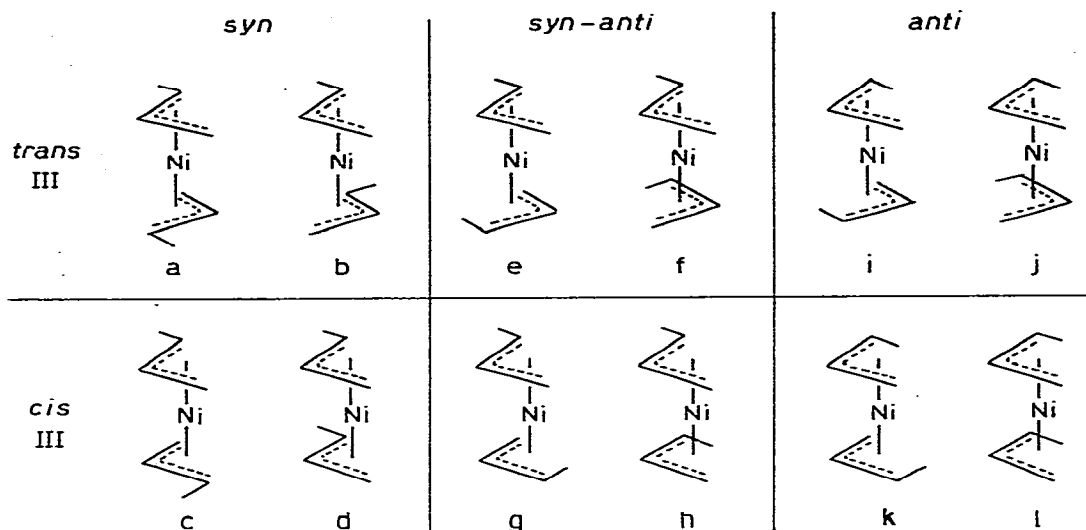


(Ia)



(Ib)

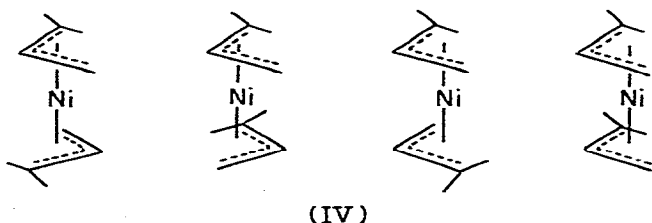
The second isomer is believed to have the structure Ib in which the  $\eta^3$ -allyl groups are mutually *cis*. Although a *cis* arrangement has been shown both crystallographically and spectroscopically to be present in the phosphine adducts  $\eta^3\text{-C}_9\text{H}_{12}\text{NiP}(\text{C}_6\text{H}_{11})_3$  [16] and  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$  (see following paper), direct evidence for its presence in the simple  $(\eta^3\text{-allyl})_2M$  complexes is still lacking, and the formulation of this isomer as Ib is based primarily upon the structure of the products of the reaction of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  (I, R = H) with diazomethane [17]. Additional isomers are possible for complexes having substituents on the C<sub>1</sub> or C<sub>3</sub> atoms. In the particular case of  $(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$  (III) a total of twelve isomers are possible due to *syn*- or *anti*-substitution of the  $\eta^3$ -allyl groups as shown below:



## Results

The  $(\eta^3\text{-allyl})_2\text{metal}$  complexes of nickel, palladium and platinum studied here were synthesized by the standard reaction between metal halide and Grignard reagent in diethyl ether (see for example [1a,9,10,18]). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are collected in Tables 4 and 5 and typical spectra are shown in Fig. 1.

All the readily soluble non-cyclic  $(\eta^3\text{-allyl})_2\text{M}$  complexes exist as a mixture of isomers. In the case of  $(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$  (III) the four isomers detected in both the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra (ratio 5 : 3 : 2 : 1) were shown by an analysis of the proton-proton coupling constants to contain exclusively *syn*-substituted  $\eta^3$ -allyl groups (IIIa-d). An absolute assignment cannot be made, but the two main isomers have been assigned the *trans*-configuration, e.g. IIIa and IIIb, by comparison of the proton chemical shifts with those for  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  (I). The situation in the case of the analogous  $\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4$ -complexes of palladium and platinum has not been completely resolved: in the case of platinum the  $^1\text{H}$  NMR spectrum proved too complex to analyze, while in the case of palladium four isomers containing *syn*-CH<sub>3</sub> groups have been identified with certainty, while two other species (formed in a total of 5% yield) probably contain *anti*-CH<sub>3</sub> groups.  $(\eta^3\text{-1,1'-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$  (IV) also exists as a mixture of the four possible isomers (Fig. 1).



Comparison of the  $^{13}\text{C}$ -chemical shifts for the  $\eta^3\text{-C}_3\text{H}_5$  and  $\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4$

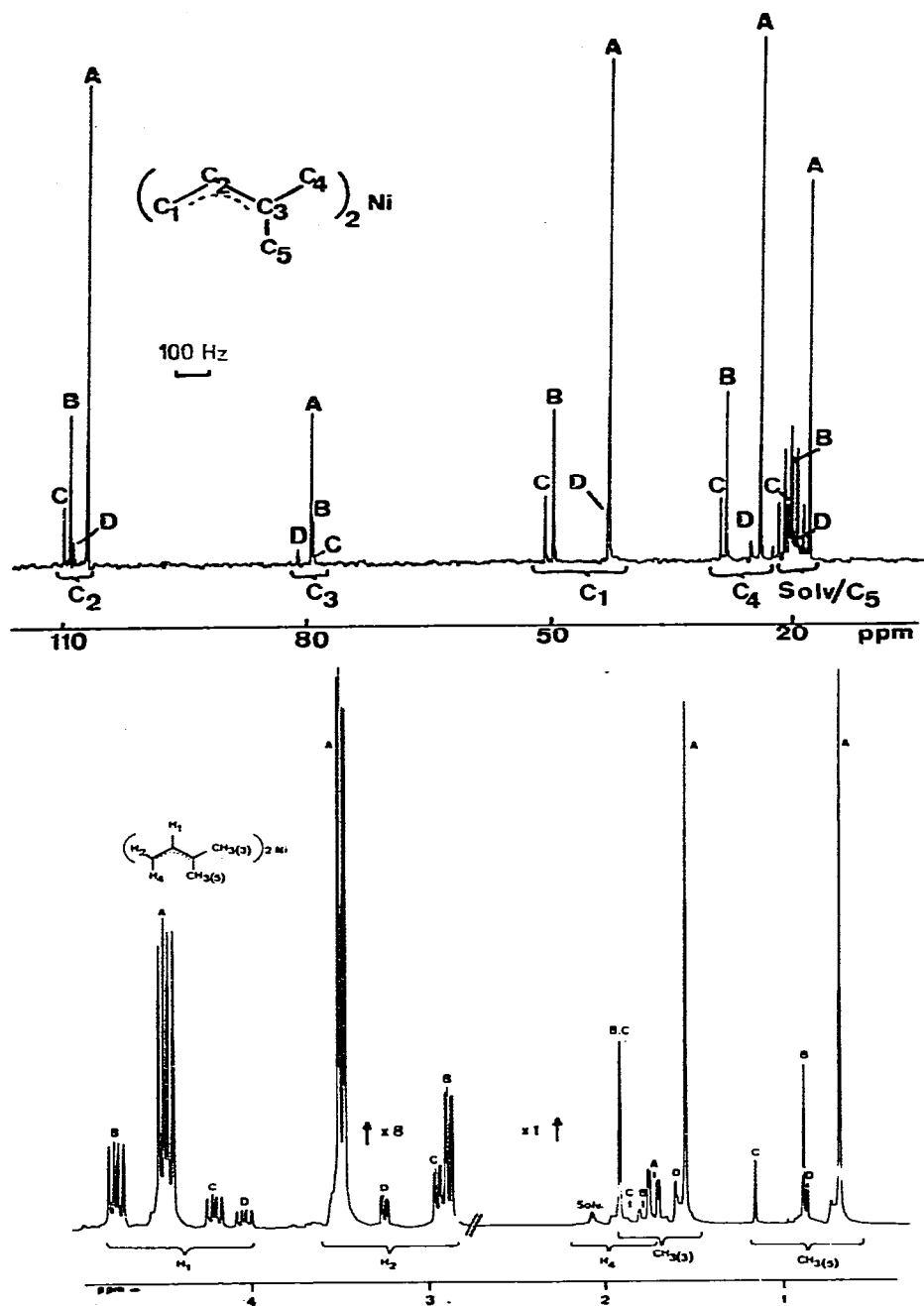


Fig. 1. The 25 MHz  $^{13}\text{C}$ - $\{^1\text{H}\}$  and 270 MHz  $^1\text{H}$  NMR spectra of  $(\eta^3\text{-}1,1'\text{-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$  (IV) in toluene- $d_8$  at  $-20^\circ\text{C}$ .

complexes of Ni, Pd and Pt (Table 5) shows, surprisingly, that the chemical shifts increase in the order  $\text{Pt} < \text{Ni} < \text{Pd}$ . The chemical shift data of the methyl-substituted  $\eta^3$ -allyl complexes given in Tables 4 and 5 show considerable regularity. If we assume that the main isomers A have the same structure (i.e. a

*trans* arrangement of the  $\eta^3$ -allyl groups), then substitution increments can be estimated. These are shown in Table 1 where a positive increment indicates that substitution causes a shift to lower field.

Repeated recrystallization (pentane,  $-78^\circ\text{C}$ ) of both  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  (I) and  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$  (II) leads to samples rich in the *trans*-isomer (6.5 : and 6.2 : 1, respectively). These samples equilibrate irreversibly on warming from  $-80^\circ\text{C}$  to RT to give the previously observed *trans* : *cis* ratios of 2.6 : 1 and 2.3 : 1. Practically pure *trans*- $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  has previously been obtained by disproportionation of  $(\eta^3\text{-C}_3\text{H}_5\text{NiCH}_3)_2$  at  $-70^\circ\text{C}$  [9]. Interestingly, the analogous reaction with  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4\text{NiCH}_3)_2$  was shown to produce *cis*- $(\eta^3\text{-2-CH}_3\text{-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$ . Equilibration on warming to room temperature was also observed in these cases. It is not known whether this process is associated with intermediate formation of a  $\eta^1$ -allyl species accompanied by *syn*  $\leftrightarrow$  *anti* exchange of the allylic protons or whether a rotation about the  $\eta^3$ -allyl metal axis occurs. This question has previously been discussed for  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$  (XIV) [11b] and it is expected that a spin saturation transfer experiment may distinguish between these alternatives.

In contrast to the simple  $(\eta^3\text{-allyl})_2\text{M}$  complexes discussed above, only one isomer can be detected in the NMR spectra of the complexes containing cyclic  $\eta^3$ -allyl groups. An X-ray crystallographic determination for  $(\eta^3\text{-cyclooctatrienyl})_2\text{Ni}$  (XI) (Fig. 2) indicates that, at least in this case, the  $\eta^3$ -allyl groups are mutually *trans*. The structures was solved by direct methods from 3111 diffractometer collected reflections  $hkl$ ,  $\overline{hkl}$  (CAD-4, nickel filtered Cu-radiation,  $\lambda$

TABLE I  
 $^{13}\text{C}$  AND  $^1\text{H}$  CHEMICAL SHIFT INCREMENTS FOR METHYL SUBSTITUTION

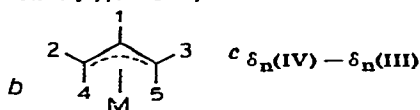
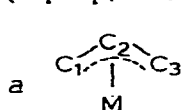
$^{13}\text{C}$ :

| $\text{CH}_3\text{-Subst.}^a$                  | Metal | $\Delta\delta\text{C}_1$ (ppm) | $\Delta\delta\text{C}_2$ (ppm) | $\Delta\delta\text{C}_3$ (ppm) |
|--|-------|--------------------------------|--------------------------------|--------------------------------|
| at $\text{C}_2$ (II)<br>(XV)<br>(XIX)          | Ni    | -1.5                           | +10.8                          | -1.5                           |
|  | Pd    | -1.0                           | +12.9                          | -1.0                           |
|  | Pt    | -0.7                           | +13.9                          | -0.7                           |
| <i>syn</i> at $\text{C}_1$ (IIIA)<br>(XVIA)    | Ni    | +18.5                          | +0.5                           | -6.6                           |
|  | Pd    | +21.0                          | +0.2                           | -7.6                           |
| additional<br><i>anti</i> at $\text{C}_1$ (IV) | Ni    | +8.1 <sup>c</sup>              | -6.0                           | -3.3                           |

$^1\text{H}$ :

| $\text{CH}_3\text{-Subst.}^b$               | Metal | $\Delta\delta\text{H}_1$ | $\Delta\delta\text{H}_2$ | $\Delta\delta\text{H}_3$ | $\Delta\delta\text{H}_4$ | $\Delta\delta\text{H}_5$ |
|---|-------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| at $\text{C}_2$ (II)<br>(XV)                | Ni    | +3.30                    |                          | +0.27                    |                          | -0.02                    |
|   | Pd    | +3.31                    |                          | +0.19                    |                          | +0.03                    |
| <i>syn</i> at $\text{C}_1$ (IIIA)<br>(XVIA) | Ni    | +0.15                    | +2.09                    | +0.23                    | -0.62                    | +0.08                    |
|   | Pd    | +0.09                    | +2.30                    | +0.28                    | -0.69                    | +0.12                    |

( $\Delta\delta_i = \delta_i(\text{subst. allyl}) - \delta_i(\text{unsubst. allyl}); i = 1-5$ )



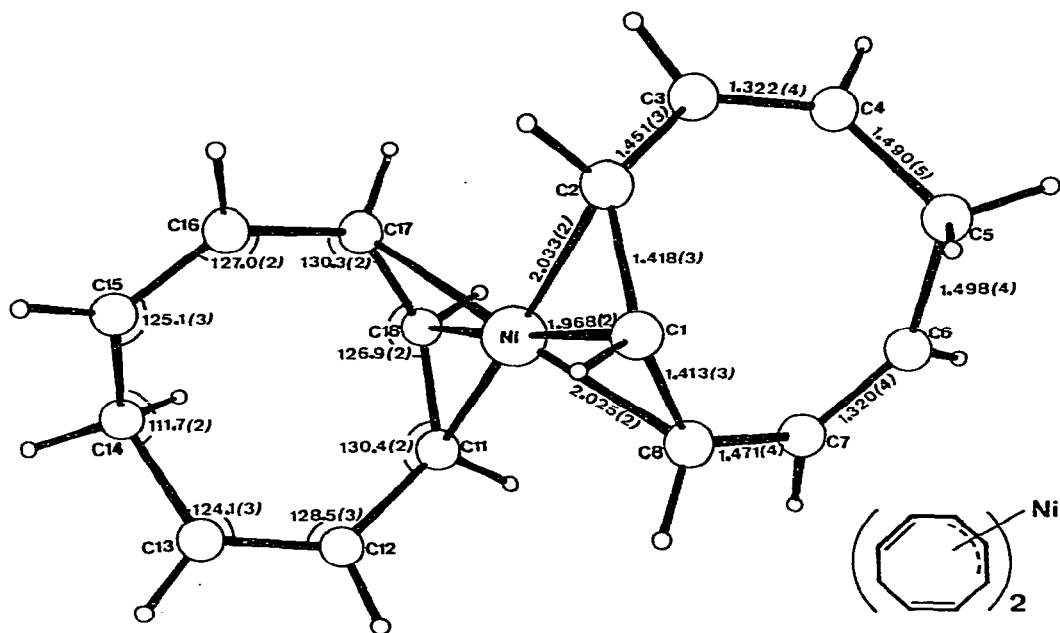


Fig. 2. The crystal structure of  $(\eta^3\text{-cyclooctatrienyl})_2\text{Ni}$  (XI) ( $a$  10.2153(7),  $b$  10.2928(4),  $c$  12.5568(6) Å;  $V$  1320.2 Å<sup>3</sup>; space group  $P2_12_12_1$ ;  $Z = 4$ ;  $d_{\text{calc}}$  1.353 g cm<sup>-3</sup>).

1.54178 Å) of which 747 were deemed unobserved ( $I \leq 2\sigma(I)$ ). An anisotropic refinement (hydrogen atoms isotropic) converged at  $R = 0.028$  ( $R_w = 0.034$ ). Experimental and computational details are given in ref. 19. The molecule, as shown in Fig. 2, is characterized by a pseudo-inversion centre occupied by nickel. Both  $\eta^3$ -allyl fragments exhibit equivalent bonding parameters while the bonding feature within the eight-membered rings are comparable. The adoption of a chiral space group by the molecule in the solid state may thus be brought about by packing forces due to some short H—H contacts. The normals to the planes of the transoid allylic fragments form an angle of only 4°, the adjacent carbon atoms being 0.75 Å above this plane. A packing diagram is shown in Fig. 3 while atomic parameters (which refer to the correct enantiomer with more than 99% probability) are given in Table 2 and selected bond distances angles in Table 3.

The <sup>13</sup>C NMR spectrum of XI at -60°C in toluene-*d*<sub>8</sub> is consistent with the structure found in the solid state. However, at ambient temperatures (32°C) the resonances for C<sub>2</sub>\* ( $\Delta\nu_{1/2}$  = peak width at half height ~ 30 Hz) and C<sub>4,8</sub> and C<sub>5,7</sub> (unresolved,  $\Delta\nu_{1/2}$  ~ 10 Hz) become broadened, while those for C<sub>1,3</sub> and C<sub>6</sub> remain sharp ( $\Delta\nu_{1/2}$  ~ 4 Hz and 3 Hz respectively). A probable explanation for this behaviour is that at higher temperature a second structure becomes populated and exchange between this and the more stable form is occurring. The resonance for C<sub>6</sub> in  $(\eta^3\text{-cyclooctenyl})_2\text{Ni}$  (X) is found at relatively high field (24.2 ppm) compared to the free cycloalkanes, indicating that the ring has adopted a boat configuration.

\* The numbering of the carbon atoms refers to the convention used in Table 5.

TABLE 2  
FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS ( $\times 10^4$ ) AND FINAL THERMAL PARAMETERS ( $\times 10^3$ )

| Atom             | X         | Y         | Z         | $U_{1,1}$ | $U_{2,2}$ | $U_{3,3}$ | $U_{1,2}$ | $U_{1,3}$ | $U_{2,3}$ |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| N <sub>1</sub>   | -3786(1)  | -1209(1)  | -4833(1)  | 56        | 41        | 47        | -3        | 5         | 2         |
| C <sub>1</sub>   | -2510(2)  | 145(2)    | -5213(1)  | 44        | 46        | 67        | -8        | 4         | 6         |
| C <sub>2</sub>   | -3111(2)  | 501(2)    | -4239(1)  | 67        | 46        | 45        | -6        | -8        | -3        |
| C <sub>3</sub>   | -4270(2)  | 1271(2)   | -4023(1)  | 84        | 45        | 52        | -0        | 12        | -7        |
| C <sub>4</sub>   | -4875(2)  | 2106(2)   | -4653(2)  | 75        | 45        | 80        | 2         | 14        | -7        |
| C <sub>5</sub>   | -4455(3)  | 2397(2)   | -5764(2)  | 69        | 43        | 76        | 1         | 1         | 16        |
| C <sub>6</sub>   | -4883(2)  | 1391(2)   | -6553(2)  | 69        | 73        | 61        | -8        | -12       | 18        |
| C <sub>7</sub>   | -4320(2)  | 248(2)    | -6684(1)  | 88        | 69        | 43        | -22       | -5        | 1         |
| C <sub>8</sub>   | -3149(2)  | -269(2)   | -6151(1)  | 73        | 46        | 50        | -9        | 15        | -1        |
| C <sub>11</sub>  | -4553(2)  | -2914(2)  | -5370(1)  | 57        | 52        | 71        | -11       | -11       | 4         |
| C <sub>12</sub>  | -3493(2)  | -3828(2)  | -5568(2)  | 69        | 55        | 67        | -11       | -4        | -12       |
| C <sub>13</sub>  | -2973(2)  | -4693(2)  | -4905(2)  | 71        | 46        | 102       | 1         | -3        | -16       |
| C <sub>14</sub>  | -3382(3)  | -4852(2)  | -3750(2)  | 71        | 48        | 98        | -3        | -8        | 14        |
| C <sub>15</sub>  | -2803(2)  | -3633(2)  | -3064(2)  | 63        | 63        | 77        | -1        | -12       | 17        |
| C <sub>16</sub>  | -3247(2)  | -2635(2)  | -2874(1)  | 75        | 62        | 51        | -7        | -0        | 9         |
| C <sub>17</sub>  | -4420(2)  | -2089(2)  | -3481(1)  | 62        | 53        | 58        | 6         | 20        | 6         |
| C <sub>18</sub>  | -5103(2)  | -2489(2)  | -4408(2)  | 42        | 50        | 80        | -1        | 6         | 12        |
| H <sub>1</sub>   | -1601(19) | -108(19)  | -5166(16) | 53        |           |           |           |           |           |
| H <sub>2</sub>   | -2593(21) | 427(20)   | -3600(17) | 57        |           |           |           |           |           |
| H <sub>3</sub>   | -4611(23) | 1159(23)  | -3306(18) | 76        |           |           |           |           |           |
| H <sub>4</sub>   | -5652(23) | 2536(18)  | -4374(17) | 61        |           |           |           |           |           |
| H <sub>5A</sub>  | -4808(23) | 3205(22)  | -5972(18) | 69        |           |           |           |           |           |
| H <sub>5B</sub>  | -3523(27) | 2401(22)  | -5869(21) | 76        |           |           |           |           |           |
| H <sub>6</sub>   | -5718(21) | 1578(20)  | -6941(16) | 59        |           |           |           |           |           |
| H <sub>7</sub>   | -4708(22) | -305(20)  | -7210(17) | 64        |           |           |           |           |           |
| H <sub>8</sub>   | -2623(20) | -789(12)  | -6589(16) | 55        |           |           |           |           |           |
| H <sub>11</sub>  | -5181(24) | -2795(21) | -5994(18) | 69        |           |           |           |           |           |
| H <sub>12</sub>  | -3155(22) | -3823(24) | -6258(20) | 70        |           |           |           |           |           |
| H <sub>13</sub>  | -2311(22) | -5216(23) | -5145(19) | 70        |           |           |           |           |           |
| H <sub>14A</sub> | -3165(25) | -5770(26) | -3542(21) | 88        |           |           |           |           |           |
| H <sub>14B</sub> | -4367(23) | -4813(21) | -3808(19) | 69        |           |           |           |           |           |
| H <sub>15</sub>  | -2016(20) | -4044(22) | -2725(18) | 64        |           |           |           |           |           |
| H <sub>16</sub>  | -2787(21) | -2018(23) | -2519(19) | 61        |           |           |           |           |           |
| H <sub>17</sub>  | -4939(22) | -1556(20) | -3019(16) | 59        |           |           |           |           |           |
| H <sub>18</sub>  | -6026(25) | -2117(22) | -4417(18) | 77        |           |           |           |           |           |



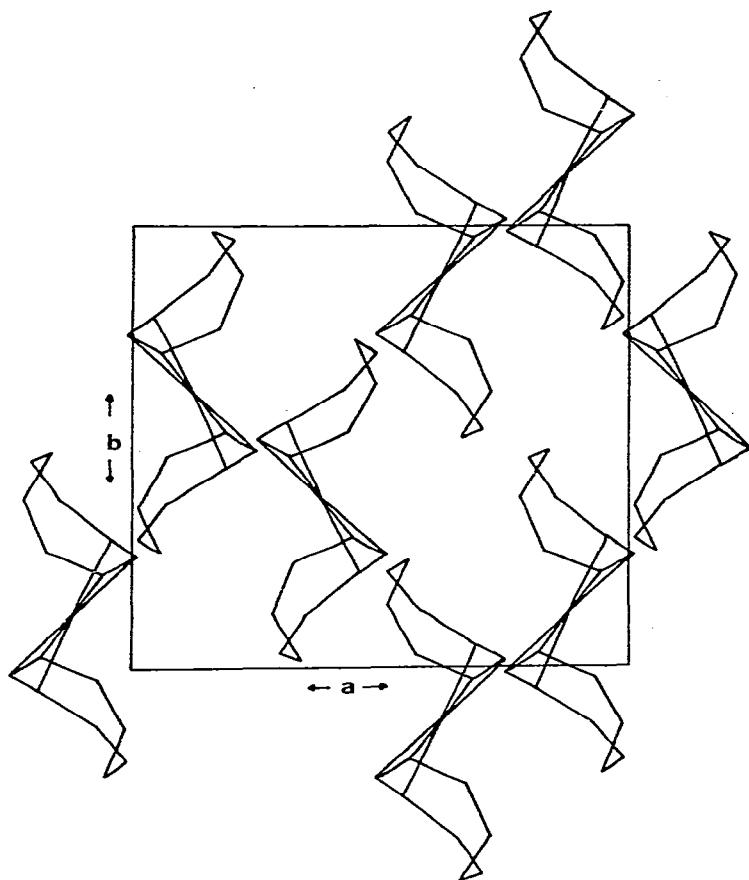


Fig. 3. Packing diagram for  $(\eta^3\text{-cyclooctatrienyl})_2\text{Ni}$  (XI).

In addition to the simple  $(\eta^3\text{-allyl})_2\text{Ni}$  complexes shown in Tables 4 and 5, we have reinvestigated the bis- $\eta^3$ -dodecatrienediyl complex (XII) which is formed on treating ligand-free zerovalent nickel complexes with butadiene, and which is involved as an intermediate in the nickel-catalyzed cyclotrimerization of butadiene to 1,5,9-cyclododecatriene [20]. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra are shown in Fig. 4. The  $^{13}\text{C}$  NMR spectra in  $\text{THF-}d_8$  and  $\text{toluene-}d_8$  are practically identical, indicating that the THF is not in this case functioning as a ligand. The  $^{13}\text{C}$  NMR spectrum shown in Fig. 4 was run in  $\text{THF-}d_8$  and demonstrates the absence of signals around 130 ppm. Assignment of the  $^{13}\text{C}$  resonances is unambiguous, and is supported by the results of selective proton decoupling experiments. The following conclusions can be drawn from the combined spectroscopic evidence:

- a) The  $\text{C}_{12}$  chain of the major component is bonded symmetrically to the metal atom; only 6 absorptions for the 12 carbon atoms and 9 absorptions for the 18 hydrogen atoms are observed.
- b) The  $\eta^3$ -allyl groups are *anti*-substituted;  $^3J(\text{H}_1, \text{H}_2)$  7 Hz (see Table 4).
- c) A second isomer (ca. 20%), which is also symmetrical, is present.

TABLE 3  
SELECTED BOND DISTANCES (Å) AND ANGLES (°)

|  |          |   |          |
|--|----------|---|----------|
| Ni—C <sub>1</sub>                              | 1.968(2) | Ni—C <sub>18</sub>                                | 1.958(2) |
| Ni—C <sub>2</sub>                              | 2.033(2) | Ni—C <sub>11</sub>                                | 2.037(2) |
| Ni—C <sub>3</sub>                              | 2.025(2) | Ni—C <sub>17</sub>                                | 2.031(2) |
| C <sub>1</sub> —C <sub>2</sub>                 | 1.418(3) | C <sub>18</sub> —C <sub>11</sub>                  | 1.402(4) |
| C <sub>2</sub> —C <sub>3</sub>                 | 1.451(3) | C <sub>11</sub> —C <sub>12</sub>                  | 1.456(4) |
| C <sub>3</sub> —C <sub>4</sub>                 | 1.322(4) | C <sub>12</sub> —C <sub>13</sub>                  | 1.331(4) |
| C <sub>4</sub> —C <sub>5</sub>                 | 1.490(4) | C <sub>13</sub> —C <sub>14</sub>                  | 1.518(5) |
| C <sub>5</sub> —C <sub>6</sub>                 | 1.498(4) | C <sub>14</sub> —C <sub>15</sub>                  | 1.481(4) |
| C <sub>6</sub> —C <sub>7</sub>                 | 1.320(4) | C <sub>15</sub> —C <sub>16</sub>                  | 1.319(4) |
| C <sub>7</sub> —C <sub>8</sub>                 | 1.471(4) | C <sub>16</sub> —C <sub>17</sub>                  | 1.470(4) |
| C <sub>8</sub> —C <sub>1</sub>                 | 1.413(3) | C <sub>17</sub> —C <sub>18</sub>                  | 1.419(4) |
| C <sub>8</sub> —C <sub>1</sub> —C <sub>2</sub> | 126.7(2) | C <sub>11</sub> —C <sub>18</sub> —C <sub>17</sub> | 126.9(2) |
| C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub> | 131.0(2) | C <sub>18</sub> —C <sub>11</sub> —C <sub>12</sub> | 130.4(2) |
| C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub> | 128.7(2) | C <sub>11</sub> —C <sub>12</sub> —C <sub>13</sub> | 128.5(3) |
| C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub> | 123.8(3) | C <sub>12</sub> —C <sub>13</sub> —C <sub>14</sub> | 124.1(3) |
| C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub> | 113.3(2) | C <sub>13</sub> —C <sub>14</sub> —C <sub>15</sub> | 111.7(2) |
| C <sub>5</sub> —C <sub>6</sub> —C <sub>7</sub> | 124.9(3) | C <sub>14</sub> —C <sub>15</sub> —C <sub>16</sub> | 125.1(3) |
| C <sub>6</sub> —C <sub>7</sub> —C <sub>8</sub> | 128.4(2) | C <sub>15</sub> —C <sub>16</sub> —C <sub>17</sub> | 127.0(2) |
| C <sub>7</sub> —C <sub>8</sub> —C <sub>1</sub> | 120.2(2) | C <sub>16</sub> —C <sub>17</sub> —C <sub>18</sub> | 130.3(2) |

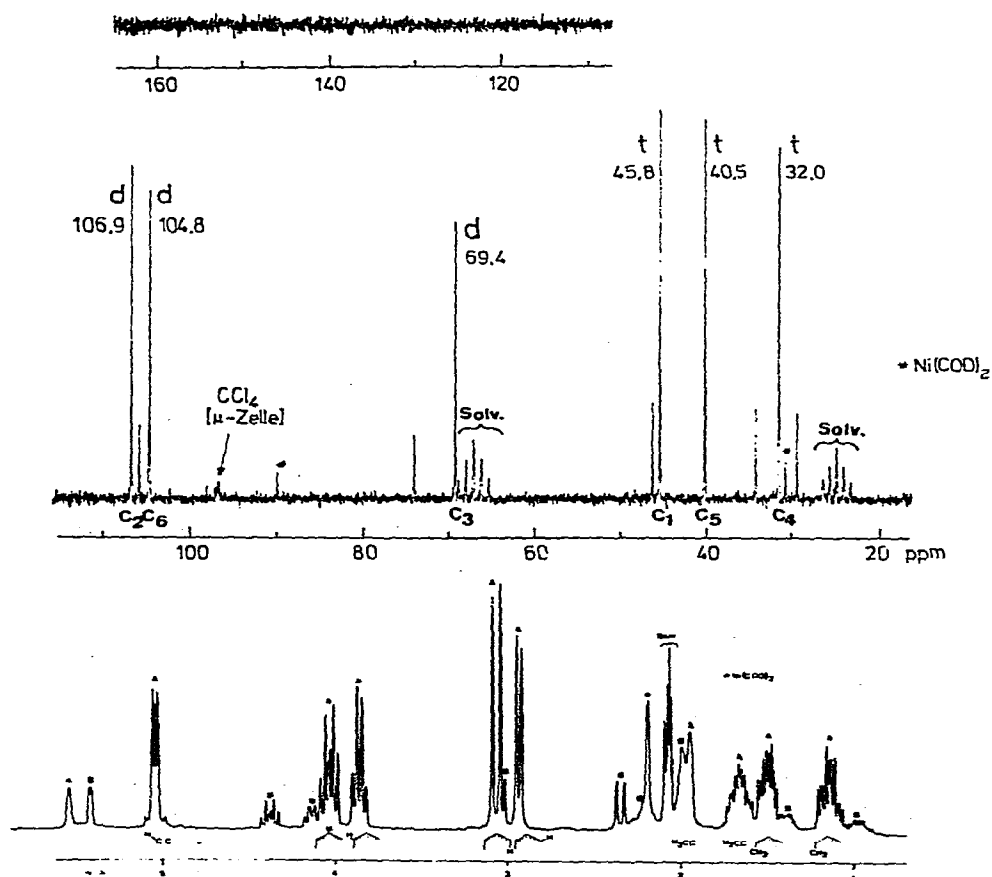
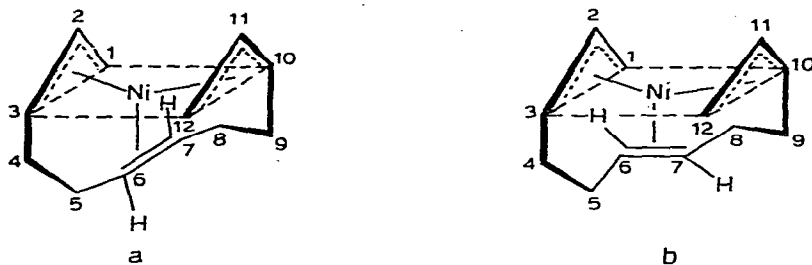


Fig. 4. The 25.2 MHz  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR and 270 MHz  $^1\text{H}$  NMR spectra of  $(\eta^3\text{-C}_{12}\text{H}_{18})\text{Ni}$  (XII).

d) The double bond is complexed to the metal atom. Complexation is associated with an upfield shift of ca. 25 ppm. This value is, however, relatively small for zerovalent nickel olefin complexes [2].

e) The complexed double bond has a *trans* configuration. Double resonance (irradiation of one of the protons on C<sub>5</sub> (and C<sub>8</sub>)) leads to an {A A' X X'} spin system for the protons on C<sub>6</sub> (and C<sub>7</sub>) and the second proton on C<sub>5</sub> (and C<sub>8</sub>). Analysis of this system gives a value of 13.3 Hz for the olefinic coupling, which is typical for a complexed double bond [21]. This value and the other calculated parameters (Table 4) were used in a computer simulation which exactly reproduced the spectrum of the {A A' X X'} spin system obtained experimentally by double resonance. We have not carried out this procedure for the olefinic protons of the second isomer, but since the form of the multiplet for the olefinic protons in this case is identical with that for the main isomer, it can be assumed that in this case also the olefin adopts a *trans*-configuration. Further evidence for the *trans*-configuration is the position of the absorption for C<sub>5</sub> (major component) at 40.5 ppm. In a *cis*-configuration it might be anticipated that  $\gamma$ -interaction between the methylene groups at C<sub>5</sub> and C<sub>8</sub> would result in a shift in this signal to a value of ca. 30 ppm.

The structures most consistent with these data are XIIa and XIIb, and we assume that these are the two species observed spectroscopically in solution. (Models indicate that two other arrangements are possible, but serious steric interference between one of the protons on C<sub>5/8</sub> and the *anti*-proton on C<sub>1/12</sub> make them less probable.) XIIa and XIIb can be formally interconverted by rotation of the complexed double bond. The assignment of the main isomers as XIIa is provisional but is suggested by spectroscopic evidence: the abnormal chemical shift of the *anti*-proton bonded to C<sub>1/12</sub> ( $\delta$  *anti*-H(C<sub>1/12</sub>) >  $\delta$  *syn*-H(C<sub>1/12</sub>)) in this isomer probably arises due to the contiguity of this atom and the olefinic H atoms on C<sub>7/6</sub>. This effect is not observed in the second isomer (XIIb) in which this interaction is absent.



(XII)

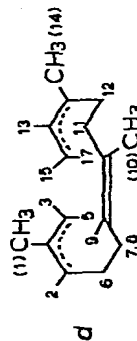
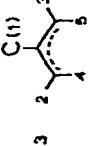
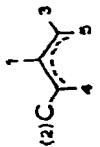
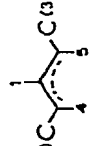
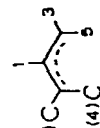
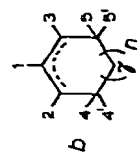
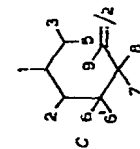
A related complex XIII has been isolated from the reaction of bis(cyclooctadiene)nickel with isoprene. The <sup>1</sup>H and <sup>13</sup>C NMR spectra (Tables 4 and 5) indicate that here also two isomers are present in the ratio 4 : 3 and that in both cases the double bond is complexed to the metal atom. The product of hydrogenation, 2,7,10-trimethyldodecane, suggests that the chain is formed by the head-head-tail coupling of three isoprene molecules. The combined NMR and chemical evidence suggests that the structure is related to XII, with methyl groups in positions 2, 7 and 10.

TABLE 4

 $^1\text{H}$  NMR SPECTROSCOPIC DATA FOR  $(\eta^3\text{-ALLYL})_2\text{M}$  COMPLEXES OF NI, Pd, Pt

| Complex <sup>a</sup>   | Temp.<br>(°C) | Solvent                | Isomer (%)                             | $\delta_1$<br>(ppm)          | $\delta_2$<br>(ppm)          | $\delta_3$<br>(ppm)          | $\delta_4$<br>(ppm)          | $\delta_5$<br>(ppm)          | Coupling Const. (Hz)   | Remarks                                |
|--|---------------|------------------------|--|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|--|--|
| $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$ (I)                             | +25           | Toluene-d <sub>8</sub> | A (72)<br>B (28)                       | 4.90<br>4.43                 | 3.76<br>3.56                 |                              | 1.67<br>2.16                 |                              | J(12) 7.6; J(14) 14.3<br>J(12) 7.6; J(14) 14.3   | See ref. 1b                            |
| $(\eta^3\text{-2-CH}_3\text{-C}_3\text{H}_4)_2\text{Ni}$<br>(II)           | +30           | Toluene-d <sub>8</sub> | trans (68)<br>cis (32)                 | 1.60<br>1.36                 | 3.49<br>3.35                 |                              | 1.69<br>2.10                 |                              |  | See ref. 1b                            |
| $(\eta^3\text{-1-CH}_3\text{-C}_3\text{H}_4)_2\text{Ni}$<br>(III)          | +10           | Toluene-d <sub>8</sub> | A (46)<br>B (27)<br>C (18)<br>D (9)    | 4.75<br>4.83<br>4.27<br>4.40 | 1.67<br>1.81<br>1.67<br>1.82 | 3.53<br>3.24<br>3.33<br>2.84 | 2.29<br>2.70<br>2.89<br>2.92 | 1.59<br>1.40<br>1.93<br>2.14 | J(14) ~ J(15) 13.3; J(13) 7.65; J(24) 6.02; J(35) 2.4<br>J(14) ~ J(15) 13.6; J(13) 7.8; J(24) 6.2; J(35) 2.0<br>J(14) ~ J(15) 13.2; J(13) 7.8; J(24) 6.1; J(35) 2.56<br>J(13) 7.9; J(15) 14.1; J(35) 2.9 | WH 270<br>Spectrometer<br>See ref. 1b  |
| $(\eta^3\text{-1,1'-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$ (IV)       | -20           | Toluene-d <sub>8</sub> | A (67)<br>B (20)<br>C (8.5)<br>D (5.0) | 4.48<br>4.76<br>4.21<br>4.04 | 1.56<br>1.92<br>1.92<br>1.61 | 3.49<br>2.89<br>2.95<br>3.25 | 0.68<br>0.88<br>1.16<br>0.86 | 1.56<br>1.92<br>1.92<br>2.00 | J(13) 7.9; J(15) 14.0; J(35) 2.5<br>J(13) 7.9; J(15) 13.9; J(35) 2.7<br>J(13) 8.0; J(15) 14.0; J(35) 2.9<br>J(13) 8.0; J(15) 14.0; J(35) 2.9   | WH 270<br>spectrometer                 |
| $(\eta^3\text{-1,3-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$ (V)         | -10           | Toluene-d <sub>8</sub> | A (76)<br>B (24)                       | 4.05<br>4.14                 | 1.74<br>1.61                 |                              | 2.15<br>2.63                 |                              | J(15) 12.4; J(24) 6.1<br>J(15) 12.3; J(24) 6.1   |  |
| $(\eta^3\text{-1-iso-C}_3\text{H}_7\text{-C}_3\text{H}_4)_2\text{Ni}$ (VI) | -10           | Toluene-d <sub>8</sub> | A (85)<br>B (15)                       | 4.82<br>4.38                 | 2.31<br>nd                   | 3.48<br>3.16                 | 2.65<br>2.91                 | 1.43<br>nd                   | J(13) 7.5; J(15) 13.5; J(35) 2.0; J(14) 13; J(24) 6<br>J(13) 7.5; J(15) 12.5; J(24) 2.0  | $\delta(\text{CH}_3)$ 1.14; 1.12       |
| $(\eta^3\text{-1-C}_6\text{H}_5\text{-C}_3\text{H}_4)_2\text{Ni}$ (VII)    | 0             | Toluene-d <sub>8</sub> | A (~85)<br>B (~15)                     | 5.55<br>4.83                 | 7.1<br>7.1                   | 3.61<br>3.23                 | 2.78<br>nd                   | 1.70<br>nd                   | J(13) 7.5; J(15) 13.5; J(35) 2; J(14) 13.5   |  |
| $(\eta^3\text{-cyclo-(VIII)hexenyl})_2\text{Ni}$ <sup>b</sup>              | -50           | Toluene-d <sub>8</sub> |  | 4.96                         | 4.62                         | 2.0                          | 1.10                         |                              | J(12) 8.2  |  |
| $(\eta^3\text{-cyclo-(IX)heptenyl})_2\text{Ni}$ <sup>b</sup>               | -10           | Toluene-d <sub>8</sub> |  | 4.4                          | 4.4                          | 1.9                          | 1.0                          |                              |  |  |
| $(\eta^3\text{-cyclo-(X)octenyl})_2\text{Ni}$ <sup>b</sup>                 | 0             | Toluene-d <sub>8</sub> |  | 4.91                         | 4.33                         | 2.0                          | 1.3                          |                              | J(12) 8.1  | $\delta(\gamma\text{CH}_2)$ 1.3        |
| $(\eta^3\text{-cyclo-(XI)octatrienyl})_2\text{Ni}$                         | +25           | Benzene-d <sub>6</sub> |  | 4.19                         | 4.42                         |                              | 5.7                          |                              |  | $\delta(\gamma\text{CH}_2)$ 3.37; 2.13 |
| $\eta^3\text{-C}_{12}\text{H}_{18}\text{Ni}$ (10) <sup>c</sup><br>(XII)    | -20           | Toluene-d <sub>8</sub> | A (80)<br>B (20)                       | 4.05<br>4.42                 | 3.88<br>4.17                 | 2.95<br>3.04                 | —<br>—                       | 3.08<br>2.36                 | J(13) 7.2; J(12) 7.2; J(15) 12.1; J(35) 0; J(26) (= J(26)') 7.3<br>J(13) 7.35; J(12) 7.35; J(15) 12.0; J(35) 0; J(26) 9.3;<br>J(26)' 6.3   | WH 270 Spectr.<br>see ref. 20          |

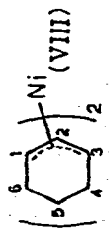
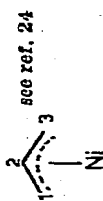
| $\eta^3\text{-C}_1\text{H}_2\text{Ni d (XIII)}$                      | +25 | Toluene-d <sub>8</sub> | A (55) | $\delta_1$ 1.27; $\delta_2$ 3.23; $\delta_9$ 5.43; $\delta_{10}$ 1.70 | See Text   |
|--|-----|------------------------|--------|---|--|
| $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd (XIV)}$                     | +25 | Benzene-d <sub>6</sub> | A (70) | $\delta_{14}$ 1.48; $\delta_{13}$ 4.10; $\delta_{15}$ 2.70            |  |
| $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pd (XV)}$         | +25 | Benzene-d <sub>6</sub> | B (30) | $\delta_1$ 1.33; $\delta_2$ 3.73; $\delta_9$ 5.71; $\delta_{10}$ 1.79 |  |
|  |     |                        | A (68) | $\delta_{14}$ 1.52; $\delta_{13}$ 4.13                                |  |
|  |     |                        | B (32) | 4.86 4.08 2.40  | J(12) 8; J(15) 13                                  |
| $(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Pd (XVI)}$        | 0   | Toluene-d <sub>8</sub> | A (48) | 4.77 1.78 3.80 3.09 2.28  | J(13) 7.2; J(15) 12.4                              |
|  |     |                        | B (21) | 4.88 2.00 3.59 3.31 2.16  | J(13) 7.2; J(15) 12.8                              |
|  |     |                        | C (16) | 4.58 1.67 3.61 3.46 2.33  | J(13) 7.0; J(15) 12.6                              |
|  |     |                        | D (8)  | 4.50 2.00 3.22 (3.46) 2.28  | J(13) 7.2  |
| $(\eta^3\text{-1,8-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Pd (XVII)}$ | -21 | Toluene-d <sub>8</sub> | A (58) | 4.77 1.89 2.94  |  |
|  |     |                        | B (36) | 4.50 1.74 3.08  |  |
| $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt (XVIII)}$                   | +25 | Benzene-d <sub>6</sub> | A (50) | 4.35 4.13 2.27  | J(12) 7; J(15) 12; J(3Pt) 27; J(5Pt) 78            |
|  |     |                        | B (50) | 3.85 3.85 2.23  | J(12) 10.5; J(3Pt) 20.5; J(5Pt) 82                 |
| $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pt (XIX)}$        | +25 | Benzene-d <sub>6</sub> | A (44) | 1.64 4.06 2.35  | J(CH <sub>3</sub> Pt) 47; J(3Pt) 24.5; J(5Pt) 79.5 |
|  |     |                        | B (56) | 1.59 3.66 2.28  | J(CH <sub>3</sub> Pt) 51; J(3Pt) 15.5; J(5Pt) 80.5 |



Isomer A:  $\delta_6$  1.13;  $\delta_6$  1.50;  $\delta_7$  1.66;  $\delta_8$  1.98;  $\delta_9$  5.07; J(66') -12.7; J(67) 13.3; J(6'8) 4.5; J(6'7) 4.9; J(6'8) 2.9; J(7.9) 4.0; J(89) 3.6; J(78) -11.7; J(99) 13.3  
 Isomer B:  $\delta_6$  0.97;  $\delta_6$  1.40;  $\delta_7$  1.95;  $\delta_8$  2.26;  $\delta_9$  5.46; J(66) -13.5; J(67) 12.75; J(88) 5.4; J(6'7) 5.4; J(6'8) 3.3; J(79) 9; J(78) -12.7; J(80) 2.6; J(99) 13.5

TABLE 5  
 $^{13}\text{C}$  NMR SPECTROSCOPIC DATA FOR  $(\eta^3\text{-ALLYL})_2\text{M}$  COMPLEXES OF Ni, Pd, Pt

| Complex   | Temp.<br>(°C) | Solvent                        | Isomer<br>(%)                              | $\delta(\text{C}_1)$<br>(ppm)    | $\delta(\text{C}_2)$<br>(ppm)        | $\delta(\text{C}_3)$<br>(ppm)    | Other signals  | Remarks   |
|---|---------------|--------------------------------|--|----------------------------------|--------------------------------------|----------------------------------|--|---|
| $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$ (I)                                | -24           | Toluene- <i>d</i> <sub>8</sub> | A (70)<br>B (30)                           | 52.61<br>53.00                   | 112.06<br>112.16                     | 52.61<br>53.00                   |  |   |
| $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$<br>(II)               | 0             | Toluene- <i>d</i> <sub>8</sub> | A (70)<br>B (30)                           | 51.14<br>51.84                   | 122.83<br>123.86                     | 51.14<br>51.84                   | 24.36 (CH <sub>3</sub> )<br>24.42 (CH <sub>3</sub> )   | The values in<br>ref. 24 are<br>incorrect   |
| $(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$                       | -60           | Toluene- <i>d</i> <sub>8</sub> | A (55)<br>B (25)<br>C (16)<br>D (5)        | 71.09<br>68.69<br>69.38<br>67.95 | 112.51<br>113.68<br>112.13<br>112.85 | 46.02<br>50.15<br>nd<br>49.86    | 17.23 (CH <sub>3</sub> )<br>19.68 (CH <sub>3</sub> )<br>17.06 (CH <sub>3</sub> )<br>nd (CH <sub>3</sub> )  | No change in isomer<br>ratio between -60<br>and +15°C   |
| $(\eta^3\text{-1,1'-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$<br>(IV)       | -20           | Toluene- <i>d</i> <sub>8</sub> | A (66.9)<br>B (20.5)<br>C (8.9)<br>D (3.7) | 79.13<br>78.95<br>80.81<br>78.80 | 106.44<br>108.54<br>109.32<br>108.20 | 42.72<br>49.55<br>50.58<br>42.89 | 24.21; 18.24<br>(CH <sub>3</sub> )<br>28.40; 20.21<br>(CH <sub>3</sub> )<br>29.06; 20.89<br>(CH <sub>3</sub> )<br>25.45; 19.50<br>(CH <sub>3</sub> ) |   |
| $(\eta^3\text{-1,9-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$<br>(V)         | -10           | Toluene- <i>d</i> <sub>8</sub> | A (80)<br>B (20)                           | 64.36<br>61.82                   | 115.04<br>113.73                     | 64.36<br>61.82                   | 17.16 (CH <sub>3</sub> )<br>16.88 (CH <sub>3</sub> )   |   |
| $(\eta^3\text{-1-iso-C}_3\text{H}_7\text{-C}_3\text{H}_4)_2\text{Ni}$<br>(VI) | -11           | Toluene- <i>d</i> <sub>8</sub> | A (90)<br>B (10)                           | 85.54<br>85.29                   | 108.40<br>107.85                     | 47.26<br>47.26                   | 31.46 (CH)<br>25.44; 24.58<br>(CH <sub>3</sub> )<br>31.69 (CH)<br>25.61; 24.60<br>(CH <sub>3</sub> )   | $\text{C}_6\text{H}_5$ and solvent<br>signals coincide,<br>Spectrum quality<br>limited by<br>solubility |
| $(\eta^3\text{-1-C}_6\text{H}_5\text{-C}_3\text{H}_4)_2\text{Ni}$<br>(VII)    | -8            | Toluene- <i>d</i> <sub>8</sub> | A (100)                                    | 77.80                            | 108.30                               | 48.31                            |  |   |
| $(\eta^3\text{-1-C}_6\text{H}_5\text{-C}_3\text{H}_4)_2\text{Ni}$<br>(VIII)   | -50           | Toluene- <i>d</i> <sub>8</sub> | A (100)                                    | 65.78                            | 103.78                               | 65.78                            | 29.03 (C <sub>4,6</sub> )<br>19.72 (C <sub>5</sub> )   |   |



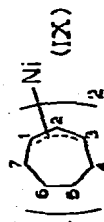
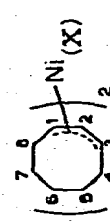

|   |     |                        |                  |                         |                  |                         |  |  |
|---|-----|------------------------|------------------|-------------------------|------------------|-------------------------|--|--|
|  | -35 | Toluene-d <sub>8</sub> | A (100)          | 74.00                   | 104.58           | 74.00                   | 34.69 (C <sub>4,7</sub> )<br>28.35 (C <sub>5,6</sub> )   | C <sub>4</sub> -7 assignment is<br>not certain             |
|  | 9   | Toluene-d <sub>8</sub> | A (100)          | 67.06                   | 106.41           | 67.06                   | 31.98 } C <sub>4,8</sub><br>30.28 } and<br>C <sub>5,7</sub><br>24.17 (C <sub>6</sub> )   |  |
|  | -60 | Toluene-d <sub>8</sub> | A (100)          | 74.35                   | 95.04            | 74.35                   | 131.26 (C <sub>4,8</sub> )<br>131.19 (C <sub>7,5</sub> )<br>28.35 (C <sub>6</sub> )  | trans-arrangement<br>confirmed by X-ray<br>crystallography |
| $\eta^3\text{-C}_{12}\text{H}_{18}\text{Ni}$ (XII)                                  | -60 | Toluene-d <sub>8</sub> | A (80)           | 69.13 (C <sub>3</sub> ) | 106.16           | 45.04 (C <sub>1</sub> ) | 31.67 (C <sub>4</sub> )<br>40.52 (C <sub>5</sub> )<br>105.11 (C <sub>6</sub> )<br>28.99 (C <sub>4</sub> )<br>33.92 (C <sub>5</sub> )<br>103.33 (C <sub>6</sub> )<br>31.98 (C <sub>5</sub> )<br>40.54 (C <sub>4</sub> )<br>104.77 (C <sub>6</sub> )<br>29.87 (C <sub>5</sub> )<br>34.54 (C <sub>4</sub> )<br>104.59 (C <sub>6</sub> ) | see formula XII  |
| $\eta^3\text{-C}_5\text{H}_5)_2\text{Pd}$ (XIV)                                     | 0   | Toluene-d <sub>8</sub> | A (73)<br>B (27) | 54.61<br>53.81          | 115.13<br>115.43 | 54.61<br>53.81          | 24.70 (CH <sub>3</sub> )<br>24.85 (CH <sub>3</sub> )<br>17.59 (CH <sub>3</sub> )<br>17.28 (CH <sub>3</sub> ) or<br>20.22 (CH <sub>3</sub> ) =<br>$J(^{195}\text{Pt}-^{13}\text{C}_1)$ =<br>225.2 Hz<br>$J(^{195}\text{Pt}-^{13}\text{C}_2)$ =<br>61.1 Hz   | see ref. 24  |
| $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pd}$<br>(XV)                     | 10  | Toluene-d <sub>8</sub> | A (67)<br>B (33) | 53.58<br>53.00          | 128.06<br>127.89 | 53.58<br>53.00          |  |  |
| $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pd}$<br>(XVI)                    | -20 | Toluene-d <sub>8</sub> | A (56)<br>B (25) | 75.64<br>72.09          | 115.36<br>115.99 | 47.01<br>46.71          |  |  |
| $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$<br>(XVIII)                               | 10  | Toluene-d <sub>8</sub> | C (20)<br>A (63) | 72.23<br>46.56          | 116.63<br>102.06 | 51.21<br>46.56          |  |  |
|   |     |                        | B (37)           | 48.37                   | 104.15           | 48.37                   | $J(^{195}\text{Pt}-^{13}\text{C}_1)$ =<br>226.0 Hz<br>$J(^{195}\text{Pt}-^{13}\text{C}_2)$ =<br>54.5 Hz  |  |

TABLE 5 (continued)

| Complex   | Temp.<br>(°C) | Solvent                        | Isomer<br>(%) | $\delta(C_1)$<br>(ppm) | $\delta(C_2)$<br>(ppm) | $\delta(C_3)$<br>(ppm) | Other signals   | Remarks |
|---|---------------|--------------------------------|---------------|------------------------|------------------------|------------------------|---|---------|
| $(\eta^3\text{-}2\text{-CH}_3\text{C}_3\text{H}_4)_2\text{Pt}$<br>(XIX) | 32            | Toluene- <i>d</i> <sub>8</sub> | A (60)        | 45.85                  | 115.51                 | 45.85                  | $J(^{195}\text{Pt}\text{-}^{13}\text{C}_1) =$<br>220.3 Hz<br>$J(^{195}\text{Pt}\text{-}^{13}\text{C}_2) =$<br>71.2 Hz<br>$J(^{195}\text{Pt}\text{-}^{13}\text{CCH}_3) =$<br>34.8 Hz |         |
|   |               |                                | B (40)        | 47.45                  | 117.15                 | 47.45                  | $J(^{195}\text{Pt}\text{-}^{13}\text{C}_1) =$<br>223.3 Hz<br>$J(^{195}\text{Pt}\text{-}^{13}\text{C}_2) =$<br>nd<br>$J(^{195}\text{Pt}\text{-}^{13}\text{CCH}_3) =$<br>34.8 Hz      |         |



### Raman Spectra

The Raman spectra of the various  $\eta^3$ -allyl-metal complexes have also been studied. Raman spectroscopy is a more suitable tool than infrared spectroscopy for investigating complexes sensitive to oxidation, hydrolysis or thermolysis since the danger of sample contamination by decomposition products is greatly reduced, while as much spectroscopic information can be obtained from the Raman spectra as from the IR and FIR spectra. There is no interaction of the internal vibrations of the individual allyl groups, and hence all the pure ligand vibrations are both IR and Raman active and the spectra can be analyzed by assuming a local  $C_s$  symmetry for the symmetrical and  $C_1$  symmetry for the unsymmetrical substituted allyl groups. The most informative with respect to the bonding within the complex are the symmetrical metal-ligand vibrations, and these can be most easily studied with the help of Raman spectroscopy; in the case of centrosymmetric complexes these can only be observed in the Raman spectra.

The spectra obtained for a variety of  $(\eta^3\text{-allyl})_2\text{M}$  complexes at low temperature (130–200 K) are shown in Table 6 and typical spectra in Fig. 5. Bands having very weak intensities or shoulders, are not included while lattice modes below  $200\text{ cm}^{-1}$  have also been excluded. The relative intensities shown are qualitative and no allowance has been made for the difference in sensitivity of the spectrometer at different wavelengths. For this reason the C–H stretching frequencies have been treated separately. The partial assignment shown in Table 6 has been made empirically with the help of published IR and Raman data [22]. These assignments should be treated with caution since various normal coordinate analyses have shown that most frequencies are the result of complex stretching and bending behaviour [22,23g].

Publications which specifically consider the low temperature, solid state, Raman spectra of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{M}$  complexes are to be found in refs. 23b,d–f. Our results, which are probably the most complete to date, agree in general with those published in refs. 23d, e with the following additions: two bands are observed in the spectrum of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$  at ca.  $900\text{ cm}^{-1}$  (885 and  $902\text{ cm}^{-1}$ , intensity ratio 2.3 : 1) while the bands at  $1220$  and  $330\text{ cm}^{-1}$  are split (these features are not mentioned in ref. 23d). As a result, the Raman spectrum of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$  is practically identical to that of the analogous nickel complex. We have been unable to detect the weak Raman absorptions at  $323$  and  $395\text{ cm}^{-1}$  which were reported [23d,f] for the spectrum of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$  and which are also infrared active. Taking account of the sensitivity of our spectrometer, the intensities of these bands would have to be more than 0.2% of that of the line at  $360\text{ cm}^{-1}$ .

The observation of only 3 Raman-active metal–ligand vibrations in the three  $(\eta^3\text{-C}_3\text{H}_5)_2\text{M}$  (M = Ni, Pd, Pt) complexes suggest that they adopt  $C_i$  (or idealized  $C_{2h}$ ) symmetry in the solid. In the case of nickel and palladium, crystal lattice interaction causes a splitting of these bands and in the case of platinum shows itself in the slightly unsymmetrical form of the band at  $360\text{ cm}^{-1}$ . Thus our spectra for all three complexes provide no indication that non-centrosymmetric isomers are present in the solid.

For none of the complexes measured was any band (other than the C–H stretching vibrations) observed above  $1530\text{ cm}^{-1}$ , indicating that in all cases a

$\eta^3$ -allyl system having delocalized double bonds is present. More specific conclusions concerning the bonding situation within the molecule are not warranted since, as we have mentioned above, the frequencies are the result of complex vibrations, the nature of which depend upon that of the substituents present. However, the lines which are most informative are the so-called C—C stretching frequencies at 1500 and 1000  $\text{cm}^{-1}$  and the metal—ligand stretching frequencies at 300–400  $\text{cm}^{-1}$ .

The symmetrical metal—ligand stretching frequencies in which all the M—C bonds are in phase can, in general, be easily identified in the Raman spectra because of their relatively high intensities. Their predictive value, however, is diminished because of coupling with low frequency ligand deformation vibrations [22]. In order to compare the frequencies of the various complexes, it must be assumed that similar kinematic effects are operative. The calculated order for the effective metal—allyl force constants is  $K(\text{Ni—allyl}) \approx K(\text{Pd—allyl}) > K(\text{Pt—allyl})$  [23f]. We find the same order for the  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{M}$  complexes (Fig. 5): the wavelengths of the symmetrical M—ligand stretching vibrations are identical for Ni and Pd (332  $\text{cm}^{-1}$ ) while that for Pt is significantly larger (362  $\text{cm}^{-1}$ ). Interestingly, these frequencies are practically identical to those observed for the corresponding  $\eta^3\text{-C}_3\text{H}_5$  complexes. This can be explained, using a simple 3-body model (L—M—L), as compensation of the influence of the increase in mass on introduction of a methyl

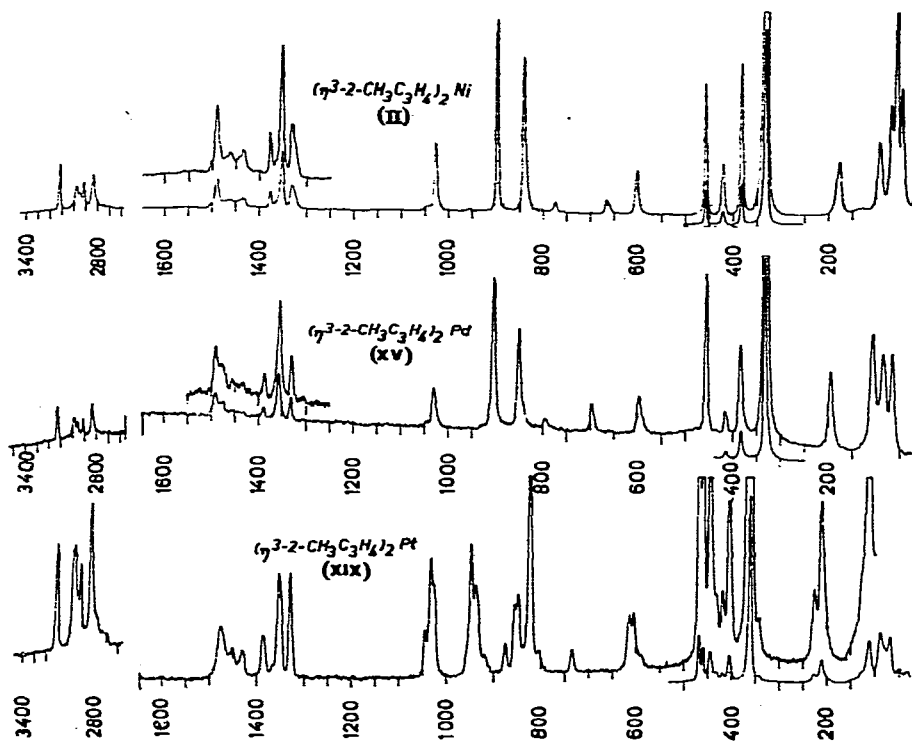


Fig. 5. The solid state Raman spectra of  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{M}$  ( $\text{M} = \text{Ni, Pd, Pt}$ ).

group by an increase in the effective force constant. This result, although based on an over-simplification, is in agreement with the observed increase in thermal stability associated with the introduction of the methyl group.

The asymmetric C—C valence vibrations for the  $\eta^3$ -2-methyl-allyl complexes are found at ca.  $10\text{ cm}^{-1}$  to longer wavelengths than those in the corresponding  $\eta^3$ -allyl complexes while the symmetrical C—C valence vibrations are shifted to shorter wavelengths. The mean square average of these two frequencies for both types of complex is, however, practically identical suggesting that the difference in wave numbers is the result of kinematic effects and not of changes in C—C bond strength.

The effect of coupling on the wavelengths of the C—C valence bands is even more apparent in those complexes in which the  $C_1$  and/or the  $C_3$  atoms of the allyl group are substituted. The effect of substitution on the asymmetric C—C valence frequency has been previously discussed for  $\eta^5$ - $C_5H_5Ti$   $\eta^3$ -allyl complexes [27]. The complexes containing the  $\eta^3$ -1,1'-( $CH_3$ )<sub>2</sub> $C_3H_3$  group show an interesting difference: the titanium complex has an asymmetric C—C valence vibration at the relatively high value of  $1558\text{ cm}^{-1}$  while that for ( $\eta^3$ -1,1'-( $CH_3$ )<sub>2</sub> $C_3H_3$ )<sub>2</sub>Ni (IV) falls at  $1510\text{ cm}^{-1}$  and is practically identical to that for ( $\eta^3$ -1,3-( $CH_3$ )<sub>2</sub> $C_3H_3$ )<sub>2</sub>Ni (V) ( $1524\text{ cm}^{-1}$ ). The suggestion that the high value observed in the titanium complex is the result of a weakened  $\pi$ -bond due to the unfavourable *anti*-substitution of the allyl group must be viewed with caution.

The lowest C—C valence vibration frequencies are observed for nickel complexes containing cyclic alkyl groups (Table 6). It is possible that this is the result of a stronger  $\pi$ -bonding between the metal and ligand in comparison to the open chain allyl groups.

## Experimental section

### Instrumentation

The  $^1H$  NMR spectra were measured at 100 and 270 MHz with Varian HA 100 CW and Bruker WH 270 FT spectrometers, respectively. The chemical shifts are relative to TMS as internal standard. Assignments were made with the aid of intensity measurements, homo-decoupling experiments and by comparison with authentic samples.

The  $^{13}C$  NMR spectra were measured at 25.2 MHz with a Varian XL-100-15-FT spectrometer. The samples were filled into 12 mm tubes at the temperatures shown in Table 5. The chemical shifts ( $\pm 0.05$  ppm) are relative to internal TMS and are positive to higher frequencies. The assignments were made with the aid of a) off-resonance decoupled and gated decoupled spectra, b) comparison with known compounds and c) intensity measurements, d) selective proton decoupling.

The Raman spectra were measured with a Coderg-LRT 800 instrument using a  $90^\circ$  scattering arrangement. The excitation source was either a Krypton-Ion-Laser ( $6471\text{ \AA}$ ) or an Argon-Ion-Laser ( $4880\text{ \AA}$ ) supplied by Spectra Physics. Plasma lines were eliminated using an interference filter. The appropriate excitation energies for each complex were determined by trial and error and lay between 50 and 100 mW. The laser was slightly defocussed to avoid damage to the samples which were measured under argon in 5 mm sealed tubes at low

TABLE 6  
THE SOLID STATE RAMAN SPECTRA OF  $(\eta^3\text{-ALLYL})_2\text{M COMPLEXES}$

| I                  | XIV                | XVIII              | II                 | XV                 | XIX                | Approximate description                          | IX                 | X                  | Approximate description                          |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--|--------------------|--------------------|--|
| 6471 Å<br>ca 170 K | 6471 Å<br>ca 170 K | 6471 Å<br>ca 170 K | 6471 Å<br>ca 130 K | 6471 Å<br>ca 170 K | 6471 Å<br>ca 200 K |  | 6471 Å<br>ca 190 K | 6471 Å<br>ca 185 K |  |
| 3060 m             | 3060 m             | 3060 } m<br>3060 } | 3060 m-s           | 3065 m-s           | 3065 m-s           | $\nu_{\text{as}} \text{CH}_2$                    |                    | 3015 s<br>3005 m   |  |
| 3015 w-m           | ~3020 w            | 3015 w             |                    |                    |                    | $\nu \text{CH}$                                  | 2995 s             | 2995 w             |  |
| 2990 w             | 2990 w             | 2999m              | 2990 m             | 2995 m             | 2980 m-s           | $\nu_{\text{s}} \text{CH}_2$                     | 2935 m             | 2975 w             | $\nu \text{CH (CH), (CH}_2\text{)}$              |
| 2950 w             | 2960 w             | 2940 w             | 2975 w             | 2980 w             | 2955 m             | $\nu_{\text{as}} \text{CH}_3$                    | 2920 m             | 2950 w             |  |
| 1495 m             | 1500 w             | 1486 m             | 2920 m-s           | 2920 m-s           | 2915 s             | $\nu_{\text{s}} \text{CH}_2$                     | 2875 } m           | 2915 s             |  |
| 1450 w             | 1450 w             | 1455 w             | 1488 m             | 1492 m             | 1475 m             | $\nu_{\text{as}} \text{CCC}$                     | 2860 } m           | 2895 m             |  |
| 1385 w             | 1390 w             | 1380 m             | 1462 w             | 1455 vw            | 1452 w             |  | 2820 m-s           | 2860 w             |  |
| 1222 m             | 1225 m             | 1218 m             | 1435 w             | 1435 vw            | 1430 w             | $\delta \text{HCH (CH}_2\text{), (CH}_3\text{)}$ | 1482 m             | 2840 w             | $\nu_{\text{as}} \text{CCC (}\eta\text{-allyl)}$ |
| 1213 m             | 1217 m             | 1205 m             | 1375 w             | 1390 w             | 1385 m             |  | 1445 m             | 1442 w             |  |
| 1012 s             | 1012 m             | 1035 } m<br>1022 } | 1350 m             | 1358 m             | 1354 s             |  | 1432 } m<br>1425 } | 1428 w             | $\delta \text{CH}_2$                             |
| 902 m              | 902 m              | 943 s              | 1330 w             | 1330 m             | 1330 s             |  | 1330 m             | 1322 m             |  |
| 886 s              | 885 s              | 910 w              |                    |                    |                    | $\nu_{\text{s}} \text{CCC}$                      | 1276 m             | 1305 w             |  |
| 773 w              | 776 w              | 820 w              | 1028 m             | 1030 m             | 1045 m             |  | 1222 w             | 1278 m             |  |
| 680 m              | 704 w              | 730 w              |                    |                    | 1034 s             |  | 1164 m             | 1264 m             |  |
| 498 m              | 505 w              | 547 m              | 896 s              | 903 s              | 948 } s<br>938 }   |  | 1150 m             | 1225 w             |  |
|                    | 494 m              |                    | 840 s              | 850 s              | 875 w              | $\rho \text{CH}_2, \delta \text{CH}$             | 1074 m             | 1150 m-s           | $\rho \text{CC (Ring),}$                         |
|                    |                    |                    | 775 w              | 795 w              | 850 m              | $\pi \text{CH, } \delta \text{CCH}_3$            | 1030 m             | 1088 m-s           | $\rho \text{CH}_2, \delta \text{CH,}$            |
|                    |                    |                    | 665 w              | 695 m              | 824 vs             |  | 986 s              | 1027 w             | $\delta \text{(Ring)}$                           |
|                    |                    |                    | 602 m              | 597 m              | 735 w              |  | 867 w              | 1005 m-s           |  |
|                    |                    |                    | 457 s              | 455 s              | 615 } m<br>606 }   |  | 807 w              | 975 s              |  |
|                    |                    |                    | 422 m              | 415 w              | 478 } s<br>460 }   | $\delta \text{CCC}$                              | 765 m              | 867 w              |  |
|                    |                    |                    | 382 s              | 382 s              | 445 s              |  | 730 w              | 838 m-s            |  |
|                    |                    |                    | 332 vs             | 332 vs             | 420 m              |  | 583 m-s            | 774 s              |  |
|                    |                    |                    | 412 m              | 410 m              | 405 s              |  | 505 m              | 636 m-s            |  |
|                    |                    |                    | 390 m              | 372 m              | 362 vs             | $\nu_{\text{s}} \text{ML}_2$                     | 408 m              | 505 m              |  |
|                    |                    |                    | 336 } s<br>328 }   | 335 } s<br>327 }   | 362 vs             | Metal-Ligand vibrations                          | 368 vs             | 425 vs             |  |
|                    |                    |                    |                    |                    |                    |  | 375 m-s            | 375 m-s            | Metal-Ligand vibrations                          |
|                    |                    |                    |                    |                    |                    |  | 342 m              | 342 m              |  |
|                    |                    |                    |                    |                    |                    |  | 295 m              | 308 m-s            |  |

temperature (130–200 K) using a liquid nitrogen based cooling system. In spite of the colour (yellow to orange) of many of the samples, it was possible to obtain reliable spectra using this arrangement. The error associated with the wave-length is dependent upon the intensity and shape of the band and in unfavourable cases can be as high as  $\pm 10 \text{ cm}^{-1}$ .

*Preparation and characterization of the  $(\eta^3\text{-allyl})_2M$  complexes*

The complexes investigated were prepared by reactions between the appropriate metal halide and allylmagnesium halide [e.g. 1a,9,10,18]. The reaction was in general carried out in diethylether and the resulting complexes crystallized from pentane.

$\eta^3\text{-C}_{12}\text{H}_{18}\text{Ni}$  was prepared by the reaction of bis(1,5-cyclooctadiene)nickel with liquid butadiene at  $-30^\circ\text{C}$  [20]. Samples for the NMR studies were ob-

TABLE 7  
ANALYTICAL DATA FOR  $(\eta^3\text{-ALLYL})_2M$  COMPLEXES OF Ni, Pd AND Pt

| Complex | Colour (Mp/dec; yield)       | Empirical formula                     | Mass spectrum (m/e 70 eV) | Analysis Found (calc.) (%)                        | Reference                             |
|---------|------------------------------|---------------------------------------|---------------------------|---|---------------------------------------|
| I       | orange yellow (0, 92%)       | $\text{C}_6\text{H}_{10}\text{Ni}$    | 140                       | Ni 41.60(41.68)                                   | 1a–d, 3, 7–9, 11a, 18, 23b, c, 24, 26 |
| II      | orange yellow (33–33; 90%)   | $\text{C}_8\text{H}_{14}\text{Ni}$    | 168                       | Ni 34.80(34.79)                                   | 1b–d, 9, 10, 14, 23b, 24, 26          |
| III     | orange yellow (–5; 88%)      | $\text{C}_8\text{H}_{14}\text{Ni}$    | 168                       | Ni 34.90(34.78)                                   | 1b–d, 10, 26                          |
| IV      | orange yellow (–10––15; 90%) | $\text{C}_{10}\text{H}_{12}\text{Ni}$ | 196                       | Ni 29.70(29.65)                                   | 1d                                    |
| V       | orange yellow (10–15; 90%)   | $\text{C}_{10}\text{H}_{12}\text{Ni}$ | 196                       | Ni 29.60(29.65)                                   | 26                                    |
| VI      | orange yellow (0–10; 85%)    | $\text{C}_{12}\text{H}_{22}\text{Ni}$ | 224                       | Ni 26.10(26.13)                                   | —                                     |
| VII     | beige yellow (0; 85%)        | $\text{C}_{18}\text{H}_{18}\text{Ni}$ | 292                       | Ni 20.00(20.10)                                   | 28                                    |
| VIII    | yellow (–35d; 75%)           | $\text{C}_{12}\text{H}_{18}\text{Ni}$ | —                         | Ni 26.50(26.60)                                   | 1c, d, 10                             |
| IX      | yellow (0–10d; 89%)          | $\text{C}_{14}\text{H}_{22}\text{Ni}$ | 248                       | Ni 23.50(23.57)                                   | 1c, d, 10                             |
| X       | yellow (89%)                 | $\text{C}_{16}\text{H}_{26}\text{Ni}$ | 276                       | Ni 21.10(21.18)                                   | 1c, d, 10                             |
| XI      | dark red (168–170; 85%)      | $\text{C}_{16}\text{H}_{18}\text{Ni}$ | 268                       | Ni 21.80(21.85)                                   | 1c, d                                 |
| XII     | red liq                      | $\text{C}_{12}\text{H}_{18}\text{Ni}$ | 220                       | Ni 26.42(26.56)                                   | 1a, c, d, 8,,20                       |
| XIII    | red liq                      | $\text{C}_{15}\text{H}_{24}\text{Ni}$ | 262                       | Ni 22.18(22.32)<br>C 67.98(68.49)<br>H 8.97(9.20) | —                                     |
| XIV     | lemon yellow (28; 85%)       | $\text{C}_6\text{H}_{10}\text{Pd}$    | 188                       | Pd 56.50(56.53)                                   | 1b, c, 10, 11a–c, 23d, 24             |
| XV      | yellow (83%)                 | $\text{C}_8\text{H}_{14}\text{Pd}$    | 216                       | Pd 49.20(49.17)                                   | 11c                                   |
| XVI     | yellow (20–23d; 75%)         | $\text{C}_8\text{H}_{14}\text{Pd}$    | 216                       | Pd 49.50(49.17)                                   | —                                     |
| XVII    | yellow (78%)                 | $\text{C}_{10}\text{H}_{12}\text{Pt}$ | 244                       | Pd 43.60(43.53)                                   | —                                     |
| XVIII   | col. (42; 90.3%)             | $\text{C}_6\text{H}_{10}\text{Pt}$    | 277                       | Pt 70.40(70.41)                                   | 1c, 10, 11a, 12b, 13, 23a, d, 24      |
| XIX     | col. (70; 81%)               | $\text{C}_8\text{H}_{14}\text{Pt}$    | —                         | Pt 63.65(63.90)                                   | 12a, b, 13                            |
| XX      | col. (81%)                   | $\text{C}_8\text{H}_{14}\text{Pt}$    | 305                       | Pt 63.00(63.90)                                   | 29                                    |

TABLE 8  
LIGAND DISPLACEMENT REACTIONS

| Complex   | Hydrogenation (%) <sup>a</sup>                                     | Pyrolysis (% °C) <sup>b</sup>   | P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> displacement (%) <sup>c</sup> | CO displacement (%) <sup>d</sup>                       |
|---|--|---|--|--|
| ( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ni (I)                                       | C <sub>3</sub> H <sub>8</sub> (96.5)                               | C <sub>3</sub> H <sub>6</sub> (92.8; 60)                                | 1,5-hexadiene (97.8)   | 1,5-hexadiene (94)                                     |
| ( $\eta^3$ -2-CH <sub>3</sub> C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Ni (II)                    | C <sub>4</sub> H <sub>10</sub> (98.7)                              | C <sub>4</sub> H <sub>8</sub> (95.8; 80)                                | 2,5-(CH <sub>3</sub> ) <sub>2</sub> 1,5-hexadiene (97)                       | 2,5-(CH <sub>3</sub> ) <sub>2</sub> 1,5-hexadiene (94) |
| ( $\eta^3$ -1-CH <sub>3</sub> C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Ni (III)                   | C <sub>4</sub> H <sub>10</sub> (95.5)                              | C <sub>4</sub> H <sub>8</sub> (98; 50)                                  | C <sub>8</sub> (95.3) <sup>e</sup>   | C <sub>8</sub> (95.5) <sup>f, g</sup>                  |
| ( $\eta^3$ -1,1'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>3</sub> H <sub>3</sub> ) <sub>2</sub> Ni (IV) | C <sub>5</sub> H <sub>12</sub> (90.4)                              | C <sub>5</sub> H <sub>10</sub> (93.2; 50) <sup>k</sup>                  | C <sub>10</sub> (90.3) <sup>l</sup>  | C <sub>10,11</sub> (98.6) <sup>m</sup>                 |
| ( $\eta^3$ -1,3'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>3</sub> H <sub>3</sub> ) <sub>2</sub> Ni (V)  | C <sub>5</sub> H <sub>12</sub> (92)                                | C <sub>5</sub> H <sub>10</sub> (95; 70) <sup>h</sup>                    | C <sub>10</sub> (91.4) <sup>l</sup>  | C <sub>10,11</sub> (92.4) <sup>j</sup>                 |
| ( $\eta^3$ -1-iso-C <sub>3</sub> H <sub>7</sub> C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Ni (VI)  | C <sub>6</sub> H <sub>14</sub> (94.3)                              | C <sub>6</sub> H <sub>12</sub> (87; 80) <sup>n</sup>                    | —  | C <sub>12,13</sub> (98) <sup>o</sup>                   |
| ( $\eta^3$ -1-C <sub>6</sub> H <sub>5</sub> C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Ni (VII)     | C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>5</sub> (89.9) | C <sub>3</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> (89.2; 100) | —  | C <sub>18</sub> (98.7) <sup>p</sup>                    |
| ( $\eta^3$ -C <sub>15</sub> H <sub>24</sub> )Ni (XIII)  | C <sub>15</sub> H <sub>30</sub> (98.5) <sup>q</sup>                | —   | —  | C <sub>15</sub> , C <sub>16</sub> <sup>r</sup>         |

(XIII)

<sup>a</sup> H<sub>2</sub> uptake detn. Product identified by mass spectroscopy. <sup>b</sup> Sample heated (in vacuo) and product either collected in gas burette or distilled into a cooled liq. N<sub>2</sub> collector. <sup>c</sup> Sample dissolved in an appropriate solvent, treated with >4 X excess of phosphine at -20 to +30°C and product collected in a gas burette or distilled out. <sup>d</sup> Sample, dissolved in an inert solvent, was attached to a gas burette and treated with CO from -78° to room temperature. <sup>e</sup> 3-methyl-1,5-*trans*-heptadiene (64.6); 3-methyl-1,5-*cis*-heptadiene (5.1); 2-*trans*,6-*trans*-octadiene (27.4); 2-*trans*,6-*cis*-octadiene (46.5); 2-*trans*,6-*cis*-octadiene (0.8); 3-methyl-1,5-*trans*-heptadiene (0.8); 3-methyl-1,5-*cis*-heptadiene (7.0); 2-*trans*,6-*trans*-octadiene (81.6); 2-*trans*,6-*cis*-octadiene (5.6); <sup>f</sup> Pentane (4.9); 1-Pentene (76.3); 2-Pentene (17.9); 3-methyl-1,5-*trans*-heptadiene (1.6); 3-methyl-1,5-*cis*-heptadiene (14.7); 4,5-dimethyl-2-*cis*,6-*cis*-octadiene (84.2); 4,5-dimethyl-2-*cis*,6-*cis*-octadiene (15.1); 2-methyl-2-butene (68.4); <sup>g</sup> 3,3,7-trimethyl-1,5-heptadiene (72.9); 2,7-dimethyl-2,6-octadiene (27.1); 2,7-dimethyl-1,6-octadiene (13.4); 2,8-dimethyl-2,7-norundien-5-one (1.1). <sup>h</sup> 2,3-dimethylbutene (30.3); 2-methylpentene (50.4); 2-methyl-1-pentene (17.7). <sup>i</sup> 3-isopropyl-7-methyl-1,5-octadiene (10.5); 2,9-dimethyl-3,7-decadiene (64.4); 3-isopropyl-8-methyl-1,6-nonadien-4-one (2.5); 2,10-dimethyl-3,8-undecadien-6-one (18.7). <sup>j</sup> 1,6-diphenylhexa-2,4-diene. <sup>k</sup> 2,7,10-trimethyldecane (80.0); 2,6,11-trimethyldecane (12.8). <sup>l</sup> 3 C<sub>15</sub> hydrocarbons, 4 CO-insertion products.

tained by subliming the red oil (0.01 mmHg) followed by recrystallization from pentane. The corresponding complex derived from isoprene ( $\eta^3\text{-C}_{15}\text{H}_{24}\text{Ni}$ ) (XIII) was prepared analogously (90% yield) as an orange red oil.

In addition to the spectroscopic characterization described in the text, full chemical characterization was carried out: analytical data are collected together in Table 7 and the results of hydrogenation, pyrolysis and displacement reactions with triphenylphosphine and CO in Table 8. The products of these reactions were identified quantitatively by MS and GC analysis.

The reaction with CO was carried out at  $-78^\circ\text{C}$ : in most cases four equivalents of CO were taken up at  $-78^\circ\text{C}$  but in some cases, e.g. ( $\eta^3\text{-1,3-(CH}_3\text{)}_2\text{-C}_3\text{H}_3\text{)}_2\text{Ni}$  (V), ( $\eta^3\text{-1,1'-(CH}_3\text{)}_2\text{C}_3\text{H}_3\text{)}_2\text{Ni}$  (IV) and ( $\eta^3\text{-1-iso-C}_3\text{H}_7\text{C}_3\text{H}_4\text{)}_2\text{Ni}$  (VI), additional CO was absorbed on allowing the sample to warm to room temperature and was accompanied by insertion of CO into the  $\eta^3$ -allyl fragment to give a ketone. Insertion occurs mainly into the least substituted carbon atom of the  $\eta^3$ -allyl group.

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