

## TRANSITION METAL ALLYLS

### IV \*. THE ( $\eta^3$ -ALLYL)<sub>2</sub>M COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM: REACTION WITH TERTIARY PHOSPHINES

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#### Summary

A series of 1 : 1 adducts have been prepared by treating the bis- $\eta^3$ -allyl complexes of nickel, palladium and platinum with tertiary phosphines. Investigations of their structure in solution as well as in the crystal have shown that both 18-electron ( $\eta^3$ -allyl)<sub>2</sub>M–L complexes as well as 16-electron ( $\eta^1$ -allyl)-( $\eta^3$ -allyl)M–L complexes may be formed.

#### Introduction

The bis( $\eta^3$ -allyl)metal complexes of nickel, palladium and platinum, whose preparation and structure have been described in the preceding paper [1], can react with donor ligands by addition followed by rearrangement or displacement of one or both  $\eta^3$ -allyl groups.

Reaction to give an 18-electron adduct has, to our knowledge, not been previously reported though such a process might, however, have occurred in the reaction with tertiary phosphine of the unstable tris(allene)nickel species reported in ref. 2. A tentative proposal [3] that ( $\eta^3$ -2-methylallyl)<sub>2</sub>Ni reacts with triethylphosphine to give ( $\eta^1, \eta^3$ -2-CH<sub>3</sub>C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>NiP(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> has not been substantiated (see below). However, a <sup>1</sup>H NMR study has shown that in the presence of N-donors such as ammonia, pyridine, and secondary amines a simplification of the <sup>1</sup>H NMR spectra occurs, indicating that  $\eta^3 \leftrightarrow \eta^1$  interconversion, rapid on the <sup>1</sup>H NMR time scale, is taking place [4,5]. The conversion of both  $\eta^3$ -allyl groups into  $\eta^1$ -allyl groups upon addition of two ligand molecules has

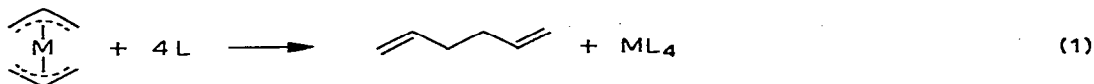
\* For Part III see ref. 1.

\*\* Spectroscopic investigations.

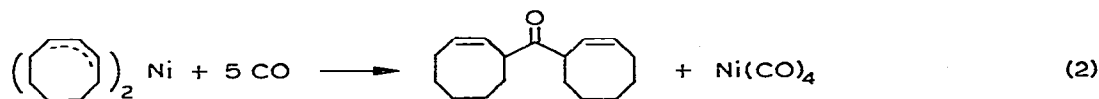
\*\*\* X-ray structural determination.

been suggested, on the basis of IR evidence, to occur in the reaction of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$  and  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pt}$  with triphenylphosphine and triphenylarsine [6]. Recently it has been shown that reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)$  with trialkylphosphines leads to formation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^1\text{-2-CH}_3\text{C}_3\text{H}_4)\text{PR}_3$ , which, moreover, is in equilibrium with the  $(\eta^1\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)\text{PR}_3$  form [7].

Reaction with excess ligand usually leads to reductive coupling of the organic groups followed by elimination (eq. 1), and is occasionally (in the case



of CO or isonitrile) accompanied by insertion of a donor molecule (eq. 2) [5].



We have been able to isolate a series of crystalline 1 : 1 adducts from the reaction of the  $(\eta^3\text{-allyl})_2\text{metal}$  complexes of nickel, palladium and platinum (Table 8) and report here the crystal structure of one of them and the behaviour in solution of representative complexes.

## Results

The results obtained for the system  $(\eta^3\text{-C}_3\text{H}_5)_2\text{M}/\text{P}(\text{CH}_3)_3$  where  $\text{M} = \text{Ni}$ ,  $\text{Pd}$  or  $\text{Pt}$  will be first presented and are followed by a discussion of the data obtained using other tertiary phosphines and of the effect of substituents in the  $\eta^3\text{-allyl}$  group upon the structure of the adduct formed.  $^{13}\text{C}$  and  $^1\text{H}$  NMR data are collected together in Tables 5 and 6.

$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  reacts with  $\text{P}(\text{CH}_3)_3$  at  $-78^\circ\text{C}$  to form an orange 1 : 1 adduct (I). The X-ray structural determination discussed below shows that in the crystal the molecule adopts the symmetrical 18-electron structure Ia. That this structure is maintained in solution at low temperatures is indicated by the NMR spectra.

The  $^{13}\text{C}$  NMR spectra (Table 5) at  $-60^\circ\text{C}$  show two sharp absorptions (intensities 2 : 1) for the carbon atoms of the allyl group. An unusual feature is that the *meso*-carbon atom, but not the terminal carbon atoms, couple to phosphorus ( $J(\text{P}, \text{C}_2)$  6.7 Hz). (Similar behaviour is observed for complex XIV (see below) in which the allyl groups are also mutually *cis* and the *meso*-carbon atom and the phosphorus atom are pseudo-*trans*.) At  $0^\circ\text{C}$  this coupling is no longer observed. The  $^1\text{H}$  NMR spectra at  $-110^\circ\text{C}$  (Fig. 1a) indicates that in solution the molecule also adopts structure Ia. On raising the temperature the spectrum simplifies to that expected for an  $\text{AM}_4\text{X}$  spin system ( $\text{X} = ^{31}\text{P}$ ) as the result of equilibration of the *syn* and *anti* protons (Fig. 1b). The observation of  $J(\text{P}, \text{H}_1)$  (5.7 Hz) and the average coupling  $J(\text{P}, \text{H}_{2-5})$  (9 Hz) during this process is direct evidence that equilibration occurs *without dissociation* of the nickel-trimethylphosphine bond and is in accord with the intermediate formation of an  $\eta^1\text{-allyl-nickel}$  species Ib (eq. 3; *syn*  $\leftrightarrow$  *anti* exchange is illustrated for only

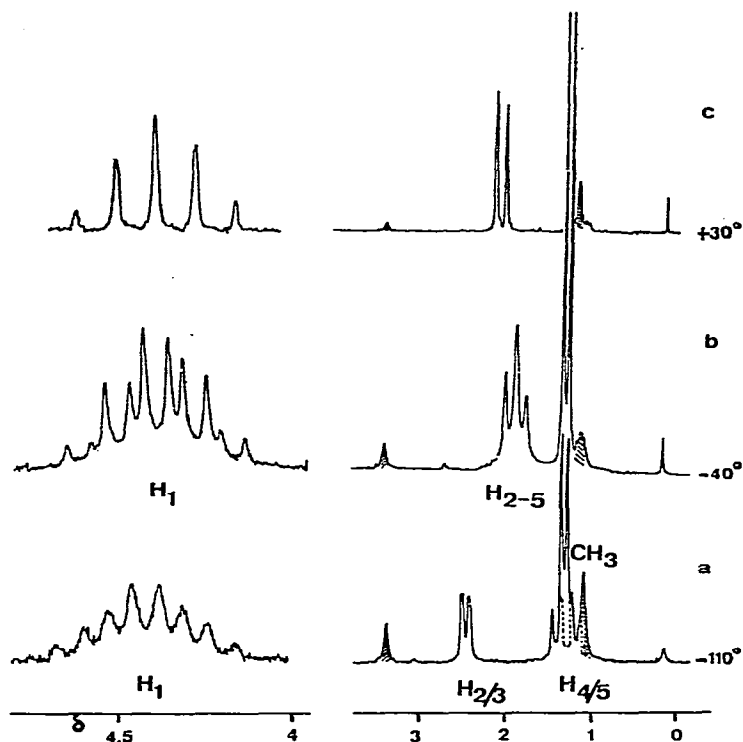
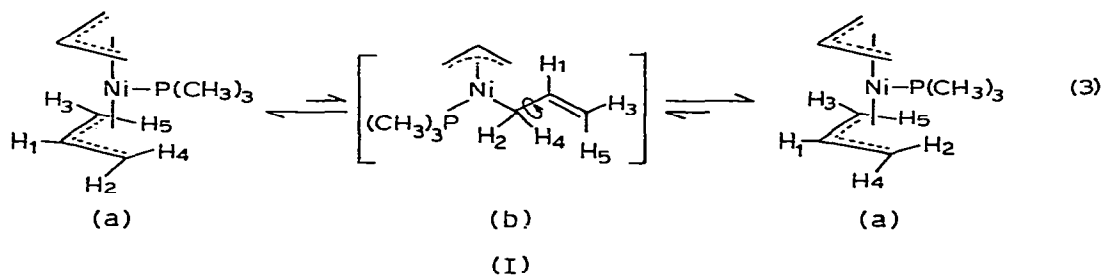


Fig. 1. The 80 MHz  $^1\text{H}$  NMR spectrum of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$  (I) in ether- $d_{10}$ .

one pair of protons). The coalescence temperature (at 80 MHz) for this process is  $-70^\circ\text{C}$  from which a free energy of activation ( $\Delta G^\ddagger$ ) of  $9.6 \pm 1.5$  kcal/mol can be calculated [8]. Above  $-40^\circ\text{C}$  the  $^{31}\text{P}$ - $^1\text{H}$  coupling disappears (Fig. 1c) indicating that above this temperature phosphine dissociation is occurring.



The structure found in solution below  $-100^\circ\text{C}$  is also observed in the crystal: an X-ray structural determination confirms the *cis*-arrangement of the two  $\eta^3$ -allyl groups. A sample was recrystallized from pentane and a single crystal mounted in a Lindemann glass capillary under argon at  $-25^\circ\text{C}$  \*. Data collection was carried out at  $-170^\circ\text{C} \pm 0.5^\circ\text{C}$  and details are to be found in the

\* This was performed by working in a refrigerated room. We thank Chem. Ing. K.H. Claus for his perseverance under difficult conditions.

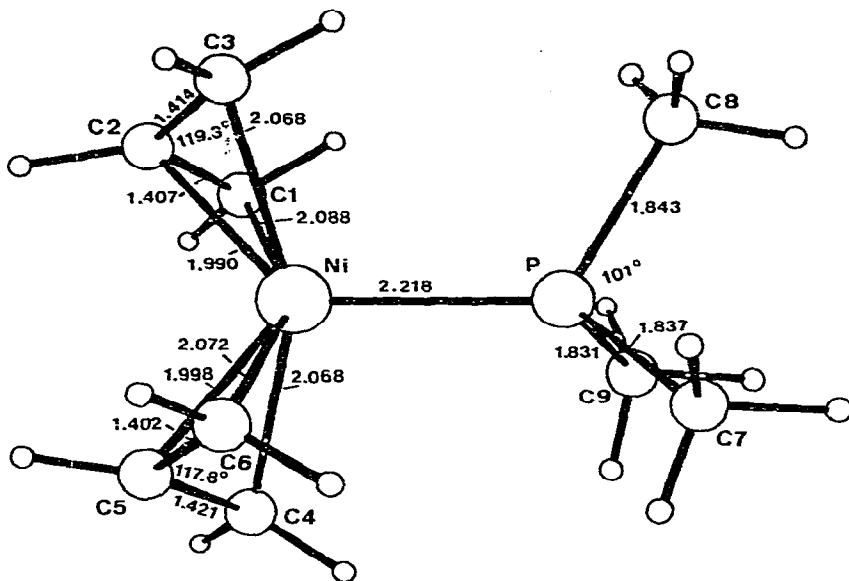


Fig. 2. The molecular structure of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$  (I).

Experimental section. The structure adopted by the molecule in the crystal is shown in Fig. 2 which shows one of the two independent molecules in the unit cell. The two molecules differ little in their molecular characteristics: bond distances and angles are compared in Table 1. The following discussion is based on the averaged geometrical parameters\*.

The molecule possesses approximate  $C_s(m)$  symmetry, the mirror plane passing through the atoms Ni, P and C<sub>9</sub>. The Ni-P distance of 2.218(1) Å is normal for a Ni<sup>II</sup>-PR<sub>3</sub> bond where R is an alkyl or aryl group. The geometry of the P(CH<sub>3</sub>)<sub>3</sub> ligand is almost identical with that of the free P(CH<sub>3</sub>)<sub>3</sub> molecule as reported in an electron diffraction study [9]; thus the P-C distance in this study (1.837(6) Å) is less than one standard deviation different from that of the free molecule (1.841(3) Å) and the C-P-C angles are similar (101.1(9)° cf. 99.1(2)°). The surprising feature about the molecule is that the two  $\eta^3$ -allyl groups bonded to the nickel lie approximately parallel to one another (Table 2) even though the nickel atom has been drawn away from between the two groups by the phosphorus atom. The  $\eta^3$ -allyl groups are separated by 3.2 Å and are arranged such that the  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  moiety has  $C_{2v}(mm)$  symmetry. This should be compared to the  $C_{2h}(2m)$  symmetry observed for bis( $\eta^3$ -2-methylallyl)nickel [10]. A recent theoretical study of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  based on this structure attributes the major part of the bonding to an interaction between the filled non-bonding  $\pi$ -orbital of the allyl group and the empty  $3d_{xz}$  orbital of the Ni atom with some backbonding through an interaction between the  $3d_{x^2-y^2}$  and  $3d_{xy}$  orbitals and the  $\sigma$ - and the  $\pi$ -orbitals of the ligand [11];  $x$

\* Estimated standard deviations from the mean are given by  $\sigma = (\sum_i^2 (\alpha_i - \bar{\alpha})^2 / (n - 1))^{1/2}$  where  $\alpha_i$  is the  $i$ 'th and  $\bar{\alpha}$  the mean of  $n$  similar types.

TABLE 1

OBSERVED BOND DISTANCES (Å) AND ANGLES (°) IN  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$  (I)

Molecule (1)		Molecule (2)	
<i>a) Distances</i>			
Ni <sub>1</sub> —P <sub>1</sub>	2.218(2)	Ni <sub>2</sub> —P <sub>2</sub>	2.217(2)
Ni <sub>1</sub> —C <sub>1</sub>	2.092(5)	Ni <sub>2</sub> —C <sub>10</sub>	2.084(5)
Ni <sub>1</sub> —C <sub>2</sub>	1.998(5)	Ni <sub>2</sub> —C <sub>11</sub>	1.981(4)
Ni <sub>1</sub> —C <sub>3</sub>	2.068(5)	Ni <sub>2</sub> —C <sub>12</sub>	2.067(5)
Ni <sub>1</sub> —C <sub>4</sub>	2.068(5)	Ni <sub>2</sub> —C <sub>13</sub>	2.067(5)
Ni <sub>1</sub> —C <sub>5</sub>	2.000(4)	Ni <sub>2</sub> —C <sub>14</sub>	1.995(5)
Ni <sub>1</sub> —C <sub>6</sub>	2.062(5)	Ni <sub>2</sub> —C <sub>15</sub>	2.081(5)
C <sub>1</sub> —C <sub>2</sub>	1.401(7)	C <sub>10</sub> —C <sub>11</sub>	1.413(7)
C <sub>2</sub> —C <sub>3</sub>	1.417(7)	C <sub>11</sub> —C <sub>12</sub>	1.410(6)
C <sub>4</sub> —C <sub>5</sub>	1.420(6)	C <sub>15</sub> —C <sub>14</sub>	1.421(7)
C <sub>5</sub> —C <sub>6</sub>	1.403(7)	C <sub>14</sub> —C <sub>13</sub>	1.401(7)
P <sub>1</sub> —C <sub>7</sub>	1.839(5)	P <sub>2</sub> —C <sub>16</sub>	1.835(7)
P <sub>1</sub> —C <sub>8</sub>	1.839(6)	P <sub>2</sub> —C <sub>18</sub>	1.846(5)
P <sub>1</sub> —C <sub>9</sub>	1.834(5)	P <sub>2</sub> —C <sub>17</sub>	1.827(5)
mean C—H	0.99(6)	mean C—H	0.98(9)
<i>b) Angles</i>			
P <sub>1</sub> —Ni <sub>1</sub> —C <sub>1</sub>	103.0(1)	P <sub>2</sub> —Ni <sub>2</sub> —C <sub>10</sub>	102.1(1)
P <sub>1</sub> —Ni <sub>1</sub> —C <sub>2</sub>	128.1(2)	P <sub>2</sub> —Ni <sub>2</sub> —C <sub>11</sub>	127.0(2)
P <sub>1</sub> —Ni <sub>1</sub> —C <sub>3</sub>	105.7(1)	P <sub>2</sub> —Ni <sub>2</sub> —C <sub>12</sub>	104.9(1)
P <sub>1</sub> —Ni <sub>1</sub> —C <sub>4</sub>	100.2(1)	P <sub>2</sub> —Ni <sub>2</sub> —C <sub>15</sub>	103.1(1)
P <sub>1</sub> —Ni <sub>1</sub> —C <sub>5</sub>	126.0(2)	P <sub>2</sub> —Ni <sub>2</sub> —C <sub>14</sub>	127.4(2)
P <sub>1</sub> —Ni <sub>1</sub> —C <sub>6</sub>	104.8(1)	P <sub>2</sub> —Ni <sub>2</sub> —C <sub>13</sub>	103.9(1)
C <sub>1</sub> —Ni <sub>1</sub> —C <sub>3</sub>	71.3(2)	C <sub>10</sub> —Ni <sub>2</sub> —C <sub>12</sub>	72.0(2)
C <sub>1</sub> —Ni <sub>1</sub> —C <sub>4</sub>	108.8(2)	C <sub>10</sub> —Ni <sub>2</sub> —C <sub>15</sub>	102.9(2)
C <sub>1</sub> —Ni <sub>1</sub> —C <sub>5</sub>	119.1(2)	C <sub>10</sub> —Ni <sub>2</sub> —C <sub>14</sub>	119.7(2)
C <sub>1</sub> —Ni <sub>1</sub> —C <sub>6</sub>	152.2(2)	C <sub>10</sub> —Ni <sub>2</sub> —C <sub>13</sub>	154.0(2)
C <sub>2</sub> —Ni <sub>1</sub> —C <sub>4</sub>	120.1(2)	C <sub>11</sub> —Ni <sub>2</sub> —C <sub>15</sub>	118.7(2)
C <sub>2</sub> —Ni <sub>1</sub> —C <sub>5</sub>	105.9(2)	C <sub>11</sub> —Ni <sub>2</sub> —C <sub>14</sub>	105.6(2)
C <sub>2</sub> —Ni <sub>1</sub> —C <sub>6</sub>	117.5(2)	C <sub>11</sub> —Ni <sub>2</sub> —C <sub>13</sub>	118.9(2)
C <sub>3</sub> —Ni <sub>1</sub> —C <sub>4</sub>	154.1(2)	C <sub>12</sub> —Ni <sub>2</sub> —C <sub>15</sub>	152.2(2)
C <sub>3</sub> —Ni <sub>1</sub> —C <sub>5</sub>	118.2(2)	C <sub>12</sub> —Ni <sub>2</sub> —C <sub>14</sub>	116.9(2)
C <sub>3</sub> —Ni <sub>1</sub> —C <sub>6</sub>	100.5(2)	C <sub>12</sub> —Ni <sub>2</sub> —C <sub>13</sub>	100.9(2)
C <sub>4</sub> —Ni <sub>1</sub> —C <sub>6</sub>	71.6(2)	C <sub>15</sub> —Ni <sub>2</sub> —C <sub>13</sub>	71.3(2)
Ni <sub>1</sub> —P <sub>1</sub> —C <sub>7</sub>	117.6(2)	Ni <sub>2</sub> —P <sub>2</sub> —C <sub>16</sub>	118.3(2)
Ni <sub>1</sub> —P <sub>1</sub> —C <sub>8</sub>	118.2(2)	Ni <sub>2</sub> —P <sub>2</sub> —C <sub>18</sub>	115.4(2)
Ni <sub>1</sub> —P <sub>1</sub> —C <sub>9</sub>	116.4(2)	Ni <sub>2</sub> —P <sub>2</sub> —C <sub>17</sub>	115.7(2)
C <sub>7</sub> —P <sub>1</sub> —C <sub>8</sub>	99.6(3)	C <sub>16</sub> —P <sub>2</sub> —C <sub>18</sub>	101.4(3)
C <sub>7</sub> —P <sub>1</sub> —C <sub>9</sub>	101.6(2)	C <sub>16</sub> —P <sub>2</sub> —C <sub>17</sub>	101.5(2)
C <sub>8</sub> —P <sub>1</sub> —C <sub>9</sub>	100.4(2)	C <sub>18</sub> —P <sub>2</sub> —C <sub>17</sub>	102.1(3)
C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	118.8(4)	C <sub>10</sub> —C <sub>11</sub> —C <sub>12</sub>	119.7(4)
C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	117.7(4)	C <sub>13</sub> —C <sub>14</sub> —C <sub>15</sub>	117.9(4)

being defined to coincide with the 2-fold axis and *y* lying parallel to the planes of the  $\eta^3$ -allyl groups.

Even though the nickel atom is shifted away from the central carbon atom of the allyl groups, the distance between these atoms (1.994(9) Å) is significantly shorter than the distance between the nickel and the terminal carbon atoms (2.073(11) Å). The C—C—C angle in the allyl group is 118.5(9)° and the C—C distance 1.411(8) Å. Correlations between geometrical structure and the number of *d*-electrons for a number of  $M(\eta^3\text{-C}_3\text{H}_5)$  complexes has been observed by Ibers et al. [12], and the parameters observed here are consistent

TABLE 2

EQUATIONS OF SELECTED LEAST-SQUARES PLANES <sup>a</sup> WITH DEVIATIONS (Å) OF ATOMS FROM THOSE PLANES IN PARENTHESES

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Plane 1 defined by atoms C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub>:  
 $0.7546x + 0.1988y + 0.6254z + 0.0672 = 0$   
 [Ni<sub>1</sub> 1.634, P<sub>1</sub> 1.752, H<sub>1A</sub> 0.129, H<sub>1B</sub> -0.533, H<sub>2</sub> 0.155, H<sub>3A</sub> 0.198, H<sub>3B</sub> -0.485]

Plane 2 defined by atoms C<sub>4</sub>, C<sub>5</sub> and C<sub>6</sub>:  
 $0.7848x + 0.1495y + 0.6015z + 3.1455 = 0$   
 [Ni<sub>1</sub> -1.612, P<sub>1</sub> -1.605, H<sub>4A</sub> 0.073, H<sub>4B</sub> 0.600, H<sub>5</sub> -0.167, H<sub>6A</sub> 0.008, H<sub>6B</sub> 0.540]

Planes 3 defined by atoms Ni<sub>1</sub>, P<sub>1</sub>, C<sub>2</sub> and C<sub>5</sub>:  
 $0.0342x + 0.9491y - 0.3130z + 2.3192 = 0$   
 [Ni<sub>1</sub> -0.021, P<sub>1</sub> 0.007, C<sub>2</sub> 0.007, C<sub>5</sub> 0.007, C<sub>8</sub> -0.683]

Plane 4 defined by atoms C<sub>10</sub>, C<sub>11</sub> and C<sub>12</sub>:  
 $0.7610x - 0.1601y + 0.6287z + 11.2651 = 0$   
 [Ni<sub>2</sub> 1.624, P<sub>2</sub> 1.704, H<sub>10A</sub> -0.474, H<sub>10B</sub> 0.113, H<sub>11</sub> 0.192, H<sub>12A</sub> 0.126, H<sub>12B</sub> -0.458]

Plane 5 defined by atoms C<sub>13</sub>, C<sub>14</sub> and C<sub>15</sub>:  
 $0.7210x - 0.1143y + 0.6834z + 15.5045 = 0$   
 [Ni<sub>2</sub> -1.632, P<sub>2</sub> -1.722, H<sub>13A</sub> -0.216, H<sub>13B</sub> 0.373, H<sub>14</sub> -0.196, H<sub>15A</sub> -0.146, H<sub>15B</sub> 0.478]

Plane 6 defined by atoms Ni<sub>2</sub>, P<sub>2</sub>, C<sub>11</sub> and C<sub>14</sub>:  
 $0.2603x + 0.9587y - 0.1150z + 5.2154 = 0$   
 [Ni<sub>2</sub> 0.006, P<sub>2</sub> -0.002, C<sub>11</sub> -0.002, C<sub>14</sub> -0.002]

Angles (°) between two planes

1-2	3.6	2-3	91.1	3-5	72.7
1-3	88.9	2-4	17.9	3-6	17.3
1-4	20.7	2-5	16.3	4-5	4.7
1-5	18.4	2-6	73.8	4-6	88.4
1-6	71.6	3-4	71.2	5-6	90.0

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<sup>a</sup> The direction cosines of the plane normal are given for a Cartesian cell, where *x*, *y* and *z* define a right handed coordinate system with *x* parallel to *a* and *y* parallel to *b* \*.

with these observations whereby the C-C-C angle is one of the smallest observed for a *d*<sup>8</sup>- $\eta^3$ -allyl complex and the Ni- $\eta^3$ -allyl centroid distance of 1.76 Å is one of the shortest (even allowing 0.1 Å for the smaller radius of Ni [13]).

The hydrogen atoms on the methyl carbon atoms attached to the phosphorus are tetrahedrally oriented with one C-H vector parallel to the Ni-P bond. Average distances of the hydrogen and nickel atoms from the plane of the allyl-carbon atom frame are shown in Fig. 3.

The *meso*-hydrogen appears to bend some 11(2)° \* towards the nickel atom while the *anti*-methylene proton is bent away from the nickel atom by 30(3)°. The *syn*-proton lies, within the accuracy of the measurements, in the allyl plane.

The crystal is chiral and the absolute configuration of that studied was determined with 99% certainty [14] to be that shown in Fig. 4. The two independent molecules are related by an approximate centre of symmetry and together form a chiral asymmetric unit. There are no unusually short intermolecular distances.

Essentially similar behaviour to that reported here for ( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>NiP(CH<sub>3</sub>)<sub>3</sub> is observed for the P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> and P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> adducts with ( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>Ni and ( $\eta^3$ -2-CH<sub>3</sub>C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>Ni. An additional reaction is observed on warming solu-

\* Whilst intramolecular distances involving H atoms located by means of X-ray diffraction are subject to systematic errors [13], directional quantities (such as elevation angles) are not.

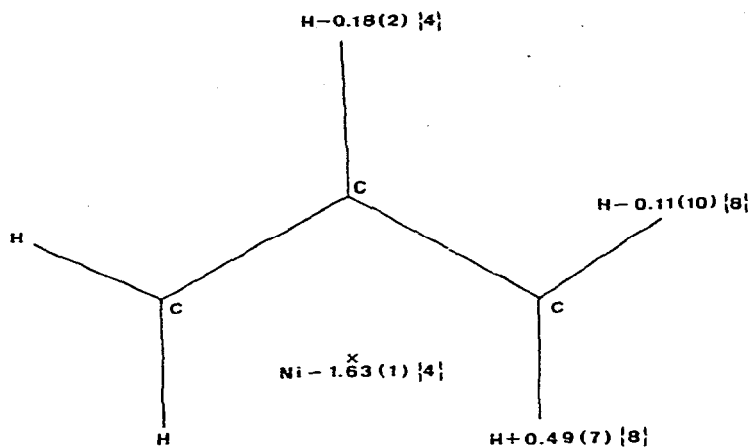


Fig. 3. The average distances (Å) of the atoms above (+) and below (−) the mean plane through the  $\eta^3$ -allyl carbon atoms (standard deviation in parentheses; { } signifies the number of atoms used in each calculation).

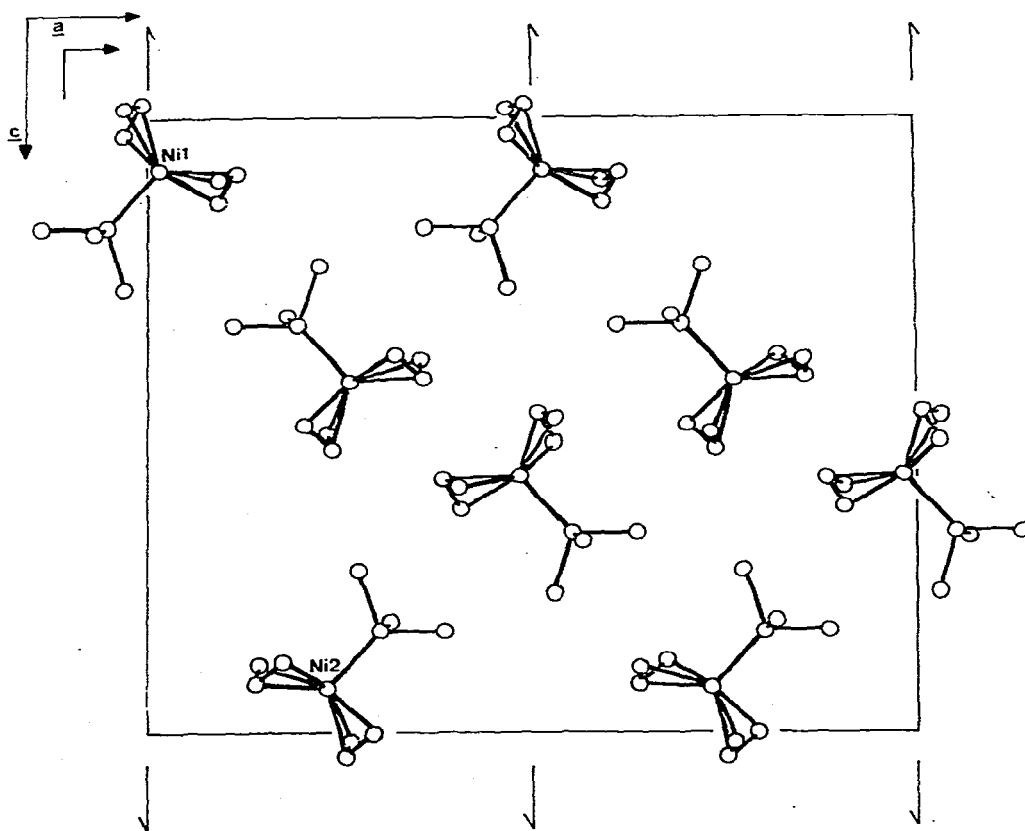
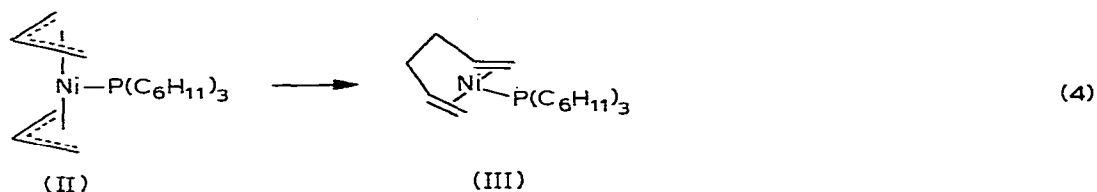


Fig. 4. The contents of one unit cell viewed down the shortest axis (b) towards the origin.

tions of  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{C}_6\text{H}_{11})_3$  (II) above  $-20^\circ\text{C}$ : reductive coupling of the allyl fragments occurs to give (1,5-hexadiene)nickel tricyclohexylphosphine (III). The absence of diastereotopic splittings in the  $^{13}\text{C}$  NMR signals for the cyclohexyl group indicates that III has the indicated  $C_s$  rather than  $C_2$  symmetry.



It has long been known that treatment of bis( $\eta^3$ -allyl)nickel complexes with excess ligand leads to coupling and displacement of the allyl groups, but no intermediate has been isolated. This reaction is reminiscent of that observed on treating  $(\eta^3\text{-C}_{12}\text{H}_{18})\text{Ni}$  with  $\text{P}(\text{C}_2\text{H}_5)_3$  [15]. That coupling occurs in the absence of an "accelerating" ligand has mechanistic implications for the nickel-catalyzed cyclooligomerization of 1,3-dienes. The triphenylphosphine adducts dissociate rather more readily than those formed by trialkylphosphines.

$(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{C}_6\text{H}_5)_3$  (IV) dissociates (in toluene- $d_8$ ) even at  $-60^\circ\text{C}$ . On allowing solutions of this complex to reach  $0^\circ\text{C}$ , reductive coupling to give the hexadiene complex (V) analogous to III is also observed. The early tentative suggestion [3] that  $\text{P}(\text{C}_2\text{H}_5)_3$  reacts with  $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$  to give a complex containing both  $\eta^1$ -allyl and  $\eta^3$ -allyl groups has not been substantiated by our investigations: at low temperatures ( $-80^\circ\text{C}$ ) a symmetrical 18-electron adduct (VI) is formed (a value of  $154 \pm 1.5$  Hz is found for  $^1J(\text{C}_1, \text{H})$  which is typical for a terminal carbon atom of a  $\eta^3$ -allyl group) while at higher temperatures dissociation occurs.

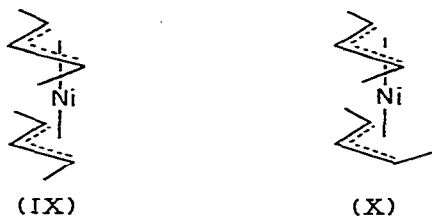
Temperature dependence of the NMR parameters is observed for most of these complexes. On raising the temperature the values approach those of the free  $(\eta^3\text{-allyl})_2\text{Ni}$  complex and free phosphine. This is the result of increasing dissociation and fast exchange. The effect is particularly marked for  $(\eta^3\text{-2-CH}_3\text{-C}_3\text{H}_4)_2\text{NiP}(\text{C}_6\text{H}_5)_3$  (VII) and changes in selected  $^{13}\text{C}$  NMR parameters are shown in Table 3. Particularly interesting is the change in  $J(\text{P}, \text{C}_4)$ : this coupling is 21.2 Hz at  $-75^\circ\text{C}$ , drops to a minimum and increases to 12.9 Hz at  $34^\circ\text{C}$ . This behaviour is consistent with fast exchange in which the weighted average value for the coupling changes with increasing dissociation;  $J(\text{P}, \text{C})$  may be expected to be positive for the complexed phosphine and negative for the free ligand [26].

The 1 : 1 adduct formed by bis( $\eta^3$ -1-methylallyl)nickel with trimethylphosphine has also been investigated. Although  $(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$  exists as a mixture of the 4 possible *syn*-substituted isomers [1], the product of the reaction with trimethylphosphine is a single symmetrical adduct — whether this has structure VIIa or VIIb remains undecided. The  $^{13}\text{C}$ — $^1\text{H}$  coupling constants in the allyl fragment were determined from a gated decoupled  $^{13}\text{C}$  NMR spectrum and fall in the range expected for an  $\eta^3$ -allyl group (151.4–156.3 Hz). Nevertheless, the  $^1\text{H}$  NMR spectrum shows that even at low temperatures ( $-60^\circ\text{C}$ ) *syn*  $\leftrightarrow$  *anti* equilibration of the terminal methylene H atoms is occurring whilst

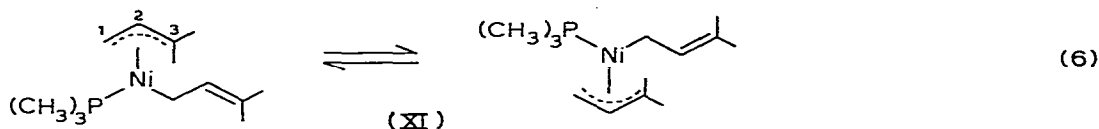




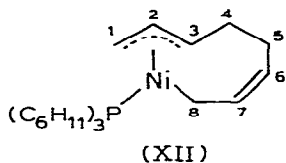
structure XI. The observation of sharp absorptions in the  $^{13}\text{C}$  NMR spectrum



even at  $-95^\circ\text{C}$  is attributable to a  $\eta^1 \leftrightarrow \eta^3$ -allyl exchange which is fast even at this temperature (eq. 6).



At a first glance the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data shown in Tables 5 and 6 do not appear to allow a distinction to be made between the situation described in eq. 6 and that in which *syn*  $\leftrightarrow$  *anti* isomerization of the methylene protons in the 18-electron adduct is occurring through the intermediacy of  $(\eta^1\text{-allyl})\text{-}(\eta^3\text{-allyl})\text{NiP}(\text{CH}_3)_3$  species (eq. 3). However, comparison of the selected data for XI with those obtained for the  $\eta^1, \eta^3$ -octadienediynickelphosphine complex XII (shown in Table 4) clearly support the formulation as a  $\eta^1$ -allyl,  $\eta^3$ -allyl complex.



Particularly convincing is the comparison of the values of  $\frac{1}{2} ({}^1J(\text{C}_{1/6}, \text{H}))$  and  $\frac{1}{2} (\delta \text{H}(\text{C}_2) + \delta \text{H}(\text{C}_7))$ : the value of 141.1 Hz for the former observed for XI is the average of that expected for an  $sp^2$ -hybridized C atom (ca. 155 Hz) and an  $sp^3$ -hybridized C atom (ca. 125 Hz) while that for the latter of 5.02 ppm is the mean of that expected for a *meso*-H atom (ca. 4 ppm) and an olefinic H atom (ca. 6 ppm). A further indication that XI has not adopted a symmetrical  $(\eta^3\text{-allyl})_2\text{NiPR}_3$  structure is provided by the  $^{13}\text{C}$  NMR chemical shifts. Typical for the symmetrical 18-electron structure is a *high-field* shift of both the terminal and *meso*-carbon absorptions of up to ca. 10 and 20 ppm respectively with respect to the phosphine free complex. In contrast in XI the absorption for the *meso*-carbon atom is shifted by ca. 7 ppm to *lower-field* and those for the two terminal carbon atoms by 11 ppm (unsubstituted) to higher field and by 15 ppm (unsubstituted) to *lower-field* respectively. We suggest that steric interaction between the *anti*- $\text{CH}_3$  groups and the ligand results in a destabilization of the expected 18-electron structure.

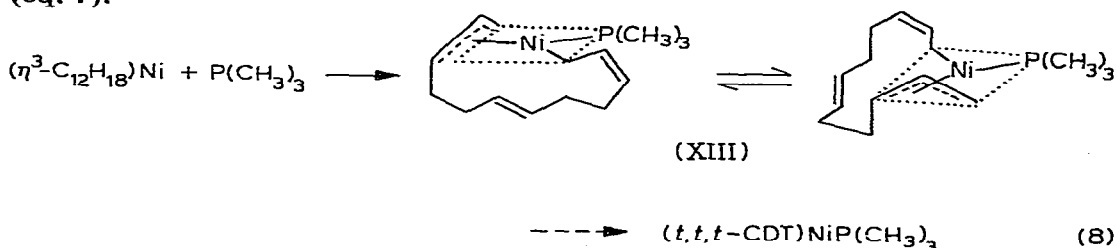
The  $\eta^3, \eta^3$ -dodecatriendiyl nickel complex discussed in the preceding publication [1] was also reacted with  $\text{P}(\text{CH}_3)_3$ . In this case it did not prove possible to

TABLE 4  
SELECTED NMR DATA FOR XI AND XII <sup>a</sup>

Complex XI		Complex XII <sup>b</sup>	
$\frac{1}{2}(\delta_1 + \delta_6)$	32.1 ppm	$\frac{1}{2}(\delta_1 + \delta_8)$	28.0 ppm
$\frac{1}{2}(\delta_2 + \delta_7)$	113.08 ppm	$\frac{1}{2}(\delta_2 + \delta_7)$	121.5 ppm
$\frac{1}{2}(\delta_3 + \delta_8)$	94.21 ppm	$\frac{1}{2}(\delta_3 + \delta_6)$	91.1 ppm
$\frac{1}{2}(^1J(\text{C}_1, \text{H}) + ^1J(\text{C}_6, \text{H}))$	141.1 Hz	$\frac{1}{2}(^1J(\text{C}_1, \text{H}) + ^1J(\text{C}_8, \text{H}))$	136 Hz
$\frac{1}{2}(^1J(\text{P}, \text{C}_1) + ^1J(\text{P}, \text{C}_6))$	broad signal	$\frac{1}{2}(^1J(\text{P}, \text{C}_1) + ^1J(\text{P}, \text{C}_8))$	8.8 or 3.3 Hz <sup>c</sup>
$\frac{1}{2}(^1J(\text{P}, \text{C}_2) + ^1J(\text{P}, \text{C}_7))$	0	$\frac{1}{2}(^1J(\text{P}, \text{C}_2) + ^1J(\text{P}, \text{C}_7))$	0.8 Hz <sup>c</sup>
$\frac{1}{2}(^1J(\text{P}, \text{C}_3) + ^1J(\text{P}, \text{C}_8))$	7.4 Hz	$\frac{1}{2}(^1J(\text{P}, \text{C}_3) + ^1J(\text{P}, \text{C}_6))$	9.8 or 8.7 Hz <sup>c</sup>
$\frac{1}{2}(\delta\text{H}(\text{C}_2) + \delta\text{H}(\text{C}_7))$	5.02 ppm	$\frac{1}{2}(\delta\text{H}(\text{C}_2) + \delta\text{H}(\text{C}_7))$	5.07 ppm

<sup>a</sup> In toluene-*d*<sub>8</sub>. <sup>b</sup> Ref. 16. <sup>c</sup> Allowance has been made for the possibility that the coupling constants have opposite signs.

isolate an adduct and instead a 1 : 1 mixture in toluene-*d*<sub>8</sub> was prepared at  $-80^\circ\text{C}$  and its behaviour studied with the help of  $^{13}\text{C}$  NMR spectroscopy. Changes in the spectrum at various temperatures are shown in Fig. 5. At  $-80^\circ\text{C}$  reaction of the principle  $\eta^3, \eta^3\text{-C}_{12}\text{H}_{18}\text{Ni}$  isomer with the phosphine has occurred leaving the second isomer unchanged. On raising the temperature, the absorption becomes broad and coalesces at  $-30^\circ\text{C}$  (at 25.2 MHz). At this temperature (Fig. 5b) the second isomer also reacts to give the same product as the first isomer. At  $-5^\circ\text{C}$  only one complex is present (Fig. 5c) and this reacts further at  $15^\circ\text{C}$  to give mainly (*t,t,t*-CDT)NiP(CH<sub>3</sub>)<sub>3</sub> [17]; a second product is also formed, probably (*t,t,c*-CDT)NiP(CH<sub>3</sub>)<sub>3</sub> \* (Fig. 5d). We interpret this behaviour as being the result of the formation of a ( $\eta^1$ -allyl)( $\eta^3$ -allyl)C<sub>12</sub>NiP(CH<sub>3</sub>)<sub>3</sub> complex (e.g. XIII) at  $-80^\circ\text{C}$ . The coalescence of the 12 absorptions due to this species (not all of which are resolved at  $-80^\circ\text{C}$ ) at  $-5^\circ\text{C}$  to give 6 absorptions indicates that exchange between the  $\eta^3$ -allyl and  $\eta^1$ -allyl group is occurring (eq. 7).



The structure of the ( $\eta^3$ -allyl)( $\eta^1$ -allyl)C<sub>12</sub>NiP(CH<sub>3</sub>)<sub>3</sub> intermediate had not been established unequivocally and the configuration of neither of the allyl groups has yet been established. The suggested structure with an *anti*-substituted  $\eta^3$ -allyl group and a  $\eta^1$ -allyl group containing a *cis*-double bond, is based upon

\* We have established that this product is not the isomer containing *t,c,c*-CDT by preparing this directly from (*t,c,c*-CDT)Ni and P(CH<sub>3</sub>)<sub>3</sub>. Unfortunately the same procedure was unsuccessful, in our hands, when applied to *t,t,c*-CDT.

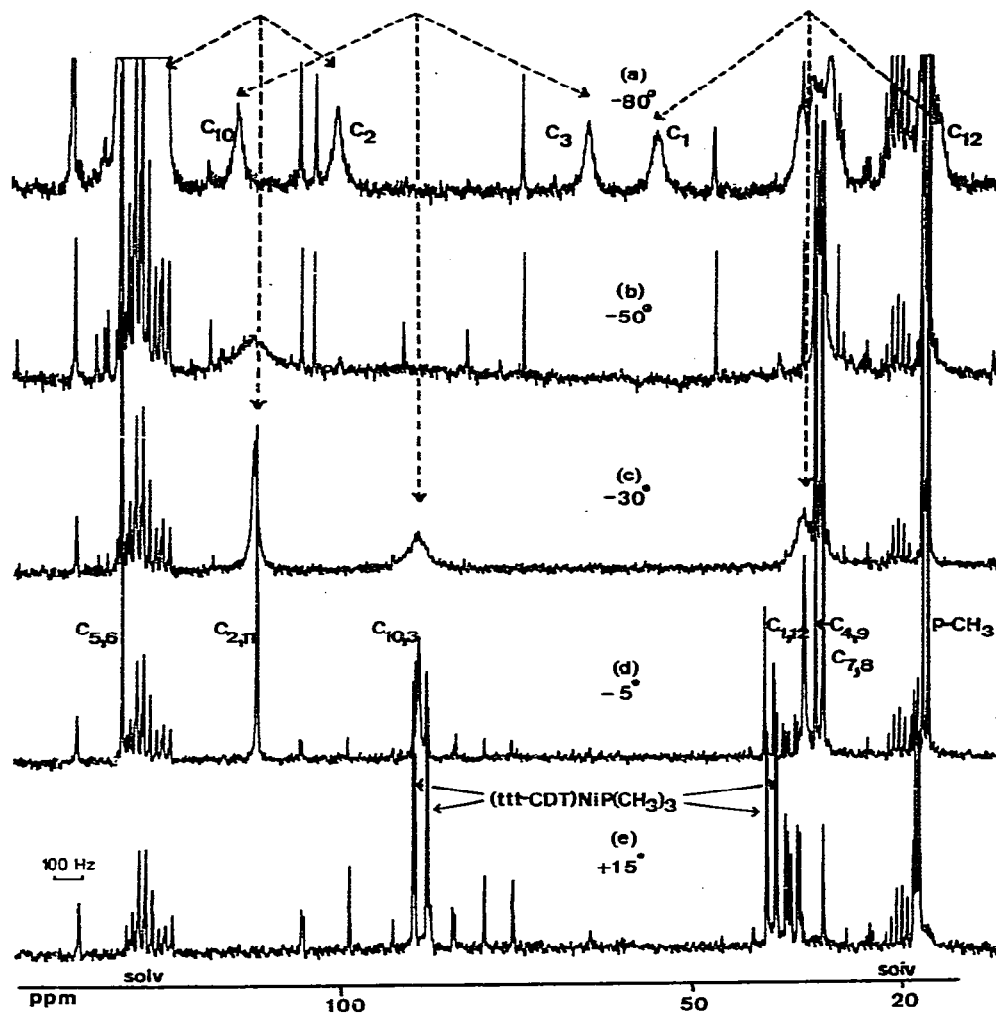
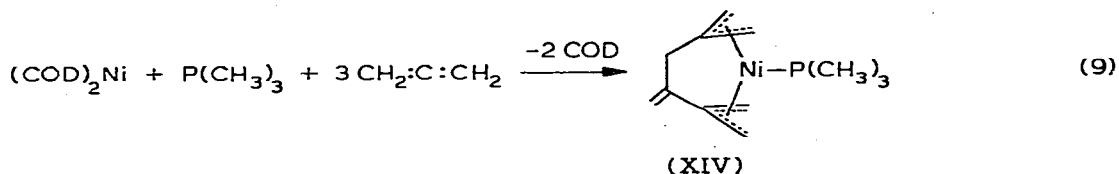


Fig. 5.  $^{13}\text{C}$  NMR spectra of  $\eta^3\text{-C}_{12}\text{H}_{18}\text{NiP}(\text{CH}_3)_3$  (XIII) at 25.2 MHz in toluene- $d_8$ .

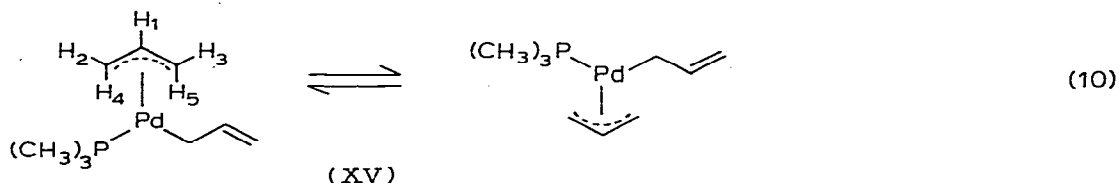
the established bis-*anti*- $\eta^3$ -allyl structure in the starting material. The product of a direct coupling reaction might have been expected to be (*t,c,c*-CDT) $\text{NiP}(\text{CH}_3)_3$  instead of the *t,t,t*-CDT isomer actually observed so that presumably isomerization of the allyl groups has occurred.

In order to assist with the assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the ( $\eta^3$ -allyl) $_2\text{Ni}$  ligand complexes, we have synthesized  $\eta^3,\eta^3\text{-C}_9\text{H}_{12}\text{NiP}(\text{CH}_3)_3$  (XIV) from the reaction of allene with bis(cycloocta-1,5-diene)nickel in the presence of trimethylphosphine.



The *cis*-arrangement of the  $\eta^3$ -allyl groups in the  $P(C_6H_5)_3$  complex analogous to XIV has been confirmed by X-ray crystallography [18]. Although the crystal structure determination indicates that the  $\eta^3$ -allyl groups are asymmetric in the solid, the NMR spectra indicate that this is not the case for either complex in solution. Coupling between  $^{13}C$  and  $^{31}P$  is observed for all carbon atoms except those terminal at the  $\eta^3$ -allyl groups.

The complexes formed by bis( $\eta^3$ - $C_3H_5$ )palladium and -platinum with trimethylphosphine are pale-yellow to white solids. Both complexes exhibit similar behaviour in solution, and the variable temperature  $^1H$  NMR spectra of the palladium complex are shown in Fig. 6\*. At  $-109^\circ C$  the molecule adopts the 16-electron structure ( $\eta^1$ - $C_3H_5$ )( $\eta^3$ - $C_3H_5$ )PdP( $CH_3$ )<sub>3</sub> (XV). On raising the temperature the allyl groups exchange (eq. 10). At  $-3^\circ C$  the spectrum for an  $AX_4$



spin-system is observed indicating that phosphine dissociation is occurring at this temperature.

The platinum complex (XVI) behaves analogously and the data are shown in Tables 5 and 6. The  $^{13}C$  chemical shifts should be compared with those for (1,2,3,8- $\eta$ -6-*cis*-octadienyl)platinum-trimethylphosphine [19]. In particular the large coupling constant  $^1J(Pt, C)$  of 720.4 Hz observed in our system is typical for a platinum-bonded methylene C atom. Above  $0^\circ C$  exchange of the allyl groups occurs. The observation that the weighted average of the  $\eta^3$ -allyl- and  $\eta^1$ -allyl-protons remains constant and that  $J(P, C)$ ,  $J(Pt, C)$ ,  $J(Pt, H)$  and  $J(Pt, P)$  are observed throughout the whole temperature range indicate that the phosphine remains bonded to the metal atom during the exchange process.  $J(Pt, P)$  was obtained from the  $^{31}P$  NMR spectrum and was measured from  $-114$  to  $102^\circ C$ ; only a relatively slight variation was observed in both  $J(Pt, P)$  (3866.1 Hz at  $-114^\circ C$ , 3940.5 Hz at  $+102^\circ C$ ) and the chemical shift ( $-21.0 \pm 0.5$  at  $-114^\circ C$ ,  $-24 \pm 0.5$  at  $102^\circ C$  relative to external  $H_3PO_4$ ).

The coalescence temperature for allyl exchange was  $50^\circ C$  (at 80 MHz) for the platinum compound and  $-50^\circ C$  (at 80 MHz or  $-67^\circ C$  at 200 MHz) for the palladium compound from which free energies of activation of  $21.1 \pm 1.5$  kcal/mol and  $9.6 \pm 1.5$  kcal/mol respectively can be calculated.

### Raman spectra

The solid state, low temperature Raman spectra of a number of the adducts formed by the ( $\eta^3$ -allyl)<sub>2</sub>M complexes with trimethylphosphine were investigated. The results are in complete agreement with those obtained by the other spectroscopic methods and the data are collected together in Table 7. The criteria used in the selection of the absorption and in the estimation of their

(Continued on p. 464)

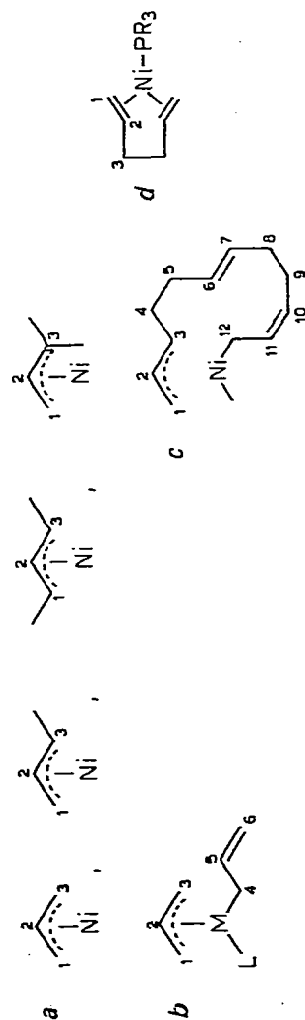
\* Similar complexes have been prepared independently by H. Werner and A. Kühn [7,20]. We thank Professor Werner for giving us information prior to publication.

TABLE 5

 $^{13}\text{C}$  NMR SPECTRAL DATA FOR THE 1 : 1 ADDUCTS FORMED BY TERTIARY PHOSPHINES WITH  $(\eta^3\text{-ALLYL})_2\text{M}$  COMPLEXES <sup>a</sup>

$(\eta^3\text{-Allyl})_2\text{M}$	$\text{PR}_3$	No. in text	Temp. ( $^\circ\text{C}$ )	Solvent	$\text{C}_1$ (ppm)	$\text{C}_2$ (ppm)	$\text{C}_3$ (ppm)	Additional data ( $\delta$ (ppm), $J$ (Hz))	Remarks
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	I	-60	toluene- $d_8$	41.73	91.54	41.73	$\delta$ 16.57 ( $\text{CH}_3$ ); $J(\text{CH}_3, \text{P})$ 17.2 $J(\text{C}_2, \text{P})$ 6.7	$2J(\text{C}_2, \text{P})$ not observed
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_{11})_3$	II	0	toluene- $d_8$	41.74	92.33	41.74	16.98 ( $\text{CH}_3$ ); $J(\text{CH}_3, \text{P})$ 16.7	
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	III	-30	toluene- $d_8$	42.50	95.77	42.50	$\delta$ 35.17 ( $J$ 8.7); 30.03; 28.13 ( $J$ 9.1), 27.07 ( $\text{C}_6\text{H}_{11}$ ) $J(\text{P}, \text{C}_1)$ 3.9, $J(\text{P}, \text{C}_2)$ 9.2, $J(\text{P}, \text{C}_3)$ 1.6; $\delta$ 36.31 ( $J$ 14.8), 30.75 ( $J$ 2.3), 28.00 ( $J$ 9.5), 27.03 ( $J$ 1.0) ( $\text{C}_6\text{H}_{11}$ )	Hexadiene complex <sup>d</sup>
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	IV	-60	toluene- $d_8$	45.78	96.3	45.78	$J(\text{C}_2, \text{P})$ 4.3; $\delta$ 135.79 ( $J$ 27.2), 134.12 ( $J$ 11.6), 128.43 ( $J$ 8.5), 128.94 ( $\text{C}_6\text{H}_5$ )	
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{C}_2\text{H}_5)_3$	V	0	toluene- $d_8$	54.50	77.79	26.87	$\delta$ 139.2 ( $J$ 26), 113.29 (12.8) $\text{C}_6\text{H}_5$ , at $-30^\circ$	Hexadiene complex <sup>d</sup>
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{C}_2\text{H}_5)_3$	VI	-50	toluene- $d_8$	43.55	107.4	43.55	$\delta$ 24.42 ( $\text{CH}_3$ ); 14.25 ( $\text{P-CH}_2$ ), $\delta$ = 12.3, 7.55 ( $\text{P-CH}_2\text{CH}_3$ )	$J(\text{C}_2, \text{P})$ 6.9 ( $-80^\circ\text{C}$ ) 0 ( $-50^\circ\text{C}$ ) see text
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	VII	-75	toluene- $d_8$	46.5	109.93	46.5	$\delta$ 24.76 ( $\text{CH}_3$ ); 134.93 ( $J$ 21.2), 134.32 ( $J$ 9.6), 128.17 ( $J$ 7.3) 128.90 ( $\text{C}_6\text{H}_5$ )	
$(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	VIII	-80	toluene- $d_8$	41.79	93.17	57.50	$\delta$ 19.85 ( $\text{CH}_3$ ); 16.51 ( $\text{P-CH}_3$ ), $J$ 17.2; $J(\text{P}, \text{C}_2)$ 6.9	<i>syn, syn</i> -isomer ( $\sim 75\%$ )
$(\eta^3\text{-1,3-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	IX	-80	toluene- $d_8$	51.76	94.09	51.76	$\delta$ 18.64 ( $\text{CH}_3$ ); 15.00 ( $\text{PCH}_3$ ), $J$ 14.8; $J(\text{P}, \text{C}_2)$ 5.9	<i>syn, anti</i> -isomer ( $\sim 25\%$ )
$(\eta^3\text{-1,1'-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	X	-65	toluene- $d_8$	54.71	93.71	54.57	$\delta$ 18.55 ( $\text{CH}_3$ ); 16.95 ( $\text{PCH}_3$ ), $J$ 15.7; $J(\text{P}, \text{C}_2)$ 5.8	one $\text{CH}_3$ group was identified
$(\eta^3\text{-1,1'-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	XI	-95	toluene- $d_8$	32.1	113.08	94.21	$\delta$ 26.86 ( <i>syn</i> $\text{CH}_3$ ); $\delta$ 20.82 ( <i>anti</i> $\text{CH}_3$ ); 16.43 ( $\text{PCH}_3$ , $J$ 23.2)	$\delta(\text{C}_1)$ broad $\eta^3, \eta^1$ -allyl exchange see text
								$J(\text{P}, \text{C}_3)$ 7.4, $^1J(\text{C}_1, \text{H})$ 141.1 ( $-60^\circ\text{C}$ )	

$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}^c$	XIII	$\text{P}(\text{CH}_3)_3$	-80	toluene- $d_8$	54.6	99.9	64.4	$\delta$ 33.9, 29.9 ( $\text{C}_4/\text{C}_9$ ); 31.7 ( $\text{C}_5/\text{C}_8$ ); 130.8 ( $\text{C}_6/\text{C}_7$ ); 114.1 ( $\text{C}_{10}$ ); 14.7 ( $\text{C}_{12}$ )	$\delta\text{C}_{11}$ not observed
$(\eta^3\text{-C}_9\text{H}_{12})\text{Ni}$	XIV	$\text{P}(\text{CH}_3)_3$	-10	toluene- $d_8$	34.2	111.9	88.9	16.38 ( $\text{PCH}_3$ , $J(\text{P}, \text{C})$ 23.5) $\delta$ 32.4 ( $\text{C}_4/\text{C}_9$ ); 31.3 ( $\text{C}_5/\text{C}_8$ ); 131.0 ( $\text{C}_6/\text{C}_7$ ); 16.67 ( $\text{PCH}_3$ , $J(\text{P}, \text{C})$ 18.9)	$\eta^3 \leftrightarrow \eta^1$ exchange see text
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}^b$	XV	$\text{P}(\text{CH}_3)_3$	-90	toluene- $d_8$	58.2	118.8	60.5	$\delta$ 43.61 ( $\text{CH}_2$ ); 16.53 ( $\text{PCH}_3$ , $J(\text{P}, \text{C})$ 19.4); $J(\text{C}_1, \text{H})$ 155.7 $\delta$ 152.64 ( $\text{CH}_2$ ; $\text{C}$ ); 109.34 ( $\overline{\text{CH}}_2$ ; $\text{C}$ ); $J(\text{C}_1, \text{H})$ 156.5	
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}^b$	XVI	$\text{P}(\text{CH}_3)_3$	-60	toluene- $d_8$	59.6	133.7	59.6	$\delta$ 16.8 ( $\text{C}_4$ ), 148.1 ( $\text{C}_5$ ), 100.0 ( $\text{C}_6$ ); 16.07 ( $\text{PCH}_3$ )/3 $\delta$ 16.63 ( $\text{PCH}_3$ , $J$ 22.6)	$\eta^3 \leftrightarrow \eta^1$ exchange see text
				toluene- $d_8$	51.62	110.20	53.55	$\delta$ 12.40 ( $\text{C}_4$ ), 149.03 ( $\text{C}_5$ ), 102.55 ( $\text{C}_6$ ), 16.04 ( $\text{PCH}_3$ , $J$ 34.2, $J(\text{Pt}, \text{C})$ 48.9) $J(\text{Pt}, \text{C}_1)$ 30.9, $J(\text{Pt}, \text{C}_2)$ 15.2, $J(\text{Pt}, \text{C}_3)$ 140.4, $J(\text{Pt}, \text{C}_4)$ 720.3, $J(\text{Pt}, \text{C}_5)$ 73.3, $J(\text{Pt}, \text{C}_6)$ 69.6, $\delta$ 18.74 ( $\text{PCH}_3$ , $J$ 33.7, $J(\text{Pt}, \text{C})$ 50.7)	



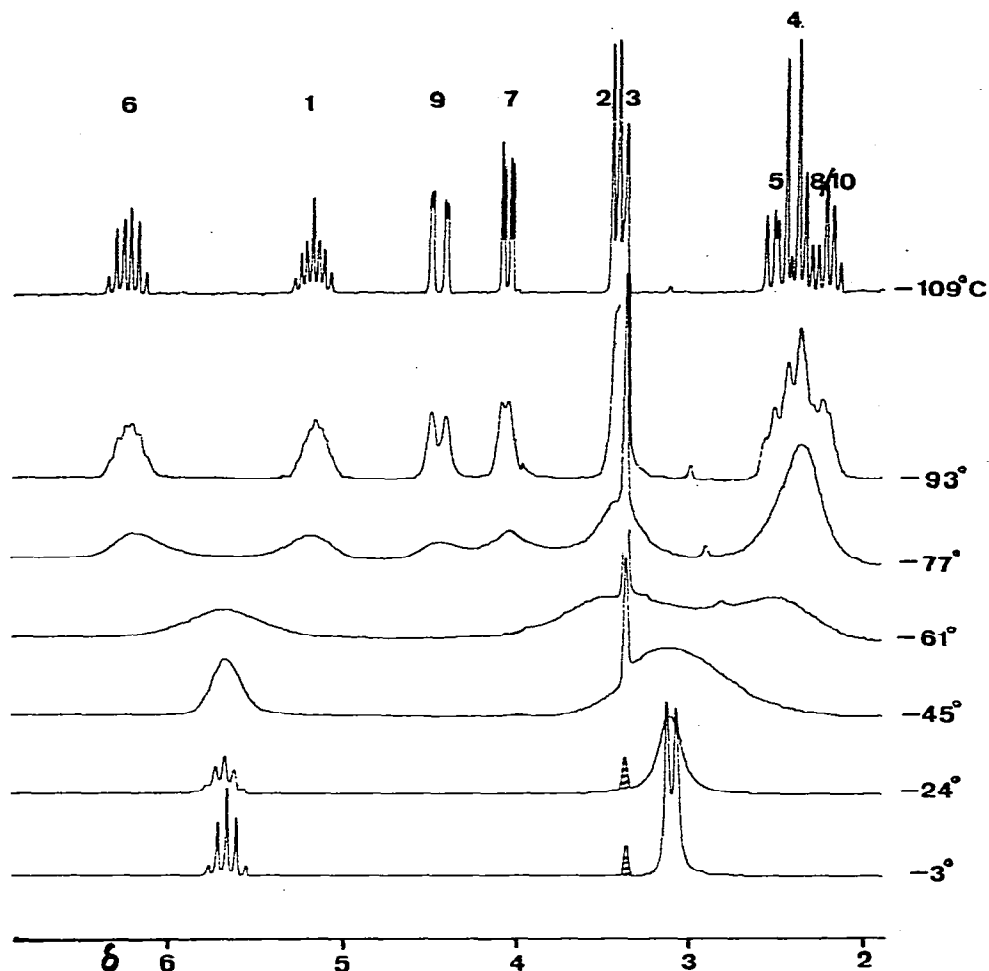


Fig. 6. The variable temperature  $^1\text{H}$  NMR spectrum of the adduct formed by  $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$  with  $\text{P}(\text{CH}_3)_3$  (ether- $d_{10}$ , 200 MHz;  $\delta$   $\text{CH}_3 \sim 1.5$  ppm).

relative intensities are the same as those described in the preceding publication [1]. A partial assignment of the absorptions to characteristic vibrations or to particular ligands has also been attempted. Typical spectra are shown in Fig. 7.

Although the spectra of the phosphine adducts are more complex than those of the corresponding  $(\eta^3\text{-allyl})_2\text{M}$  complexes, a number of characteristic absorptions enable significant structural proposals to be made. All the nickel complexes studied, with one exception (see below), show the absorptions typical of a  $\eta^3\text{-allyl}$  group. The wavelengths of the characteristic absorptions at around 1500, 1020 and 800–900  $\text{cm}^{-1}$  differ only slightly from those observed in the parent compounds. The adduct formed by  $\text{P}(\text{CH}_3)_3$  to  $(\eta^3\text{-1,1'-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$  shows, in addition to the absorptions for a  $\eta^3\text{-allyl}$  group, a very intense band at 1630  $\text{cm}^{-1}$  which is undoubtedly associated with the localized double bond of a  $\eta^1\text{-allyl}$  group and hence fully supports the assignment of this compound as



TABLE 6

 $^1\text{H}$  NMR SPECTRAL DATA FOR THE 1 : 1 ADDUCTS FORMED BY TERTIARY PHOSPHINES WITH  $(\eta^3\text{-ALLYL})_2\text{M}$  COMPLEXES

$(\eta^3\text{-ALLYL})_2\text{M}$	PR <sub>3</sub>	No. in text	Temp. (°C)	Solvent	$\delta$ (ppm)	Mult. <sup>b</sup>	J (Hz)	Assignment <sup>c</sup>	Remarks
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	P(CH <sub>3</sub> ) <sub>3</sub>	I	-110	ether-d <sub>10</sub>	4.46	t, t, d	$^3J(1,2(3)) 6.4, ^3J(1,4(5)) 11.1, J(1, P) 5.7$	meso-H(1)	WP 80
					2.48	d	$^3J(1,2(3)) 6.4$	syn-H(2,3)	
					(1.36)	d, d	$^3J(1,4(5)) 11.1, J(P, 4(5)) 18$	anti-H(4,5)	
					1.36	d	$^2J(P, CH_3) 5.8$	P-CH <sub>3</sub>	
			-40	ether-d <sub>10</sub>	4.41	d, q	$^3J(1,2-5) 8.8, J(1, P) 5.7$	meso-H(1)	$T_C \sim -70^\circ\text{C}$
					1.92	d, d	$J(P, 2-5) 9$	syn, anti-H 2-5	$\Delta G^\ddagger = 9.6 \pm 1.5$ kcal/mol
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	II	-83	toluene-d <sub>8</sub>	1.34	d	$^2J(P, CH_3) 5.7$	P-CH <sub>3</sub>	for syn anti exchange
					4.56	q	$^3J(1,2-5) 9.8$	meso-H(1)	
					2.47	d		syn, anti-H(2-5)	
			0	toluene-d <sub>8</sub>	2.83	d, d	$^3J(1,3) 8.5, ^3J(1, P) 5.8$	H <sub>1</sub>	Hexadiene complex <sup>d</sup>
					3.13	d, d	$^3J(2,3) 13.3, ^3J(2, P) 5.0$	H <sub>2</sub>	
					4.67	br s		H <sub>3</sub>	
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	IV	-78	toluene-d <sub>8</sub>	4.41	t, t, d	$^3J(1,4(5)) 13.4, ^3J(1,2(3)) 6.1, J(1, P) 5.4$	meso-H(1)	
					2.95	d	$^3J(1,2(3)) 6.1$	syn-H(2,3)	
			0	toluene-d <sub>8</sub>	1.60	d, d	$^3J(1,4(5)) 13.4, J(P, 4(5)) 13$	anti-H(2,3)	
					3.14	d	$^3J(1,3) 8.5$	H <sub>1</sub>	Hexadiene complex <sup>d</sup>
$(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	VI	-80	ether-d <sub>10</sub>	2.90	d	$^3J(2,3) 12.9$	H <sub>2</sub>	
					4.20	m		H <sub>3</sub>	
					1.83	br, s		CH <sub>2</sub> <sup>d</sup>	
					1.62	d	$J(P, 1) 7$	CH <sub>3</sub> <sup>d</sup>	
					1.87	d	$J(P, 2-5) 12$	syn, anti-H	see text
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	VII	-70	toluene-d <sub>8</sub>	1.61	br, s		CH <sub>3</sub>	
					2.86	br, s		meso-H(2,3)	
					1.79	br, s		anti-H(4,5)	
					1.55	s		CH <sub>3</sub>	
			-10	toluene-d <sub>8</sub>	2.57	s		meso, anti-H	
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	P(CH <sub>3</sub> ) <sub>3</sub>	VIII	-110	ether-d <sub>10</sub>	4.50	d, d, d, d	$J(1,2) 6.0, J(1,4) 11.7, J(1,5) 10.1, J(1, P) 5.5$	meso-H(1)	

TABLE 6 (continued)

$(\eta^3\text{-Allyl})_2\text{M}$	$\text{PR}_3$	No. in text	Temp. (°C)	Solvent	$\delta$ (ppm)	Mult.	$J$ (Hz)	Assignment <sup>c</sup>	Remarks
$(\eta^3\text{-1,3-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$	$\text{P(CH}_3)_3$	IX	-70	toluene-d <sub>8</sub>	1.42	d	$^3J(3,5)$ 6.1	<i>syn</i> -H(2)	WH 270
					1.33	d	$J(4, P)$ 22.5	<i>syn</i> -CH <sub>3</sub>	
					1.20	d, d	$J(5, P)$ 16.1	<i>anti</i> -H(4)	
					2.20	d, q, d	$^2J(P, \text{CH}_3)$ 5.9	<i>anti</i> -H(5)	
					1.30	d	$^3J(1,2(4))$ 8.8	PCH <sub>3</sub>	
					4.37	d, tr	$J(P, 2(4))$ 10.6	<i>meso</i> -H(1)	$T_c$ 91°C
					1.33	d		<i>syn, anti</i> -H(2,4)	$\Delta G^\ddagger = 8.7$ kcal/mol
					1.28	d		<i>syn</i> CH <sub>3</sub>	(exchange of 2 with 4)
					2.23			<i>anti</i> -H(5)	
					1.30			PCH <sub>3</sub>	
$(\eta^3\text{-1,1'-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$	$\text{P(CH}_3)_3$	X	-70	toluene-d <sub>8</sub>	4.08	d, tr	$^3J(1,4(5))$ 9.7, $J(1, P)$ 5.5	<i>meso</i> -H(1)	WH 270 <i>syn, syn</i> - isomer (75%)
					1.31	d	$^3J(2(3), 4(5))$ 6.3	CH <sub>3</sub> (2,3)	
					1.75	d, d, q	$J(P, 4(5))$ 18.0	<i>anti</i> -H(4,5)	
					0.75	d	$^2J(P, \text{CH}_3)$ 5.06	PCH <sub>3</sub>	
					3.94	d, tr	$^3J(1,4(5))$ 9.7, $J(1, P)$ 5.3	<i>meso</i> -H(1)	
					1.47	d		CH <sub>3</sub> (2)	
					2.39	d, q	$J(3,5)$ 6.3	<i>anti</i> -H(5)	
					4.50	d, d, d	$^3J(6,8)$ 7.6, $^3J(6,9)$ 11.0, $J(6, P)$ 4.8	<i>meso</i> -H(6)	
					1.42	d		<i>syn</i> -CH <sub>3</sub> (7)	
					2.49	d, d, q	$^3J(9,7)$ 6.0, $J(9, P)$ 5	<i>anti</i> -H(9)	
1.14	d	$^3J(8,10)$ 6.6	<i>anti</i> -CH <sub>3</sub> (10)						
$(\eta^3\text{-1,1'-(CH}_3)_2\text{-C}_3\text{H}_3)_2\text{Ni}$	$\text{P(CH}_3)_3$	XI	-90	toluene-d <sub>8</sub>	0.84	d	$^2J(P, \text{CH}_3)$ 5.2	P-CH <sub>3</sub>	$\eta^3 \leftrightarrow \eta^1$ exchange
					5.02	tr	$^3J(1,2(4))$ 9.8	<i>meso</i> -H(1)	see text
					1.78	d		<i>syn, anti</i> -H (2,4)	
					1.83	s		<i>syn</i> -CH <sub>3</sub> (3)	
					1.48	s		<i>anti</i> -CH <sub>3</sub> (5)	
					0.86	d	$^2J(P, \text{CH}_3)$ 8	P-CH <sub>3</sub>	
					2.96	d	$J(P, 2(3))$ 0.43, $J(P, 2'(3'))$ 0.92	{ <i>syn</i> -H	WP 80
					2.80	d		}	

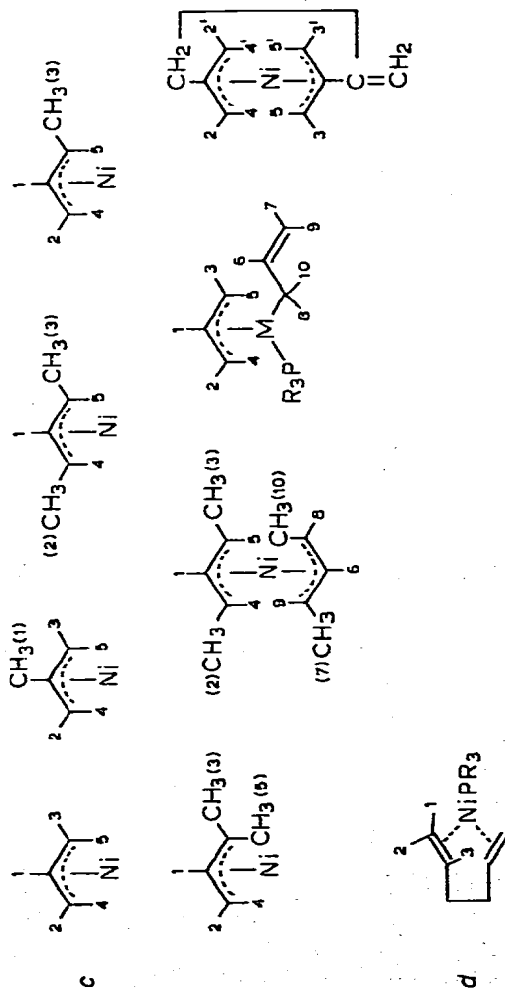
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$	P(CH <sub>3</sub> ) <sub>3</sub>	XV	-1.09	ether-d <sub>10</sub>	1.59	d }	J(P, 4(5) 12.6, J(P, 4'(5') 12.6	[anti-H -CH <sub>2</sub> - :CH <sub>2</sub> meso-H(1) syn-H(2) syn-H(3) anti-H(4) anti-H(5) H <sub>6</sub> H <sub>8</sub> or H <sub>10</sub> H <sub>7</sub> H <sub>10</sub> or H <sub>8</sub> H <sub>9</sub> P-CH <sub>3</sub> meso-H(1) syn-H(2) syn-H(3) syn-H(3) anti-H(4) anti-H(5) H <sub>6</sub> H <sub>8</sub> or H <sub>10</sub> H <sub>7</sub> H <sub>10</sub> or H <sub>8</sub> H <sub>9</sub> P-CH <sub>3</sub> H <sub>1</sub> , H <sub>6</sub>
					1.62	d	J(P, CH <sub>2</sub> ) 4.2	
					2.88	d, tr	4J(CH <sub>2</sub> ) 1.2, 2J(vic) 1.2,	
					5.03	tr, d, d }	J(P) 1.9	
					4.65	d, tr	3J(1,2) 7.3, 3J(1,4) 13.7	
					5.16	tr, tr	3J(1,3) 7.3, 3J(1,5) 13.4	
					3.47	d	J(3, P) 6.3	
					3.45	d, d	J(5, P) 9.3	
					2.40	d	3J(6,8) 8.5, 3J(6,10) 8.5	
					2.49	d, d	3J(8,10) 8.5, 3J(8, P) 8.0	
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$	P(CH <sub>3</sub> ) <sub>3</sub>	XVI	-4.0	toluene-d <sub>8</sub>	6.23	d, d, d, d	3J(6,7) 9.8	WP 80, WH 270
					2.34	d, d, d	J(3, P) 5.0, 2J(3, Pt) 15(?)	
					4.05	d, d	3J(1,4) 12.8, J(4, Pt) 43,	
					2.18	d, d, d	3J(1,5) 12.8,	
					4.44	d, d	J(5, P) 12.0, J(5, Pt) 56	
					1.48	d	3J(6,9) 17.0, 3J(6,7) 9.8,	
					4.35	m	3J(6,8(10)) 8, 3J(6, Pt) 23.4	
					3.21	m	2J(8,10) 9, 3J(6,8) 8.5, 2J(8, P) 8	
					3.59	m	J(9, Pt) 97.5	
					2.04	m	3J(7,6) 9.8, 2J(7,9) 3.0,	
2.29	m	4J(8, Pt) 32.0						
6.84	m	2J(8,10) 9, 3J(10,6) 8.5, 2J(10,P) 8						
2.86	A/B	2J(9, Pt) 97.5						
4.75	m	4J(9, Pt) 30.0						
3.08	A/B	2J(P, CH <sub>3</sub> ) 9.8, 3J(Pt, CH <sub>3</sub> ) 36.6						
5.03	m							
1.00	d							
5.40	br, s							

$\eta^1 \leftrightarrow \eta^3$   
exchange

TABLE 6 (continued)

$(\eta^3\text{-Allyl})_2\text{M}$	$\text{PR}_3$	No. in text	Temp. ( $^\circ\text{C}$ )	Solvent	$\delta$ (ppm)	Mult.	$J$ (Hz)	Assignment $c$	Remarks
					3.26	br, s		$\text{H}_2\text{-5, 7-10}$	$T_c$ (80 MHz) = $63^\circ\text{C}$
					1.00	d	$^3J(\text{CH}_3\text{P})$ 36	P- $\text{CH}_3$	$\Delta G^\ddagger$ 16.7 kcal/mol

<sup>a</sup> Chemical shifts rel. to solvent methyl or methylene absorption. <sup>b</sup> Multiplicity: d = doublet, t = triplet, q = quintet, br = broad. <sup>c</sup>



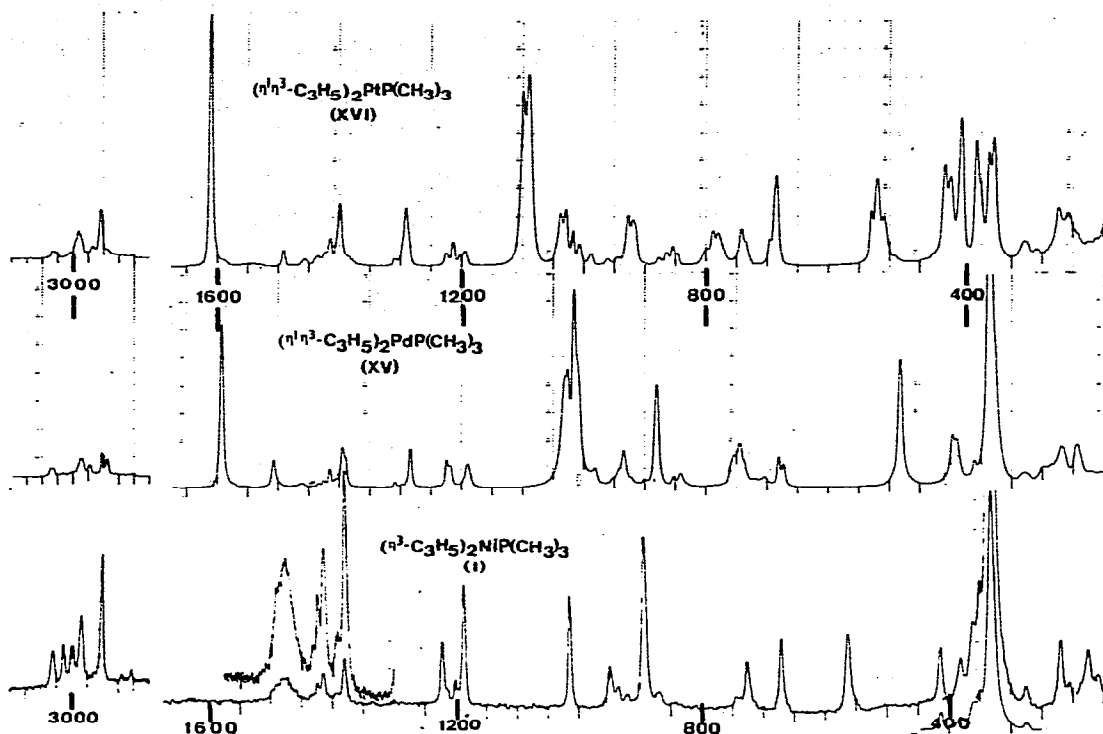


Fig. 7. The solid state Raman spectra of the 1 : 1 adducts formed by  $P(CH_3)_3$  to the  $(\eta^3-C_3H_5)_2M$  complexes of Ni, Pd and Pt.

$(\eta^1, \eta^3-1,1'-(CH_3)_2C_3H_3)_2NiP(CH_3)_3$  (XI). The results obtained for the complexes formed by  $P(CH_3)_3$  with the bis- $\eta^3-C_3H_5$  and bis- $\eta^3-2-CH_3C_3H_4$  complexes of palladium and platinum indicate that these also contain both  $\eta^1$ - and  $\eta^3$ -allyl groups (Table 7).

## Experimental section

### Instrumentation

The instrumentation and techniques employed are described in the preceding publications [1]. The NMR spectrum of compound XV was recorded on a Varian XL 200 spectrometer.

### Preparation of the $(\eta^3\text{-allyl})_2M/PR_3$ adducts

$(\eta^3-C_3H_5)_2NiP(CH_3)_3$  (I).  $P(CH_3)_3$  (404 mg, 5.31 mmol) was added dropwise to  $(\eta^3-C_3H_5)_2Ni$  (743.3 mg, 5.31 mmol) in pentane (5 ml) at  $-78^\circ C$ . The yellow solution slowly turned red and an orange complex was precipitated. After several hours stirring the products was filtered off, washed with a little cold pentane, and dried under high vacuum. Yield: 1.044 g (90.8%). Analysis: Found C, 49.53; H, 8.80; Ni, 27.26; P, 14.31.  $C_9H_{10}NiP$  calcd.: C, 49.83; H, 8.83; Ni, 27.06; P, 14.28%.

The other complexes listed in Table 8 were prepared similarly.

(Continued on p. 472)

TABLE 7

THE SOLID STATE RAMAN SPECTRA OF THE 1:1 ADDUCTS FORMED BY TRIMETHYLPHOSPHINE WITH ( $\eta^3$ -ALLYL)<sub>2</sub>M COMPLEXES (cm<sup>-1</sup>)

( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> - NiP(CH <sub>3</sub> ) <sub>3</sub> (I)	( $\eta^1$ $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> - PdP(CH <sub>3</sub> ) <sub>3</sub> (XV)	( $\eta^1$ $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> - PtP(CH <sub>3</sub> ) <sub>3</sub> (XVI)	( $\eta^1$ $\eta^3$ -2-CH <sub>3</sub> - C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Ni- P(CH <sub>3</sub> ) <sub>3</sub>	( $\eta^1$ $\eta^3$ -2-CH <sub>3</sub> - C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Pd- P(CH <sub>3</sub> ) <sub>3</sub>	( $\eta^1$ $\eta^3$ -2-CH <sub>3</sub> - C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub> Pt- P(CH <sub>3</sub> ) <sub>3</sub>	( $\eta^3$ -1,3- (CH <sub>3</sub> ) <sub>2</sub> - C <sub>3</sub> H <sub>3</sub> ) <sub>2</sub> Ni- P(CH <sub>3</sub> ) <sub>3</sub> (VIII)	( $\eta^3$ -1,3- (CH <sub>3</sub> ) <sub>2</sub> - C <sub>3</sub> H <sub>3</sub> ) <sub>2</sub> Ni- P(CH <sub>3</sub> ) <sub>3</sub> (IX)	( $\eta^3$ -1,1,1'- (CH <sub>3</sub> ) <sub>2</sub> - C <sub>3</sub> H <sub>3</sub> ) <sub>2</sub> Ni- P(CH <sub>3</sub> ) <sub>3</sub> (XI)	Assignment and Approx. Description
6471 A ca. 210 K	6471 A ca. 170 K	4880 A ca. 170 K	4880 A ca. 170 K	4880 A ca. 170 K	4880 A ca. 170 K	6471 A ca. 220 K	6471 A ca. 220 K	6471 A ca. 190 K	
3062 m	3070 w	3065 w	3065 m	3060 w	3050 w	3050 w	3050 w	3050 w	$\eta^3$ -Allyl, $\nu$ (CH)
3030 m		3040 m			3015 w				
3000 m		2985 m							
		2978 m							
2970 s	2970 m	2965 m	2975 m	2980 m	2967 m	2967 m	2967 m	2970 w	P(CH <sub>3</sub> ) <sub>3</sub> , $\nu_{as}$ (CH <sub>3</sub> )
—	2940 w	—	2950 w	2950 w	2935 w	2935 w	2935 w	2935 w	
2900 s	2910 m	2905 } s	2910 s	2918 m	2903 s	2903 s	2903 s	2905 m	P(CH <sub>3</sub> ) <sub>3</sub> , $\nu_3$ (CH <sub>3</sub> )
		2898 } s			~2870 w	~2870 w	~2870 w	~2890	
	2886 m		2878 s	2878 m	2845 w	2845 w	2845 w	~2870 w	
2805 w			2805 w	2805 w	2805 w	2805 w	2805 w	~2850	P(CH <sub>3</sub> ) <sub>3</sub>
—	1593 s	—	1600 s	1612 s	—	—	—	1630 s	$\eta^1$ -Allyl, $\nu$ (C=C)
1480 w-m	1506 w-m	1475 m	1495 w	1482 vw	$\eta^3$ -Allyl, $\nu_{as}$ (CCC)	1497 s	1497 s	1514 m	$\eta^1$ -Allyl, $\nu_{as}$ (CCC)
		1440 w				1450 m	1450 m	1455 m	
1424 } w-m	1425 vw	1428 } w		1430 } w				1445 w	
1414 } w-m	1415 w	1420 } w		1417 } w				1425 w	
1380 m	1394 m	1380 m		1392 m				1425 w	
				1380 vw				1395 m	
				1365 vw				1368 w	
				1352 w				1375 m	
		1345 m		1320 w-m				1370 w	
		1328 w-m		1278 m					
		—							
1222 m	1222 m	1213 w						1294 w	$\eta^3$ -Allyl
								1232 s	
								1240 w	
								1220 vw	

1200 w	1190 w-m	1195 w	1098 w	1110 vs	1177 s	1193 m	1198 w	} $\eta^1$ -Allyl	$\eta^2$ -Allyl, $\nu_s(\text{CCC})$	$\eta^2$ -Allyl, $\nu_s(\text{CCC})$ { $\eta^1$ -1,1-( $\text{CH}_3$ ) <sub>2</sub> C <sub>3</sub> H <sub>3</sub> , $\nu(\text{C}-\text{C})$
—	1028 s	1098 } s 1090 } s	1053 vs	1113 w	1119 w	1113 m	1113 m			
1015 s	1018 s	1038 } m 1030 } m	1018 vs	1030 m 1000 m	1027 s	1038 s	1060 w 1002 vs			
949 m	935 m	1007 w 990 w	992 s 973 s	972 m	978 w	947 w				
936 w	880 s	927 m	885 s 840 s	915 s 876 w 840 s	890 m 865 s	878 w 862 m	878 w 862 m	} $\eta^2$ -Allyl	$\eta^2$ -Allyl	$\eta^2$ -Allyl
893 s	880 s	842 s	822 w 802 s	822 w 802 s	865 s	840 m	840 m			
726 m	745 m	790 } m 780 } m	785 } w 770 } w	746 } w-m 738 } w-m	726 m 672 m	722 w 670 m	702 w-m 737 m 720 w 680 w-m			{ $\nu(\text{PCH}_3)_3, \nu(\text{P}-\text{O})$
670 m	680 } m 672 } m	685 m-s	670 m 670 m	685 m	566 s 487 m	534 s 457 m	572 s			
563 m	482 s	520 m-s	466 m-s 444 s	592 s 475 m-s 445 s	420 w	440 w 420 s	440 w 420 s			
414 m	395 m	410 } m-s 400 } m-s	430 m 405 w-m	395 m-s	372 vs	365 vs	365 vs			Metal-Ligand
382 m	360 w	382 s	365 w	375 vs	372 vs	365 vs	358 m			vibrations
360 w	360 w	358 s	365 w	375 vs	344 vs	365 vs	358 m			+
350 w	336 vs	337 } s 330 } s	345 vs 335 s	345 vs	344 vs	365 vs	358 m			+
381 vs	280 w	280 w	270 w	280 w-m	295 w-m	250 m	295 w-m			Ligand
275 w	220 m	224 m	215 w-m	215 w-m	275 w	220 m	275 w			deformations
220 m	220 m	208 m	205 m	220 m	230 w	200 m	220 m			
205 w	195 m	188 s	188 s	220 m	230 w	200 m	202 m			

*(1,2,5,6-η-1,5-hexadiene)nickel tricyclohexylphosphine (III)*

$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$  (3.04 g, 21.70 mmol) in ether (23 ml) was added to  $\text{P}(\text{C}_6\text{H}_{11})_3$  (5.73 g, 20.45 mmol) in toluene (15 ml) at  $-78^\circ\text{C}$ . The solution was allowed to reach  $-15^\circ\text{C}$  and stirred for two days. The yellow precipitate was filtered off at  $-30^\circ\text{C}$ , washed with ether ( $2 \times 15$  ml) and dried under high vacuum. Yield: 6.75 g (78.3%). Analysis: Found Ni, 13.76; P, 7.52.  $\text{C}_{24}\text{H}_{43}\text{PNi}$  calcd.: Ni, 13.94; P, 7.35%. MW in benzene 450 (calcd. 421.3).

Reaction of a toluene solution of III with CO led to the displacement of hexa-1,5-diene (99.6% yield) with absorption of 2.99 mol CO/mol Ni. Hydrogenation in the presence of bis(cycloocta-1,5-diene)nickel as catalyst in THF led to the formation of n-hexane (96% yield) with absorption of 2.66 mol  $\text{H}_2$ /mol Ni.

*The crystal structure determination of I*

Since  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$  (I) was unstable at room temperature, crystals of the complex were recrystallized from pentane and mounted in Lindemann glass capillaries under an atmosphere of argon at  $-25^\circ\text{C}$ . The orange crystal chosen for data collection was transferred at this temperature to an Enraf-Nonius

TABLE 8

ANALYTICAL DATA FOR THE 1 : 1 ADDUCTS FORMED BY TERTIARY PHOSPHINES WITH  $(\eta^3\text{-ALLYL})_2\text{M}$  COMPLEXES

$(\eta^3\text{-allyl})_2\text{M}$	PR <sub>3</sub>	No. in Text	Colour (yield, %)	Analysis (calcd. (%))	
				M (Ni, Pd or Pt)	P
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	I	orange (90.6)	27.26 (27.06)	14.31 (14.28)
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_{11})_3$	II	orange (90.6)	14.00 (13.94)	7.37 (7.35)
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	IV	orange (78.4)	14.51 (14.56)	7.55 (7.68)
$(\eta^3\text{-2-CH}_3\text{-C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	—	orange (92.5)	23.72 (23.96)	12.56 (12.64)
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{C}_2\text{H}_5)_3$	VI	orange (88.8)	20.46 (20.40)	10.79 (10.79)
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_{11})_3$	—	orange (82.2)	13.14 (13.07)	7.12 (6.89)
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	VII	orange (79.2)	13.49 (13.62)	7.24 (7.18)
$(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	VIII	orange (93.6)	23.78 (23.96)	12.64 (12.64)
$(\eta^3\text{-1-iso-C}_3\text{H}_7\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	—	orange (91.8)	20.00 (20.31)	10.50 (10.71)
$(\eta^3\text{-1-C}_6\text{H}_5\text{C}_3\text{H}_4)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	—	red (91.1)	15.95 (15.90)	8.40 (8.39)
$(\eta^3\text{-1,1'-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	XI	orange (90.3)	23.46 (21.53)	11.20 (11.36)
$(\eta^3\text{-1,1'-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_{11})_3$	—	yellow (89.1)	12.40 (12.30)	6.61 (6.49)
$(\eta^3\text{-1,1'-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	—	yellow (87.8)	12.84 (12.79)	6.71 (6.75)
$(\eta^3\text{-1,3-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	IX, X	orange (91.8)	21.61 (21.53)	11.30 (11.36)
$(\eta^3\text{-1,3-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{C}_2\text{H}_5)_3$	—	orange (90.0)	18.49 (18.64)	9.77 (9.83)
$(\eta^3\text{-1,3-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_{11})_3$	—	yellow (90.2)	12.39 (12.30)	6.58 (6.49)
$(\eta^3\text{-1,3-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$	$\text{P}(\text{C}_6\text{H}_5)_3$	—	yellow (87.1)	12.51 (12.79)	6.55 (6.75)
$(\eta^3\text{-cyclohexenyl})_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	—	yellow (87.5)	22.00 (22.00)	11.00 (10.44)
$(\eta^3\text{-cycloheptenyl})_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	—	yellow (88.0)	17.95 (18.08)	9.50 (9.54)
$(\eta^3\text{-cyclooctenyl})_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	—	yellow (89.0)	16.91 (16.62)	8.68 (8.77)
$(\eta^3\text{-C}_{12}\text{H}_{18})_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	XIII	red liquid		
$(\eta^3\text{-C}_9\text{H}_{12})_2\text{Ni}$	$\text{P}(\text{CH}_3)_3$	XIV	red (75)	21.60 (23.0)	
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$	$\text{P}(\text{CH}_3)_3$	XV	pale yellow (91.1)	40.36 (40.21)	12.00 (11.71)
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$	$\text{P}(\text{C}_6\text{H}_{11})_3$	—	pale yellow (88.8)	22.60 (22.64)	6.50 (6.59)
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pd}$	$\text{P}(\text{C}_6\text{H}_5)_3$	—	yellow (91.1)	23.65 (23.60)	6.62 (6.87)
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pd}$	$\text{P}(\text{CH}_3)_3$	—	pale yellow (93.4)	36.25 (36.35)	10.25 (10.58)
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$	$\text{P}(\text{CH}_3)_3$	XVI	white (93.2)	55.20 (55.21)	8.40 (8.76)
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Pt}$	$\text{P}(\text{CH}_3)_3$	—	white (94.4)	51.00 (51.15)	8.00 (8.12)



CAD-4 automatic diffractometer equipped with a gas flow (N<sub>2</sub>) low temperature device. The crystal was maintained at a temperature of  $-170^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$  during the course of the data collection. Intensities were measured by a coupled  $\theta-2\theta$  technique with scan speeds varying from  $1.3-10.0^{\circ}\text{min}^{-1}$ , depending on the standard deviation to intensity ratio of a preliminary  $10^{\circ}\text{min}^{-1}$  scan. The intensity of a reflection and its standard deviation were calculated from  $INT-2(BGL+BGR)$  and  $(INT-4(BGL+BGR))^{1/2}$  respectively, where  $INT$ ,  $BGL$  and  $BGR$  are the peak intensity, the left and the right backgrounds, and the time spent measuring the background was half that taken to measure the peak. A Zr filter was inserted in front of the detector if the peak count was greater than  $50,000\text{ counts sec}^{-1}$ . The intensities of three monitor reflections remeasured after every 90 minutes of X-ray exposure showed no significant variation during the course of data collection. Intensities were corrected for Lorentz polarisation and absorption effects [21]. Pertinent crystal data is given in Table 9; the cell parameters were obtained by a least-squares fit to the  $\theta$  values of 75 automatically centred reflections ( $8 < \theta < 32^{\circ}$ ).

The structure was solved by Patterson (Ni and P) and Fourier methods (C and H). Refinement was by blocked least-squares, and Ni, P and C were allowed anisotropic thermal motion. The  $z$  fractional coordinate for Ni<sub>1</sub> was fixed at 0.0815 during refinement to emphasize the pseudo-centrosymmetric relationship between molecule 1 and molecule 2 (the molecules, whose fractional coordinates are given in Table 9, are related by a pseudo centre of symmetry at  $0.25a$ ,  $0.72b$ ,  $0.50c$  where  $a$ ,  $b$  and  $c$  are the unit cell vectors). Refinement with 5042 observed reflections [ $I > 2.0\sigma(I)$ ] resulted in a final  $R = 0.055$

TABLE 9

CRYSTALLOGRAPHIC DATA FOR  $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$  (I)

$\text{C}_9\text{H}_{19}\text{NiP}$	$M = 216.9$ a.m.u.
Crystal size: $0.51 \times 0.38 \times 0.31$ mm	Crystal system, orthorhombic
Crystals shape: faced defined by $\{100\}$ , $\{01-1\}$ and $\{011\}$	Space group $Pca2_1$
$a$ 20.110(11) Å	$F_{000} = 928$ e
$b$ 6.247(3) Å	$V$ 2215.1 Å <sup>3</sup>
$c$ 17.632(6) Å	$T$ $-170^{\circ}\text{C}$
$Z = 8$	
$D_c = 1.30$ gcm <sup>-3</sup>	
Monochromated (graphite) Mo- $K_{\alpha}$ X-radiation: $\lambda$ 0.71069 Å	
Reflections measured 8178 [ $\pm h, k, l$ ]	Take off angle: $\theta = 6.15^{\circ}$
$\mu(\text{Mo}-K_{\alpha}) = 18.31$ cm <sup>-1</sup>	$\theta$ limits: $1.0 < \theta < 40.0^{\circ}$
Absorption correction: Gaussian	$\theta - 2\theta$ scan technique (43 steps)
Integration with 343 sampling points	Horizontal detector aperture:
Crystal volume 0.132 mm <sup>3</sup>	3.2 + 1.25 tan $\theta$ mm
Transmission: max 0.161	Vertical aperture: 4.0 mm
min 0.476	( $\Omega$ )-scan range $0.7 + 0.35 \tan \theta$
$\sigma(I) = (\sigma(I)_{\text{poisson}}^2 + (Ik)^2)^{1/2}/2F$ , $k = 0.02$	
Number of variables ( $P$ ) 351	
observed reflections ( $N$ ) 5042, $I > 2.0\sigma(I)$	
$R = 0.055$	
$R' (\omega = 1/\sigma^2(F_0)) = 0.048$	
$(\Sigma\omega( F_0  -  F_c )^2)^{1/2}/(N - P) = 1.9$	
$R = 1.0120$	
$R1,4691,0.005 = 1.0009$	

TABLE 10

FINAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS ( $\times 10^4$ )

Atom	x	y	z
Ni <sub>1</sub>	150(1)	4617(1)	815(1)
Ni <sub>2</sub>	2356(1)	9792(1)	9257(1)
P <sub>1</sub>	-526(1)	5607(1)	1743(1)
P <sub>2</sub>	3030(1)	8871(1)	8317(1)
C <sub>1</sub>	-320(2)	5814(8)	-153(2)
C <sub>2</sub>	-87(2)	3713(7)	-236(2)
C <sub>3</sub>	-323(2)	2120(7)	267(2)
C <sub>4</sub>	929(2)	6722(7)	991(2)
C <sub>5</sub>	1144(2)	4589(7)	358(2)
C <sub>6</sub>	909(2)	2989(7)	1348(2)
C <sub>7</sub>	-281(2)	4943(8)	2719(2)
C <sub>8</sub>	-1379(2)	4542(7)	1744(4)
C <sub>9</sub>	-697(2)	8482(7)	1821(3)
C <sub>10</sub>	1457(2)	8453(7)	8914(2)
C <sub>11</sub>	1405(2)	10582(6)	9177(2)
C <sub>12</sub>	1772(2)	12214(7)	8817(2)
C <sub>13</sub>	2960(2)	11503(8)	9986(2)
C <sub>14</sub>	2575(2)	9960(8)	10359(2)
C <sub>15</sub>	2652(2)	7788(7)	10137(2)
C <sub>16</sub>	3886(3)	9883(8)	8331(4)
C <sub>17</sub>	3166(2)	5999(8)	8197(3)
C <sub>18</sub>	2756(2)	9685(8)	7360(2)
H <sub>1A</sub>	-91(26)	6846(85)	-467(29)
H <sub>1B</sub>	-805(25)	5961(79)	15(28)
H <sub>2</sub>	322(23)	3256(69)	-608(24)
H <sub>3A</sub>	-125(24)	822(76)	320(29)
H <sub>3B</sub>	-799(22)	2243(67)	468(24)
H <sub>4A</sub>	1124(30)	7739(90)	680(37)
H <sub>4B</sub>	923(24)	7188(78)	1524(29)
H <sub>5</sub>	1379(23)	4117(73)	392(26)
H <sub>6A</sub>	1060(22)	1626(73)	1251(23)
H <sub>6B</sub>	874(21)	3313(71)	1881(25)
H <sub>7A</sub>	-294(28)	3364(85)	2741(31)
H <sub>7B</sub>	143(20)	5402(68)	2828(23)
H <sub>7C</sub>	-609(25)	5616(78)	3151(29)
H <sub>8A</sub>	-1604(28)	5089(79)	1302(30)
H <sub>8B</sub>	-1405(24)	3179(82)	1836(31)
H <sub>8C</sub>	-1630(25)	5142(75)	2199(27)
H <sub>9A</sub>	-300(36)	9271(102)	1963(42)
H <sub>9B</sub>	-1004(32)	8887(105)	1385(36)
H <sub>9C</sub>	-980(28)	8805(91)	2320(31)
H <sub>10A</sub>	1490(25)	7891(81)	8389(29)
H <sub>10B</sub>	1260(26)	7144(79)	9170(30)
H <sub>11</sub>	1220(21)	10943(70)	9638(24)
H <sub>12A</sub>	1769(19)	13664(63)	9066(20)
H <sub>12B</sub>	1839(27)	12261(80)	8317(31)
H <sub>13A</sub>	2802(26)	13108(89)	10093(31)
H <sub>13B</sub>	3328(28)	11341(93)	9844(32)
H <sub>14</sub>	2196(24)	10463(75)	10682(27)
H <sub>15A</sub>	2341(24)	6752(78)	10329(27)
H <sub>15B</sub>	3036(28)	7153(83)	10035(32)
H <sub>16A</sub>	3898(26)	11651(88)	8444(29)
H <sub>16B</sub>	4110(28)	9266(81)	8836(31)
H <sub>16C</sub>	4122(29)	9034(88)	7860(31)
H <sub>17A</sub>	3389(33)	5473(87)	8627(36)
H <sub>17B</sub>	2752(29)	5316(79)	8273(36)
H <sub>17C</sub>	3415(29)	5564(80)	7849(32)
H <sub>18A</sub>	2285(25)	8788(86)	7303(27)
H <sub>18B</sub>	2750(25)	11223(86)	7256(26)
H <sub>18C</sub>	3070(30)	8895(92)	6986(33)

( $R'(\omega = 1/\sigma^2(F_0)) = 0.048$ ) at a data variable ratio of 14.4. The quantity minimised was  $\Sigma\omega(F_0 - F_c)^2$  with  $\omega = 1/\sigma^2(F_0)$ . In the final refinement cycle the mean shift to error ratio was 0.005, and the final Fourier synthesis was essentially featureless except for several peaks ( $\leq 0.8 \text{ e}\text{\AA}^{-3}$ ) in the vicinity of the nickel and phosphorus atoms. Neutral atom scattering factors for all non-hydrogen atoms were those of Cromer and Waber [23] while the best spherical scattering factors were used for hydrogen [24]. The real and imaginary components of the anomalous scattering factors for Ni and P were included in the structure factor calculation [25]. Final positional and thermal parameters appear in Table 10. A list of observed and calculated structure amplitudes is obtainable from the authors (C.K.).

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