

TRANSITION METAL ALLYLS

VI *. THE STOICHIOMETRIC REACTION OF 1,3-DIENES WITH LIGAND MODIFIED ZEROVALENT-NICKEL SYSTEMS **

R. BENN, B. BÜSSEMEIER ***, S. HOLLE, P.W. JOLLY*, R. MYNOTT, I. TKATCHENKO ‡ and G. WILKE

Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a. d. Ruhr (F.R.G.)

(Received March 26th, 1984)

Summary

Butadiene and methyl substituted 1,3-dienes react with zerovalent-nickel-ligand complexes in a stoichiometric manner to give octadienediynickel-ligand complexes. The structure, rearrangement and reactions with CO and P-donor ligands of these species have been studied with the help of ^1H and ^{13}C NMR spectroscopy. The results provide an insight into the mechanism of the nickel-catalysed cyclodimerization of 1,3-dienes.

Introduction

It has been plausibly argued that octadienediynickel-ligand species are involved as intermediates in the nickel-catalysed cyclodimerization of 1,3-dienes [1]. We isolated examples of these species over a decade ago by reacting 1,3-dienes in a stoichiometric manner, at low temperature, with zerovalent-nickel-ligand complexes. Although essential information has been made available in the form of short communications and a doctoral thesis [2–7], thereby allowing general access to these systems (see, for example, [8] and [9]), an in extenso publication is overdue.

We report herein the present state of our investigations concerning the preparation, structure and reactions of the octadienediynickel-ligand complexes and discuss their relevance to the catalytic cyclodimerization of 1,3-dienes.

* For part V see ref. 22.

** Dedicated to Prof. Jack Halpern on the occasion of his 60th birthday.

*** Present address: Ruhrchemie AG, D-4200 Oberhausen (F.R.G.).

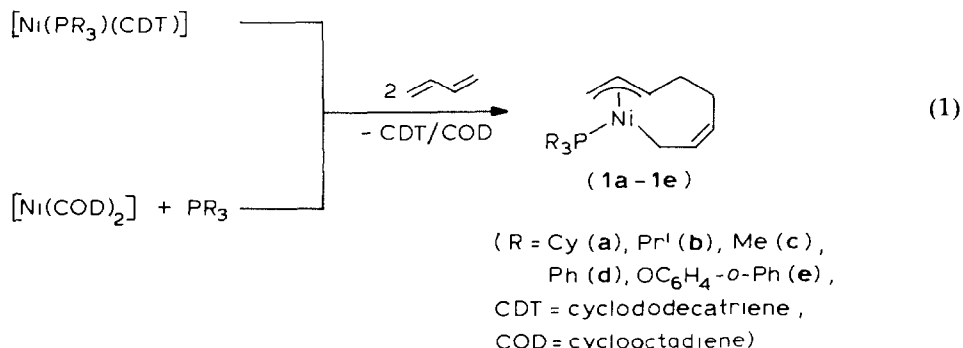
‡ Present address: Institut de Recherches sur la Catalyse, CNRS, 2 Avenue Einstein, 69626 Villeurbanne (France).

Results

1. Reactions involving butadiene

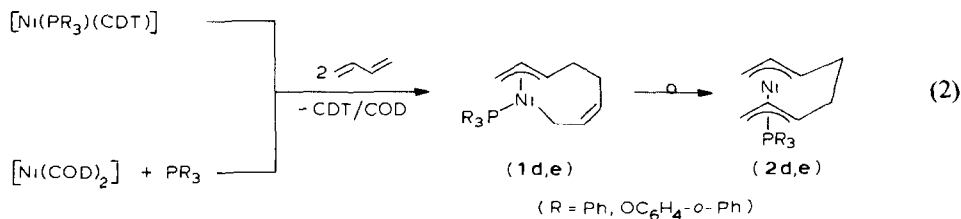
The structure of the product of the reaction of butadiene with ligand-stabilized zerovalent-nickel complexes is dependent upon the nature of the ligand.

In the presence of the bulky, basic phosphines tricyclohexylphosphine and



triisopropylphosphine, complexes **1a,b** containing an η^1, η^3 -octadienediyl group could be isolated (eq. 1). An analogous reaction when carried out in the presence of the less bulky trimethylphosphine resulted in the formation of a mixture of complexes which was shown by ¹³C NMR spectroscopy to consist of 85% of the expected η^1, η^3 -octadienediylnickel complex (**1c**) and 15% of a symmetrical η^3, η^3 -octadienediylnickel species (**2c**), presumably structurally related to the examples discussed below. This mixture showed no tendency to isomerize on warming a sample from -30 to its decomposition point at $+60^\circ\text{C}$.

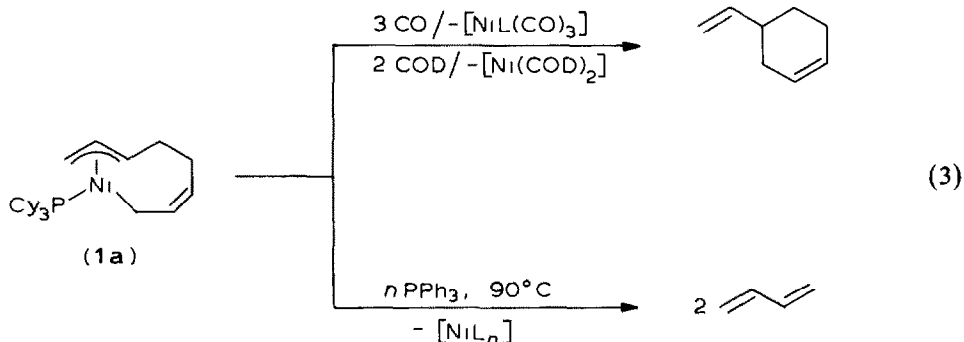
The initial product of the low-temperature reaction of butadiene with zerovalent-nickel complexes stabilized by the less basic ligands triphenylphosphine and tri-*o*-biphenylphosphite also contains an η^1, η^3 -octadienediyl group (**1d,e**), which, however, rearranges irreversibly at temperatures above -10°C to give complexes **2d,e** containing a symmetrical η^3, η^3 -octadienediyl group. NMR evidence (presented in section 2) indicates that the η^3 -allyl groups in this moiety are *syn*-substituted (eq. 2) and that the structure resembles that of $[\text{Ni}(\text{PMe}_3)(\eta^3\text{-C}_3\text{H}_5)_2]$, which has been studied by X-ray crystallography [10]. At room temperature the η^3, η^3 -octadienediyl species



reacts further, with ring closure, to give cyclooctadienenickel complexes: $[\text{Ni}(\text{COD})_2]$ (and presumably $[\text{Ni}(\text{PPh}_3)_2]$) in the case of triphenylphosphine and a mixture of $[\text{Ni}(\text{COD})_2]$ and $[\text{Ni}(\text{PR}_3)_2(\text{COD})]$ (**3**) in the case of the phosphite.

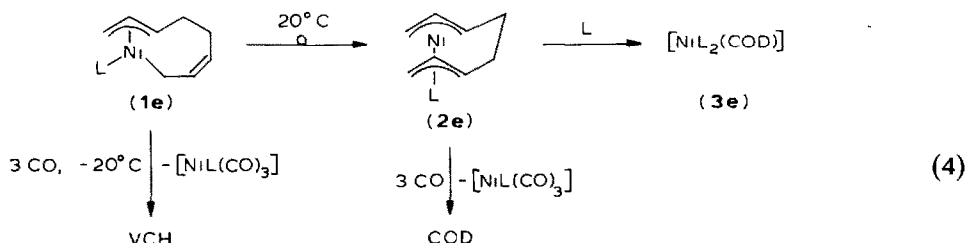
The suggested structures for the various complexes mentioned above have been established by the NMR results discussed in a following section and are supported by a number of chemical reactions. For example, treatment of $[\text{Ni}(\text{PCy}_3)(\eta^1, \eta^3\text{-}$

$C_8H_{12}]$ (**1a**) with CO at $-78^\circ C$ in toluene results in the absorption of 3 equiv. of CO to give $[Ni(PCy_3)(CO)_3]$ with quantitative liberation of vinylcyclohexene (VCH). Similar behaviour is observed in the reaction with 1,5-cyclooctadiene at $50^\circ C$ (eq. 3).

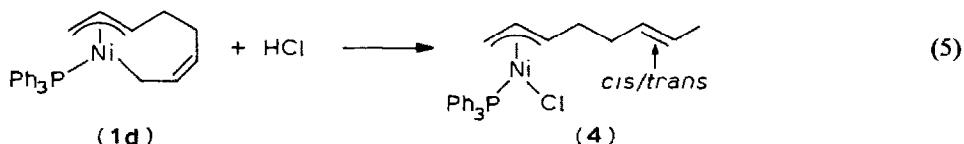


In contrast, reaction with excess triphenylphosphine at $90^\circ C$ leads to the almost exclusive liberation of butadiene.

The product of the reaction of the tris-*o*-biphenylphosphite complex with CO is, as one would expect, temperature-dependent (eq. 4): at $-20^\circ C$ (at which temperature an $\eta^1, \eta^3-C_8H_{12}$ arrangement (**1e**) is present) vinylcyclohexene is practically the only organic product whereas treatment of a sample which has been allowed to reach room temperature briefly (and which will have structure **2e**) gives mainly 1,5-cyclooctadiene. Furthermore, if one equivalent of tris-*o*-biphenylphosphite is added to an ethereal solution at $-30^\circ C$ and the reaction mixture is allowed to reach room temperature, then $[Ni\{P(OC_6H_4-o-Ph)_3\}_2(COD)]$ (**3e**) is formed in 89% yield.



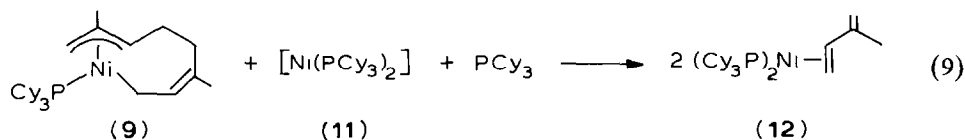
Analogous behaviour is observed for the triphenylphosphine-stabilized complexes: reaction with CO at $-78^\circ C$ leads to displacement of vinylcyclohexene, whereas at $25^\circ C$ a mixture of 1,5-cyclooctadiene, divinylcyclobutane and vinylcyclohexene is formed (23/20/57) in a total yield of 66%. Butadiene (77%) is liberated on treatment of an ethereal solution at $-70^\circ C$ with excess triphenylphosphine and is accompanied with the formation of $[Ni(PPh_3)_4]$ (96%). Hydrogenation in benzene at room temperature in the presence of Raney-nickel leads to the formation of a 2/1 mixture of butane and *n*-octane in 52% yield. The isomer containing the $\eta^1, \eta^3-C_8H_{12}$ moiety (**1d**) reacts with HCl at $-30^\circ C$ to give the triphenylphosphine-stabilized η^3 -allylnickel-chloro complex (**4**) in which partial isomerization of the expected *cis*-double bond has occurred, as indicated by 1H NMR spectral evidence (eq. 5).



3,7-positions, is apparently not formed. The crystal structure of $[\text{Ni}(\text{PCy}_3)(\eta^1, \eta^3\text{-2,6-Me}_2\text{C}_8\text{H}_{10})]$ (**9**) has been confirmed by an X-ray structural determination [4].

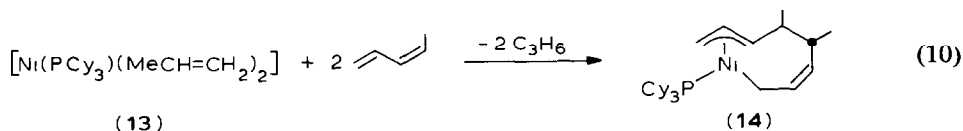
Analogous reactions have been carried out in the presence of PMe_3 , PPr_3^i , PPh_3 and $\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3$ but only in the cases of PMe_3 and PPr_3^i has the initial formation of a complex related to **8** been observed; in the other cases the product consists of one of the other two isomers or a mixture of both. The ratio of the 2,6- and 2,7-substituted complexes in the final reaction mixture is apparently ligand-dependent, being 75/25 for PCy_3 , 70/30 for $\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3$ and 50/50 for PMe_3 whereas only the 2,6-isomer has been detected in the systems involving PPr_3^i and PPh_3 . However, these ratios are somewhat dependent upon the experimental conditions.

As expected, treatment of **9** with CO at -30°C leads to ring closure to give dipentene (89%) as well as $[\text{Ni}(\text{PCy}_3)(\text{CO})_3]$. The reaction with excess triphenylphosphine at 90°C , in contrast, results in practically quantitative cleavage of the C_8 -chain to give isoprene. A related reaction is observed upon treatment with tricyclohexylphosphine and bis(tricyclohexylphosphine)nickel (**11**) [12] from which the bis-ligand nickel isoprene complex (**12**) may be isolated in high yield (eq. 9). The reaction of **12** with excess isoprene leads to regeneration of **9**.



3. Reactions involving piperylene

The reaction of *cis*-piperylene with zerovalent-nickel-ligand complexes is complicated by the isomerization to *trans*-piperylene which is known to be catalyzed by nickel. A partial crystal structure determination (slow decomposition in the X-ray beam prevented exact determination of bond lengths and angles [7]) of the product (**14**) of the reaction involving tricyclohexylphosphine-nickel(bis- η^2 -propene) (**13**) established the presence of an η^1, η^3 -dimethyloctadienediyl group as well as the *trans*-arrangement of the methyl groups bonded to C(4) and C(5) (eq. 10). However,

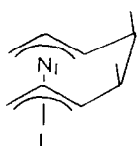


a ^{13}C NMR spectrum of the crude reaction mixture shows that at least three other components are present, all of which contain the η^1, η^3 -octadienediyl group. The exact nature of these species is not known but they are presumably the product of the head-head, head-tail or tail-tail dimerization or codimerization of the piperylene isomers.

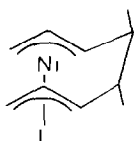
trans-Piperylene reacts with tricyclohexylphosphine-modified systems to give an orange-red crystalline solid whose ^{31}P NMR spectrum shows it to consist, in solution, of a mixture of isomers. The ^{13}C NMR spectrum suggests that the main isomer contains an η^1, η^3 -dimethyloctadienediyl arrangement (nickel-bonded carbon absorption at 8.5 ppm, $J(\text{C}, \text{P})$ 13.8 Hz), while reaction of the mixture of isomers with excess triphenylphosphine at 100°C leads to liberation of *trans*-piperylene

(62%) and *trans*-3,4-dimethyl-1,5-cyclooctadiene (8%) and only traces of *cis*-piperylene.

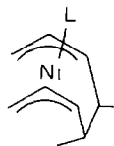
In contrast to the reactions involving PCy_3 , those between *cis*- or *trans*-piperylene and zerovalent-nickel-ligand complexes modified by trimethylphosphine and triphenylphosphine lead predominantly to species containing η^3, η^3 -dimethyloctadienediyl groups. The main product of the reaction between *cis*-piperylene and PPh_3 -modified systems has been shown by NMR spectroscopy to have a symmetrical structure (one possibility is **15**) while that between *cis*-piperylene and PMe_3 -modified systems or between *trans*-piperylene and PMe_3 - or PPh_3 -modified systems gives complexes in which all ten carbon atoms of the organic ligand are magnetically inequivalent. A variety of structures meet this requirement, e.g. **16** and **17**. Although a final decision has still to be made, the ^1H NMR data discussed below is the most consistent with *syn*-substitution of the η^3 -allyl groups.



(15)



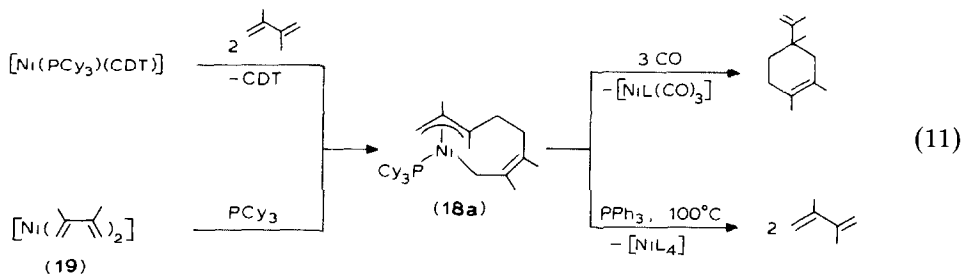
(16)



(17)

4. Reactions involving 2,3-dimethylbutadiene

Reactions of 2,3-dimethylbutadiene with zerovalent-nickel complexes modified by tricyclohexylphosphine or trimethylphosphine lead to complexes containing an η^1, η^3 -2,3,6,7-tetramethyloctadienediyl group (**18a,b**). The tricyclohexylphosphine derivative has also been prepared by reacting bis(η^4 -2,3-dimethylbutadiene)nickel (**19**) with the phosphine (eq. 11) [13]. This complex reacts with CO and excess triphenylphosphine in a manner analogous to that observed for the other members of the series: the reaction with CO leads to liberation of 2,4-dimethyldipentene (65%) as well as 2,3-dimethylbutadiene (12.6%) while the diene is practically the sole product (90.3%) of the reaction with triphenylphosphine at 100°C .



(11)

Discussion

Although the stoichiometric reactions described above lead to well-defined products under relatively mild conditions (-30 to 0°C) it should not be automatically assumed that these are necessarily involved as intermediates in the catalytic dimerization of 1,3-dienes at 60 to 80°C . Bearing in mind that the complexes can be

formed in either thermodynamically or kinetically controlled reactions and, where several intermediates are involved, that having the highest reactivity would be present in lowest concentration, we should perhaps at best regard the isolated complexes as good models for individual steps in the catalytic cycle. Some idea of the possible complexity of the catalytic system can be gained by consulting the publications of Heimbach and co-workers [14].

The principle differences between the stoichiometric and catalytic reactions are the reaction temperature and the concentration of the nickel component. In addition, in the catalytic systems, the reactant and products are generally present in high concentrations and will presumably occupy vacant coordination sites on the metal.

Needless to say, the isolated complexes are certainly not involved in the transition state of the final C–C coupling step. However, the geometry of the C₈-fragment may well be maintained in the various catalytic intermediates and a simplified, schematic mechanism for the cyclodimerization of butadiene, which takes into account our results, and which implicates five-coordinate complexes, is shown in Fig. 1; the squares indicate sites which are presumably occupied by the reactant (butadiene) or products (COD, DVCB, VCH). Although a bis(butadiene)nickel-ligand species has never been isolated, bis(mono-olefin)nickel-ligand complexes are well known [1,2]. The mechanism by which the two complexed butadiene molecules couple is still the source of speculation. An early suggestion was that the coupling reaction occurs outside the complex sphere and is instigated by at least partial separation of the non-complexed olefinic electrons [1a]. The geometry of the product of the reactions involving substituted 1,3-dienes may be understood by applying the metallalogy

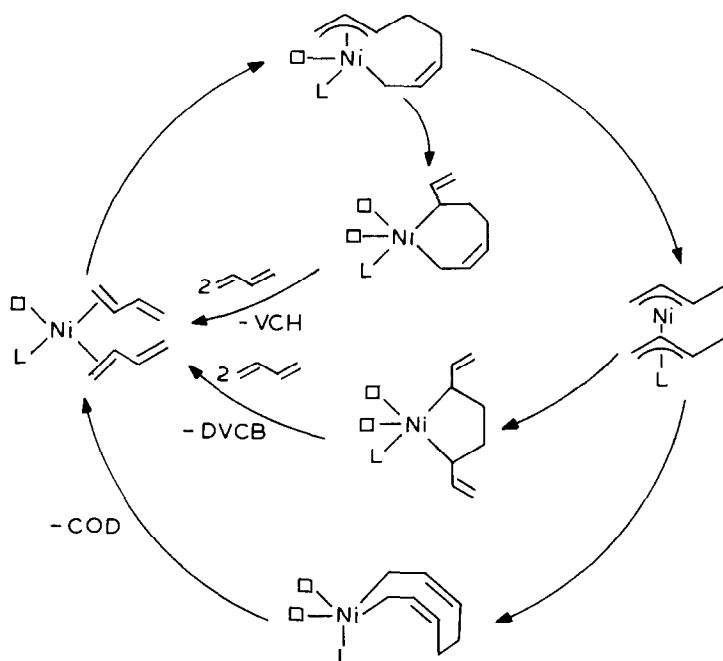
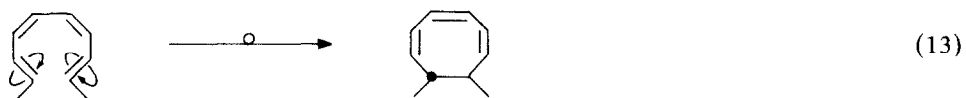
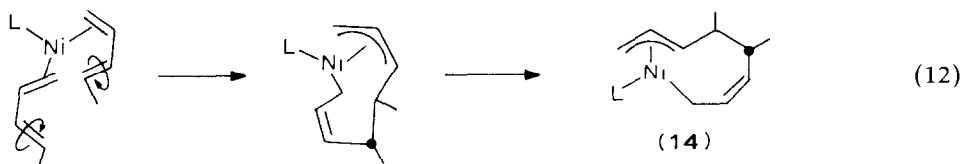


Fig. 1. A schematic mechanism of the Ni-ligand catalysed cyclodimerization of butadiene (VCH = vinylcyclohexene; DVCB = *cis*-1,2-divinylcyclobutane; COD = cyclooctadiene).

principle introduced by Heimbach [14]: the reaction of *trans*-piperylene to give **14** can be formulated as a conrotatory process (eq. 12) analogous to the thermal cyclization of dimethyloctatetraene to give *trans*-7,8-dimethylcycloocta-1,3,5-triene (eq. 13) [15].

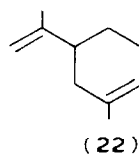
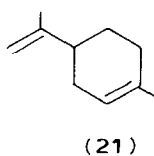
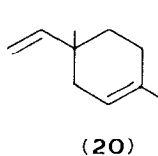


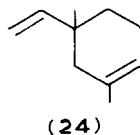
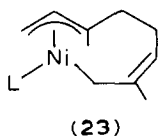
The final ring-closure step in the catalytic cycle may reasonably be supposed to involve a bis- η^1 -allyl-nickel species whose structure determines the nature of the product. Initially, the cyclic dimer formed will remain complexed to nickel until displaced by butadiene molecules. Conventional wisdom ascribes the geometry of the double bonds (*trans* or *cis*) in these intermediates and in the product to the *syn* or *anti* arrangement of the allyl groups directly involved (necessary interconversion proceeding through η^1 -allylnickel species in the familiar manner).

It is, perhaps, surprising that the initial product of the reaction with less basic phosphines, e.g. PPh_3 , $\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3$, has an η^1, η^3 -arrangement of the octadienediyl moiety (**1d,e**) which then rearranges to the η^3, η^3 -form (**2d,e**). Presumably the former is the product of a kinetically controlled reaction and the latter is thermodynamically more stable. The reverse reaction – the conversion of an η^3 -allyl group into its η^1 -allyl form in the presence of donor ligands – is well-documented [10].

The suggestion that the mechanism of the formation of DVCB is related to those of COD and VCH is supported by the observation that the isolated $[\text{Ni}(\text{PR}_3)_2(\text{DVCB})]$ complexes (**6**) rearrange at room temperature to give octadienediylnickel species in which the conformation of the organic group is dependent upon the nature of the donor-ligand in a predictable manner.

Additional support for the suggested intermediacy of octadienediylnickel species in the catalytic processes is found in the structures of the complexes isolated from the reactions involving methyl-substituted dienes. In the case of isoprene, the three dimethyloctadienediylnickel complexes **8–10** isolated from the reaction involving tricyclohexylphosphine can be regarded as precursors of the dipentene isomers **20–22**, which are indeed generated in the catalytic reaction; the fourth possible nickel complex (**23**) is not observed in the stoichiometric reaction nor has the associated cyclic dimer (**24**) ever been detected in the catalytic reaction [1,11].





The interconversion of **8** into **9** and **10** necessarily involves cleavage of the C(4)–C(5) bond of the octadienediyl chain followed by rearrangement of the bis(isoprene)nickel-ligand intermediate. That facile cleavage of this bond can indeed occur is demonstrated by the liberation of the appropriate 1,3-diene on treatment of these organonickel complexes with excess phosphine (see above). This is undoubtedly related to the observation that the nickel-ligand catalyzed rearrangement of DVCB (or dimethyl-DVCB) to VCH and COD is accompanied by the liberation of considerable quantities of butadiene (or piperylene) [16,17].

NMR Investigations

The data from the ^1H and ^{13}C NMR spectra of the complexes discussed previously have been brought together in Tables 1–4 (^1H NMR) and Tables 5–10 (^{13}C NMR). The assignments were made with the aid of established techniques such as off-resonance decoupling, gated decoupling, intensity measurements, homo-decoupling, saturation transfer as well as comparison of data with those for known compounds, and we limit ourselves here to a discussion of the more unusual results.

The ^1H NMR spectra of the various octadienediylnickel-ligand complexes have not been investigated in as much detail as the ^{13}C NMR spectra, which are in general easier to analyse. However, examples of each type of complex have been studied and a perusal of the data assembled in Tables 1–4 indicates the usefulness of high-field spectrometers; in some cases, spectra measured at 270 or 400 MHz have provided additional information which has allowed an unequivocal assignment to be made.

Diagnostic in the ^1H NMR spectra of the various η^1, η^3 -octadienediylnickel complexes listed in Tables 1 and 3 are the characteristic shifts of the *syn*- and *anti*-protons and the magnitude of the vicinal coupling constants $^3J(1,5)$ (data for vicinal *syn*- and *anti*-protons have been presented in ref. 18) and $^3J(10,11)$ (~ 8 Hz). The latter, together with the chemical shifts, indicates that the *cis*-double bond in the chain does not interact directly with the metal atom.

In the case of $[\text{Ni}(\text{PPh}_3)(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ (**1d**), it proved possible to assign all 12 protons in the C_8 -chain and to determine all the vicinal coupling constants (Table 1 and Fig. 2). These data indicate that the molecule adopts the conformation shown in the figure, in which the double bond and the *meso*-carbon atom of the η^3 -allyl group are on the same side of the molecular plane. Characteristic of this arrangement are the relatively large coupling constants $^3J(5,7)$, $^3J(7,8)$ and $^3J(8,10)$, which is an indication that these pairs of protons adopt an essentially *anti*-parallel arrangement.

A detailed ^1H NMR study also enabled the conformation of the symmetrical octadienediyl chain in $[\text{Ni}(\text{PPh}_3)(\eta^3, \eta^3\text{-C}_8\text{H}_{12})]$ (**2d**) to be assigned (Table 2 and Fig. 3). The symmetrical arrangement of the chain follows from the observation of only five multiplets for the protons (the signals $\delta(\text{H}(6))$ and $\delta(\text{H}(7))$ are degenerate even at 400 MHz). The vicinal coupling constant between the *meso*-proton H(1) and *anti*-proton H(4) is surprisingly low ($^3J(1,4)$ 10 Hz); however, comparison with published data [18] suggests that this is the result of an alteration in the geometry of

(Continued on p. 75)

TABLE 1

¹H NMR DATA FOR η¹,η³-OCTADIENEDIYLNICKEL-PR₃ COMPLEXES **1a-1e** (R = Cy (a), Ph (b), Me (c), Prⁱ (d), OC₆H₄-*o*-Ph (e)) FORMED IN REACTIONS INVOLVING BUTADIENE^a

δ (ppm) ^c	1c ^b (T = 38°C)	1b ^c (T = 40°C)	1a ^b (T 27°C)	1e ^b (T = 30°C)	1d ^d (T = 33°C)
δ ₁	4.08 (³ J(1,4) ~ ³ J(1,5) 12.9, ³ J(1,2) 7.4)	4.13	4.13 (³ J(1,4) 12.5, ³ J(1,2) 7.8)	3.49 (³ J(1,4) ~ ³ J(1,5) 12.8, ³ J(1,2) 7.4)	4.26 (³ J(1,2) 7.9, ³ J(1,4) 13.3, ³ J(1,5) 12.9)
δ ₂	2.53 (³ J(1,2) 7.4, ³ J(P,2) ~ 1.0)	2.54	2.56 (³ J(1,2) 7.6)	2.46 (³ J(2,1) 7.4)	2.57 (³ J(2,4) 2.0)
δ ₄	1.57 (³ J(1,4) 13.1)	-	-	(1.65)	1.82 (⁴ J(4,5) ~ 1.0)
δ ₅	-	-	-	-	2.60 (³ J(5,6) 5.6, ³ J(5,7) 10.0)
δ ₆	-	-	-	-	2.24 (³ J(6,7) 13.0, ³ J(6,8) 2.6, ³ J(6,9) 5.8)
δ ₇	-	-	-	0.44	1.06 (³ J(7,8) 12.6, ³ J(7,9) 2.5)
δ ₈	-	-	-	1.41	1.88 (³ J(8,9) 12.8, ³ J(8,10) 8.0, ⁴ J(8,11) 1.8)
δ ₉	-	-	-	-	2.51 (³ J(9,10) 8.3)
δ ₁₀	4.95 (³ J(10,11) 7.5, ³ J(10,9/8) 8.3)	5.16	5.02 (³ J(10,11) 8.4, ³ J(10,9/8) 7.9)	4.68 (³ J(10,11) 8.5, ³ J(10,9/8) ~ 8)	~ 5.03
δ ₁₁	6.07 (³ J(11,10) 7.4, ³ J(11,12/13) 9.9)	6.15	6.02 (³ J(11,10) 8.4, ³ J(11,12/13) 9.6)	4.89 (³ J(11,10) 8.5, ³ J(11,12/13) ~ 9.5)	5.78 (³ J(11,10) 9.6, ³ J(11,12) 10.8, ³ J(11,13) 7.3)
δ ₁₂	-	-	-	-	2.01 (³ J(12,13) 6.2)
δ ₁₃	-	-	-	0.89(?)	1.71 (³ J(13,P) ~ 0.5)
Δ _R	0.78 (² J(P,H) 7.8)	0.95(Me)	-	-	7.49(<i>o</i> -H) 7.02(<i>m</i> , <i>p</i> -H)

^a Measured in toluene-d₈. ^b Bruker WH 270 spectrometer. ^c Bruker WH 80 spectrometer. ^d Bruker WH 400 spectrometer. ^e

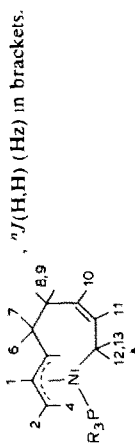


TABLE 2

¹H NMR DATA FOR η^3, η^3 -OCTADIENEDIYLNICKEL-PR₃ COMPLEXES **2d** AND **2e** (R = Ph (**d**), OC₆H₄-*o*-Ph (**e**)) FORMED FROM BUTADIENE ^a

δ (ppm) ^b	2d ^c (T 0°C)	2e ^d (T -30°C)
δ_1	5.04 (³ J(1,P) 4.7, ³ J(1,2) 7.0, ³ J(1,4) 12.0, ³ J(1,5) 10.0)	4.35 (³ J(1,P) 6.4, ² J(1,2) 6.6, ³ J(1,4) 12.6; ³ J(1,5) 9.6)
δ_2	3.06 (³ J(2,P) 2.0)	2.25 (³ J(2,1) 6.6)
δ_4	1.50 (³ J(4,P) 14.0, ⁴ J(4,5) 0.6)	1.15 (³ J(4,1) 12.6, ³ J(4,P) 18.4)
δ_5	3.03 (³ J(5,P) 14.0)	2.76
δ_6	} 2.16 (J(6/7,P) 0, ³ J(5,6/7) 10.4)	} 1.76
δ_7		
δ_R	7.58(<i>o</i> -H) 7.05(<i>m, p</i> -H)	

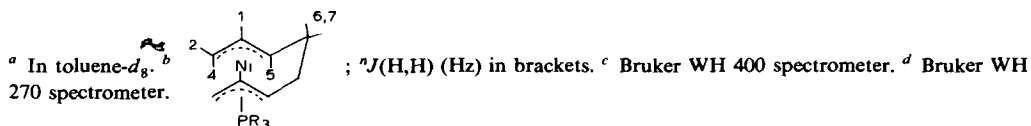


TABLE 3

¹H NMR DATA FOR η^1, η^3 -DIMETHYLOCTADIENEDIYLNICKEL-PR₃ COMPLEXES **8** AND **9** (R = Cy) FORMED IN REACTIONS INVOLVING ISOPRENE ^a

δ (ppm) ^b	(8) (T -20°C)	(9) (T 0°C)
δ_1	4.26 (³ J(1,2) 8.1)	(1.45)
δ_2	2.47 (³ J(1,4) 13.2)	2.41
δ_5	(1.20)	2.71 (³ J(5,6/7) ~ 6, ³ J(5,P) ~ 7)
δ_{10}	1.86	1.79
δ_{11}	5.69 (³ J(11,12/13) ~ 9)	5.82
δ_{12}	} 1.2	-
δ_{13}		

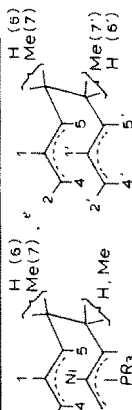
^a In toluene-*d*₈; Bruker WH 270 spectrometer. ^b ⁿJ(H,H) (Hz) in brackets.

TABLE 4

 ^1H NMR DATA FOR η^3, η^3 -DIMETHYLOCTADIENEDINICKEL- PR_3 COMPLEXES 15-17 FORMED IN REACTIONS INVOLVING PIPERYLENE

δ (ppm)	R = Ph ^{a,b,d} (T - 15°C)		R = Ph ^{c,e,g} (T - 25°C)		R = Me ^{a,c,e} (T - 28°C)	
	δ	J	δ	J	δ	J
δ_1	5.04 ($^3J(1,2)$ 6.8, $^3J(1,5)$ 9.2, $^3J(1,4)$ 12.4, $^3J(4,P)$ 4.3)		4.98		4.68	4.68
δ_2	3.04 ($^3J(2,1)$ 6.8)	3.15 ^f ($^3J(2,1)$ 6.9, $^3J(2,P)$ 1.73)		2.76 ^f ($^3J(2,1')$ 6.9)	2.96 ^f ($^3J(2,1)$ 6.8, $^3J(2,P)$ 2.6)	2.65 ^f ($^3J(2,1')$ 6.9)
δ_4	1.38 ($^3J(4,1)$ 12.4, $^3J(4,P)$ 13.6)	1.79 ($^3J(4,1)$ 12.5, $^3J(4,P)$ 12.5)		0.83 ($^3J(4,1')$ 12.5, $^3J(4',P)$ 17.0)	1.62 ($^3J(4,1)$ 12.2, $^3J(4,P)$ 14.2)	1.09 ($^3J(4',P)$ 19.1, $^3J(4,1')$ 12)
δ_5	(2.60)	2.61 ($^3J(5,P)$ 12.4, $^3J(5,1)$ 9.2, $^3J(5,6)$ 9.2)		2.36 ($^3J(5',P)$ 15.5, $^3J(5',1')$ 9.7, $^3J(5',6')$ 6.4)	2.83 ($^3J(5,P)$ 15.5, $^3J(5,1)$ 8.7, $^3J(5,6)$ 8.7)	2.26 ($^3J(5',P)$ 19.0, $^3J(5',1')$ 9.4, $^3J(5',6')$ 6)
δ_6	~ 2	2.18		1.92	-	-
δ_7	0.98 ($^3J(6,7)$ 6.6)	1.00 ($^3J(7,6)$ 6.6)		0.95 ($^3J(7',6')$ 6.6)	0.99 ^f ($^3J(7,6)$ 7.0)	0.97 ^f ($^3J(7',6')$ 7.0)
δ_R	-	7-8(br)			0.90 ($^3J(P,H)$ 5.9)	

^a In toluene- d_6 ; ^b $J(\text{H,H})$ (Hz) in brackets; Bruker WH 270 spectrometer. ^b From *cis*-piperylene. ^c From *cis*-piperylene. ^d From *trans*-piperylene. ^e From *trans*-piperylene. ^f Assignment could be reversed. ^g In Et₂O- d_{10} .



the allyl fragment upon incorporation in the chain. The position occupied by the PPh_3 molecule in the complex is indicated by the coupling between phosphorus and the *meso*-proton (${}^3J(1,\text{P})$ 4.7 Hz) as well as with the *anti*-protons (${}^3J(4,\text{P}) = {}^3J(5,\text{P}) = 14$ Hz). (Coupling constants of a similar magnitude have been found for $[\text{Ni}(\text{PMe}_3)(\eta^3\text{-C}_3\text{H}_5)_2]$ and in this case the structure has been confirmed by X-ray crystallography [10].) Additional support for the suggested arrangement comes from the Nuclear-Overhauser-Difference-Spectra shown in Fig. 3. The normal spectrum is shown as trace A. The difference spectra (traces B–E) are the difference between the normal spectrum and spectra obtained by saturating one group of signals – negative signals arise from the saturated multiplet and positive signals from those protons which are in the immediate vicinity of the saturated proton [19]. Spectra B and C indicate that the ligand is in the vicinity of the *anti*-protons H(4) and H(5). This interpretation is supported by spectrum D; saturation of the *ortho*-phenyl proton of the ligand results in positive signals for H(4) and H(5) as well as for the remaining aromatic protons. The *syn*-substitution of the η^3 -allyl groups follows from spectrum E, which indicates an interaction between H(6) and the *meso*-proton H(1).

syn-Substitution of the η^3 -allyl groups present in the dimethyloctadienediynickel complexes formed in the reactions involving piperylene (Table 4) is suggested by the magnitude of the vicinal coupling constants; although the coupling between the *meso*-proton H(1) and the *anti*-proton H(5) is unusually small, the chemical shift $\delta(\text{H}(5))$ is typical. In the case of the symmetrical complexes (Table 4, column 1), the coupling between H(5) and the proton attached to C(4) (H(6)) could not be resolved and hence supply no information concerning the conformation of the methyl group. In the case of the unsymmetrically substituted complexes (Table 4, columns 2 and 3), a staggered conformation of the methyl groups follows from the two different values for ${}^3J(5,6)$ and ${}^3J(5',6')$. A further point of interest is the two different coupling constants observed between the phosphorus atom and the *anti*-protons (e.g. ${}^3J(4,\text{P})$ and ${}^3J(4',\text{P})$) which could be interpreted as indicating asymmetry in the η^3 -allyl groups.

The assignment of the ${}^{13}\text{C}$ NMR data for the various η^1, η^3 -octadienediynickel complexes shown in Tables 5 and 7–9 rests upon the results obtained for $[\text{Ni}(\text{PCy}_3)(\eta^1, \eta^3\text{-2,6-Me}_2\text{C}_8\text{H}_{10})]$ (**9**), for which a crystal structure determination has been carried out [4]. The sample studied contained only this one isomer and the data are fully consistent with the expected structure: the signals for C(1)–C(3) and C(6)–C(8) fall in the range typical for η^3 - and η^1 -allyl systems [20] while the coupling constants $J(\text{P},\text{C}(1))$ (5.1 Hz) and $J(\text{P},\text{C}(3))$ (19.3 Hz) are consistent with a square-planar geometry in which the phosphorus atom is *trans* to C(3). Analysis of the ${}^{13}\text{C}$ NMR spectrum of the initial product formed in the reaction involving isoprene (**8**) indicates that the two methyl groups occupy 3,6-positions. Characteristic is the resonance at ca. 17 ppm, which is in the range expected for an *anti*-methyl substituent, and the shift of C(3) by ca. 10 ppm to lower field in comparison with the unsubstituted system. In addition, C(1) and C(2) are shifted slightly to higher field while the introduction of a β -substituent causes C(4) to be shifted to lower field. The 2,7-substitution of the third isomer (**10**) formed in the reaction with isoprene follows from the expected low-field shift for C(7) and C(8) and the upfield shift for C(6) relative to the unsubstituted system.

The ${}^{13}\text{C}$ NMR spectra of the unsubstituted η^1, η^3 -octadienediynickel complexes (**1**) (Table 5) show the typical low-field absorption for the nickel-bonded methylene

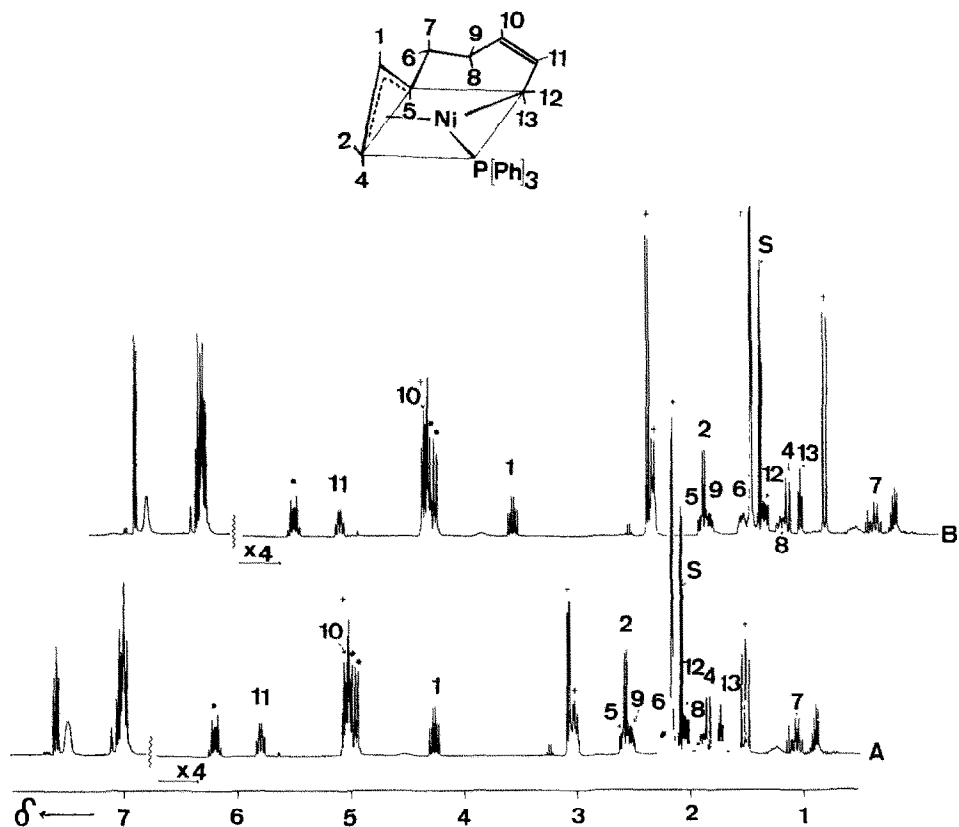


Fig. 2. 400 MHz ^1H NMR spectrum of $[\text{Ni}(\text{PPh}_3)(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ (**1d**) in toluene- d_8 at -13°C . (A) normal spectrum, (B) $\{^{31}\text{P}\}$ broadband decoupled spectrum. The scale refers to spectrum A. Signals marked with \star , $+$ and S correspond to butadiene, $[\text{Ni}(\text{PPh}_3)(\eta^3, \eta^3\text{-C}_8\text{H}_{12})]$ (**2d**) and solvent, respectively.

group (C(8)) with a large coupling (12–18 Hz) to phosphorus, while the variations in the chemical shifts of the η^3 -allylic carbon atoms C(1)–C(3) as well as the coupling to phosphorus upon varying the ligand run parallel to the results obtained for the $[\text{NiBr}(\text{L})(\eta^3\text{-cyclooctenyl})]$ complexes [20]. The rearrangement of the η^1, η^3 -octadienediyl group to a symmetrical η^3, η^3 -octadienediyl arrangement is shown in Fig. 4 for the system involving $\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3$ (**1e** \rightarrow **2e**). At -40°C , the complex exists almost exclusively in the η^1, η^3 -form (A). On raising the temperature to 0°C , four new signals (B) appear, which are assigned to the symmetrical η^3, η^3 -form. These signals remain sharp over the whole range of the measurement, indicating that the two forms do not undergo rapid exchange. At higher temperatures, further reaction occurs to give $[\text{Ni}(\text{COD})_2]$ and $[\text{NiL}_2(\text{COD})]$ (**3**).

The intensity, chemical shift, multiplicity and magnitude of $^1J(\text{CH})$ for complex B are fully consistent with its formulation as the symmetrical bis- η^3 -allyl-nickel complex **2e**, in which the allyl groups are linked by two methylene groups. The chemical shift of the methylene-C atom (37.5 ppm) is not consistent with *anti*-substitution while a proton-coupled ^{13}C NMR spectrum of the analogous PPh_3 complex suggests

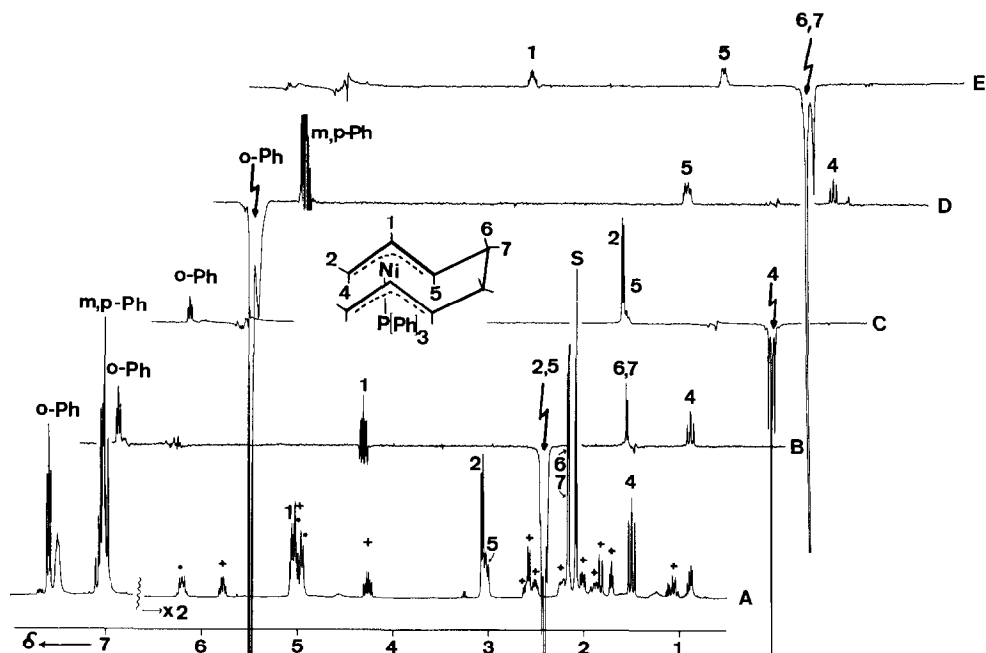


Fig. 3. 400 MHz ^1H NMR spectrum of $[\text{Ni}(\text{PPh}_3)(\eta^3, \eta^3\text{-C}_8\text{H}_{12})]$ (**2d**) in toluene- d_8 at 0°C . (A) normal spectrum, (B)–(E) Nuclear-Overhauser-Difference Spectra. Saturated multiplets are in emission and are indicated by a broken arrow; protons in the immediate vicinity show up as absorptions. Signals marked with \star , $+$ and S correspond to butadiene, $[\text{Ni}(\text{PPh}_3)(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ (**1d**) and solvent, respectively.

that the methylene groups occupy *syn* positions: the vicinal coupling $^3J(\text{CH})$ between C(3) and the protons is strongly dependent upon the dihedral angle [21] and the value of 3.5 Hz observed is typical for a system in which the C-atom is associated with an *anti*-substituted proton (i.e. *syn*-substituted methylene group). A similar conclusion has been reached from the ^1H NMR measurements discussed above. The suggestion that the P-donor ligand occupies a coordination position pseudo-*trans* to the *meso*-carbon atom is underlined by comparison with $[\text{NiL}(\eta^3\text{-C}_3\text{H}_5)_2]$ complexes in which, in the case where $\text{L} = \text{PMe}_3$, this arrangement has been confirmed by X-ray crystallography [10]: in both classes of compound the largest P–C coupling is that involving the *meso*-carbon atom while a similar dependence of C(1)–C(3) upon the nature of the ligand is observed.


The products of the reactions involving *cis*- or *trans*-piperylene also contain an η^3, η^3 -octadienediyl group with methyl substitution at C(4) and C(5). Although the basic pattern remains the same as that observed for the unsubstituted complex, the chemical shifts are strongly perturbed and have defied rationalization using the existing incremental information. For example, in the case of the unsymmetrically substituted complex $[\text{Ni}(\text{PMe}_3)(\eta^3, \eta^3\text{-4,5-Me}_2\text{C}_8\text{H}_{10})]$ (formed from the reaction with *trans*-piperylene), the two absorptions for the terminal C atoms C(1) and C(1') are shifted, relative to the unsubstituted chain, by 6.6 ppm to lower field and by 3 ppm to higher field, respectively, indicating some form of geometrical distortion.

(Continued on p. 82)

TABLE 5

^{13}C (^1H) NMR DATA FOR η^1, η^3 -OCTADIENEDIYLNICKEL- PR_3 COMPLEXES **1a–1e** ($\text{R} = \text{Cy}$ (**a**), Pr^i (**b**), Me (**c**), Ph (**d**), OC_6H_4 -*o*- Ph (**e**)) FORMED IN REACTIONS INVOLVING BUTADIENE^{*a*}

δ (ppm)	1c ($T - 30^\circ\text{C}$)	1b ($T - 40^\circ\text{C}$)	1a ($T 35^\circ\text{C}$)	1e ($T - 30^\circ\text{C}$)	1d ($T 0^\circ\text{C}$)
δ_1 ^{<i>b</i>}	50.9	49.1(5.2)	49.0(5.4)	53.2	57.3
δ_2	108.6 ^{<i>c</i>}	107.4	107.8	110.0 ^{<i>c</i>}	109.4 ^{<i>c</i>}
δ_3	69.2(20.7)	71.8(18.4)	72.3(18.5)	75.2(31.6)	70.9
δ_4	27.6 ^{<i>f</i>}	27.4(2.1)	27.3(2.2)	26.5 ^{<i>f</i>}	27.2 ^{<i>f</i>}
δ_5	24.7 ^{<i>f</i>}	24.3(2.4)	24.4(2.6)	23.9 ^{<i>f</i>}	24.7 ^{<i>f</i>}
δ_6	108.3 ^{<i>c</i>}	109.4(1.2)	109.9(1.1)	109.8 ^{<i>c</i>}	109.5 ^{<i>c</i>}
δ_7	132.7	135.0(1.2)	135.1(1.6)	133.2	133.3
δ_8	9.9(12.6)	6.8(12.2)	6.9(12.1)	6.5(17.6)	11.4
δ_{R}	15.3(26.2)	25.2(18.9, C(9)) ^{<i>d</i>}	35.9(17.8, C(9)) ^{<i>e</i>}	– ^{<i>f</i>}	136.5(29.4, C(9))
		19.8(1.9, C(10))	30.6(4.4, C(10))		133.9(11.8, C(10))
		19.5(1.4, C(10'))	28.2(9.9, C(11))		128.4(9.5, C(11))
			27.0(C(12))		129(C(12))

^{*a*} Measured in toluene- d_8 ; $J(\text{C}, \text{P})$ (Hz) in brackets. ^{*b*} . ^{*c*} C(2)/C(6) assignment provisional.

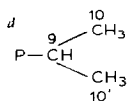
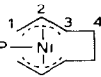


TABLE 6

^{13}C (^1H) NMR DATA FOR η^3, η^3 -OCTADIENEDIYLNICKEL- PR_3 COMPLEXES **2b–2e** ($\text{R} = \text{OC}_6\text{H}_4$ -*o*- Me (**b**), Me (**c**), Ph (**d**), OC_6H_4 -*o*- Ph (**e**)) FORMED IN REACTIONS INVOLVING BUTADIENE^{*a, b*}

δ (ppm)	2c ($T - 30^\circ\text{C}$)	2d ($T 0^\circ\text{C}$)	2b ($T - 30^\circ\text{C}$)	2e ($T - 43^\circ\text{C}$)
δ_1	38.7 ^{<i>c</i>}	42.4	44.1	44.2
δ_2	96.3(6.2)	100.8(4.8)	99.5(8.0)	99.8(7)
δ_3	71.0(1.4)	75.2(1.4)	74.7(2.6)	74.6(– 2)
δ_4	38.3 ^{<i>c</i>}	38.4	37.5	37.6
δ_{R}	17.5(18.8)	– 134.8(C(5)) ^{<i>d</i>}	151.2(5.1, C(5)) ^{<i>e</i>}	–
		134.0(12.4, C(6))	121.5(5.4, C(6))	
		128.3(8.3, C(7))	126.9(C(7))	
		129.7(1.4, C(8))	124.3(C(8))	
			131.4(C(9))	
			17.1(C(11))	

^{*a*} Measured in toluene- d_8 ; $J(\text{C}, \text{P})$ in brackets. ^{*b*} . ^{*c*} C(1)/C(4) assignment provisional.

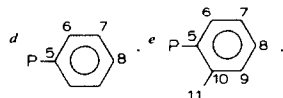
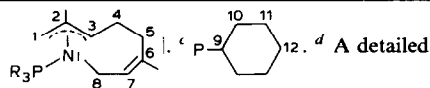


TABLE 7. ^{13}C (^1H) NMR DATA FOR η^1, η^3 -2,6-DIMETHYLOCTADIENEDIYLNICKEL- PR_3 COMPLEXES FORMED IN REACTIONS INVOLVING ISOPRENE a, b

	R = Me ($T - 30^\circ\text{C}$)	R = Cy (9) ($T 35^\circ\text{C}$)	R = OC_6H_4 - <i>o</i> -Ph ($T - 10^\circ\text{C}$)	R = Ph ($T 0^\circ\text{C}$)
δ_1	52.4(3.7)	50.4(5.1)	55.1	58.3(2.9)
δ_2	117.2	114.7(0.9)	114.3	114.6 e
δ_3	70.0(22.0)	73.2(19.3)	76.4(33.1)	72.2(21.3)
δ_4	—	20.7(1.9)	19.6(2.9?)	20.2(1.5)
δ_5	—	29.6(2.6)	29.1	30.0(2.3)
δ_6	—	115.9	119.7(2.6)	118.6 e
δ_7	—	131.2(1.8)	—	—
δ_8	10.2(12.6)	7.0(12.4)	6.8(16.9)	11.9(11.7)
δ_{Me}	—	20.3(Me-C(2))	19.6(Me-C(2)?)	20.5(Me-C(2))
	—	24.5(Me-C(6))	23.9(Me-C(6))	24.3(Me-C(6))
δ_{R}	—	35.7(17.7, C(9)) c	— d	135.3(39.5, C(9)) f
		30.7(C(10))		133.9(11.8, C(10))
		28.2(9.8, C(11))		128.4(9.5, C(11))
		27.1(C(12))		129.6(1.4, C(12))

a Measured in toluene- d_8 ; $J(\text{C}, \text{P})$ (Hz) in brackets. b



assignment of the aromatic abs. has not been made. e Provisional assignment. f $\text{P}-\text{C}_6\text{H}_5$.

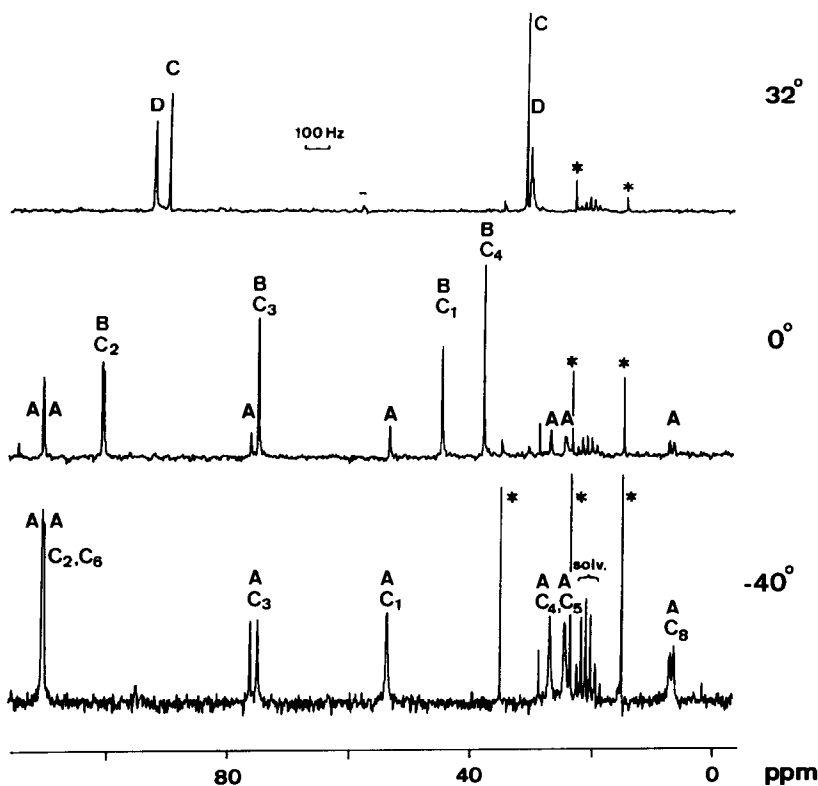


Fig. 4. The rearrangement of $[\text{Ni}(\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3)(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ (**1e**). ^{13}C (^1H) NMR spectra at 25.2 MHz in toluene- d_8 . The absorptions labelled A, B, C and D are due to $[\text{Ni}(\text{PR}_3)(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ (**1e**), $[\text{Ni}(\text{PR}_3)(\eta^3, \eta^3\text{-C}_8\text{H}_{12})]$ (**2e**), $[\text{Ni}(\text{COD})_2]$ and $[\text{Ni}(\text{PR}_3)_2(\text{COD})]$ (**3**), respectively (\star = pentane) [20].

TABLE 8

 ^{13}C $\{^1\text{H}\}$ NMR DATA FOR $\eta^1\text{-}\eta^3\text{-}2,7\text{-}$ AND $3,6\text{-DIMETHYLOCTADIENEDIYLNICKEL-PR}_3$ COMPLEXES FORMED IN REACTIONS INVOLVING ISOPRENE^a

δ (ppm)	R = Me ^b ($T = -11^\circ\text{C}$)	R = Me ^c ($T = -30^\circ\text{C}$)	R = Pr ^c ($T = -40^\circ\text{C}$)	R = Cy ^b (10) ($T = 14^\circ\text{C}$)	R = Cy ^c (8) ($T = -30^\circ\text{C}$)	R = OC ₆ H ₄ - <i>o</i> -Ph ($T = -10^\circ\text{C}$)
δ_1	51.6(4.2)	47.2(3.5)	44.3(5.5)	49.2(5.5)	44.9(5.3)	54.1
δ_2	117.6	106.7	105.7	—	106.1	114.3
δ_3	69.5(22)	79.9(20.2)	81.6(17.1)	73.9(19.4)	81.1(17.3)	75.7(33.1)
δ_4	22.1(2.8)	34.6(1.9)	34.5(1.8)	—	34.6	—
δ_5	25.7(3.0)	28.1(2.1)	27.6(1.9)	—	—	—
δ_6	106.2(1.3)	115.9(1.8)	117.2(1.1)	—	—	—
δ_7	144.0(1.7)	—	130.3(1.5)	—	117.2	108.6
δ_8	12.4(12.1)	14.0(12.7)	10.4(12.7)	10.0(10.8)	130.4	—
δ_{Me}	20.5(Me-C(2))	17.3(3.3, Me-C(3))	17.6(2.6, Me-C(3))	—	10.8(12.1)	10.4(16.0)
	27.3(Me-C(7))	24.9(Me-C(6))	25.3(Me-C(6))	—	17.2(2.5, Me-C(3)?)	—
δ_{R}	16.4(25.1)	15.6(26.1)	25.2(18.9, C(9)) ^d	—	25.3(Me-C(6)?)	—
			19.8(1.8, C(10))	—	35.4(18.7, C(9)) ^e	—
			19.6(1.7, C(10'))	—	30.4(C(10))	—
				—	28.0(10.1, C(11))	—
				—	27.0(C(12))	—

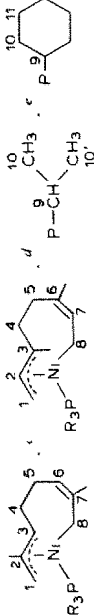
^a Measured in toluene-*d*₈; $J(\text{C,P})$ (Hz) in brackets. ^b


TABLE 9

^{13}C (^1H) NMR DATA FOR η^1, η^3 -4,5-DIMETHYL- AND -2,3,6,7-TETRAMETHYLOCTADIENEDIYLNICKEL- PR_3 COMPLEXES FORMED IN REACTIONS INVOLVING PIPERYLENE a,b AND 2,3-DIMETHYLBUTADIENE a,c

δ (ppm)	R = Cy b (14) ($T - 30^\circ\text{C}$)	R = Me c (18) ($T - 30^\circ\text{C}$)	R = Cy c (18) ($T 35^\circ\text{C}$)
δ_1	50.4(4.7)	49.0(4.6)	45.2(6.4)
δ_2	106.6	113.1	111.9
δ_3	92.3(18.8)	78.1(21.2)	81.2(17.8)
δ_4	37.4	30.7(2.8)	31.1(2.5)
δ_5	33.1	27.3(2.4)	27.9(2.3)
δ_6	118.6	108.9(1.6)	111.8(1.5)
δ_7	139.8	136.2(1.9)	137.6(1.5)
δ_8	9.8(11.4)	17.9(11.9)	14.7(10.5)
δ_{Me}	18.9(Me-C(4)) 21.6(Me-C(5))	22.8(1.2) 22.0 19.8 19.7(3.7)	22.6 22.1(1.3) 20.7(3.0) 20.1
δ_{R}	35.2(18.1, C(9)) d 30.4, 30.2(C(10,10')) 28.0(10.1, C(11)) 26.9(C(12))	16.6(25.6)	35.7(17.2, C(9)) d 30.8(C(10)) 28.3(10.0, C(11)) 27.2(C(12))

a Measured in toluene- d_8 ; $J(\text{C}, \text{P})$ (Hz) in brackets. b

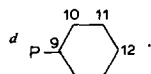
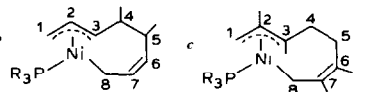
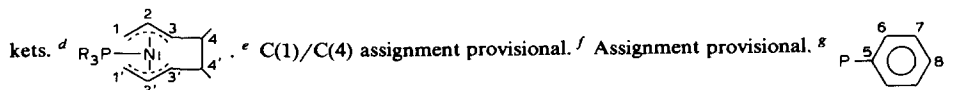


TABLE 10

^{13}C (^1H) NMR DATA FOR η^3, η^3 -4,5-DIMETHYLOCTADIENEDIYLNICKEL- PR_3 COMPLEXES FORMED IN REACTIONS INVOLVING PIPERYLENE a,b,c

δ (ppm)	R = Me a,f ($T - 10^\circ\text{C}$)	R = Me b ($T - 10^\circ\text{C}$)	R = Ph a ($T - 20^\circ\text{C}$)	R = Ph b ($T - 30^\circ\text{C}$)
$\delta_{1(1')}$ d	45.2, 44.2 e	45.3(1.9), 35.6(1.5) e	44.0	47.9, 39.4
$\delta_{2(2')}$	101.3(5.7), 94.5(6.3)	99.2(6.1), 90.0(6.3)	100.3(5.3)	102.5(4.5), 94.5(5.2)
$\delta_{3(3')}$	74.1(2.0), 64.1(1.1)	76.2, 66.8(2.9)	76.8(1.2)	80.7, 71.1(1.4)
$\delta_{4(4')}$	54.8, 41.6 e	55.7, 46.8 e	48.2	55.4, 47.0
δ_{Me}	23.1(Me-C(4)) 19.9(Me-C(4')?)	23.0(Me-C(4)) 21.6(Me-C(4'))	17.5(Me-C(4))	23.0(Me-C(4)) 21.7(Me-C(4'))
δ_{R}	17.7(11.5)	17.6(18.9)	137.1(29.3, C(5)) g 134.0(12.2, C(6)) 128.3(8.5, C(7)) 129.0(C(8))	136.9(29.5, C(5)) g 134.1(12.4, C(6)) 128.3(8.2, C(7)) 129.0(C(8))

a Involving *cis*-piperylene. b Involving *trans*-piperylene. c Measured in toluene- d_8 ; $J(\text{C}, \text{P})$ (Hz) in brackets. d



Experimental

Most of the complexes described below are air-sensitive and so all operations were carried out under argon. Solvents were dried and freed from dissolved oxygen by distillation from sodium-potassium alloy.

The displacement of the organic ligands bonded to nickel by CO was carried out in toluene or ether at -78 to -20°C using a gas-burette to measure the volume of CO absorbed. The organic product and solvent were removed by vacuum distillation and analysed by gas chromatography. Displacement by reaction with triphenylphosphine was carried out (in general) in the absence of solvent by mixing the complex and a ca. three-fold excess of phosphine at low temperature, attaching the reaction vessel to a collection flask and evacuating the apparatus. The reaction was then carried out by plunging the reaction vessel into an oil bath at 100°C while simultaneously cooling the collector in liquid nitrogen. The condensed product was analysed by gas chromatography or mass spectrometry.

The ^{13}C NMR spectra were measured at 25.2 MHz with a Varian XL-100-15-FT spectrometer. The samples were filtered into 12 mm tubes at the temperatures shown in the tables. The chemical shifts (± 0.05 ppm) are relative to internal TMS and are positive to higher frequencies. The ^1H NMR spectra were measured on Bruker WH 80, 270 and 400 MHz spectrometers. Chemical shifts are relative to internal TMS.

η^1, η^3 -Octadienediylnickeltricyclohexylphosphine (**1a**)

2.41 g (4.82 mmol) $[\text{Ni}(\text{PCy}_3)_2(\text{CDT})]$ was suspended in 40 ml of liq. butadiene at -20°C and stirred for 3 d. The original yellow suspension slowly dissolved to give a red solution from which the product precipitated as a yellow solid having a characteristic sweet smell. The product was filtered off, washed several times with cold ether, and dried under vacuum. Yield 1.9 g (88%).

Found: Ni, 13.2; P, 7.1. $\text{C}_{26}\text{H}_{45}\text{PNi}$ (447) calcd.: Ni, 13.12. P, 6.94%. Mol. wt. (cryoscopic) 445.

The same complex could also be prepared by treating $[\text{Ni}(\text{COD})_2]$ and PCy_3 (1/1) in a butadiene/toluene solution (1/2) or by dissolving $[\text{Ni}(\text{PCy}_3)(\text{cis-DVCB})]$ in toluene at room temperature [2,3].

Reaction of the complex with CO at -78°C resulted in the absorption of 3 equiv. and the quantitative liberation of VCH. A 60% yield of VCH was obtained on treatment with COD at 50°C for 36 h while the reaction with triphenylphosphine at 100°C gave mainly butadiene (65%) along with VCH, COD and DVCB (26/16/1).

η^1, η^3 -Octadienediylnickeltriisopropylphosphine (**1b**)

This complex was prepared as a yellow solid by treating equimolar amounts of $[\text{Ni}(\text{COD})_2]$ and PPr_3 with butadiene at -40°C . Yield ca. 50%. Found: Ni, 17.7. Calcd.: Ni, 18.0%.

η^1, η^3 - and η^3, η^3 -Octadienediylnickeltrimethylphosphine (**1c, 2c**)

These complexes were prepared as a mixture of low-melting, orange-red crystalline solids by treating $[\text{Ni}(\text{PMe}_3)_2(\text{CDT})]$ with butadiene in an autoclave at RT for 2 d. Yield ca. 30%. Found: Ni, 21.8. Calcd.: Ni, 24.2%.

The ^{13}C NMR spectrum measured at -30°C showed that the $\eta^1, \eta^3\text{-C}_8\text{H}_{12}$ and $\eta^3, \eta^3\text{-C}_8\text{H}_{12}$ forms **1c** and **2c** were present in the ratio 85/15.

η^1, η^3 - and η^3, η^3 -Octadienediylnickel tris-*o*-biphenylphosphite (**1e, 2e**)

These complexes were prepared as an orange solid by treating equimolar amounts of $[\text{Ni}(\text{COD})_2]$ and $\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3$ with liq. butadiene at -30°C for 14 h. Yield ca. 90%. Found: Ni, 8.3; P, 4.3. Calcd.: Ni, 8.33; P, 4.4%.

The same complexes could be prepared by treating butadiene with $[\text{Ni}(\text{CDT})]$ and the phosphite. The conversion of the η^1, η^3 - into the η^3, η^3 -form and its further reaction was monitored by NMR spectroscopy and is discussed in Section 2.

At -20°C in toluene, 3 equiv. of CO was absorbed, with liberation of vinylcyclohexene (87%) and formation of $[\text{NiP}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3(\text{CO})_3]$ (98%). The product of the reaction with CO of a sample dissolved in toluene at 25°C was cyclooctadiene (80.9%) with lesser amounts of butadiene (12.8%) and vinylcyclohexene (6.3%). Reaction with 1 equiv. of $\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3$ in ether at -30°C to RT gave $[\text{Ni}\{\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Ph})_3\}_2(\text{COD})]$ (**3**) (89%).

η^1, η^3 - and η^3, η^3 -Octadienediylnickeltriphenylphosphine (**1d, 2d**)

This mixture of complexes was prepared as an orange solid by treating equimolar amounts of $[\text{Ni}(\text{COD})_2]$ and PPh_3 with liq. butadiene at -30°C for 14 h. Yield ca. 90%. Found: Ni, 13.7; P, 7.2. MW (cryoscopic) 448. Calcd.: Ni, 13.68; P, 7.24%. MW 429.

The same complexes could be prepared by treating butadiene with $[\text{Ni}(\text{PPh}_3)(\text{CDT})]$ or $[\text{Ni}(\text{PPh}_3)_4]$. The isomerization of the η^1, η^3 -form into the η^3, η^3 -form and its further reaction was monitored by ^1H and ^{13}C NMR spectroscopy.

Reaction with CO at -78°C in toluene led to liberation of vinylcyclohexene (97.5%) while at 25°C a 66% yield of divinylcyclobutane, vinylcyclohexene and cyclooctadiene (20/57/23) was obtained. Reaction of an ethereal solution with excess triphenylphosphine at -10°C led to liberation of butadiene (76%) and formation of $[\text{Ni}(\text{PPh}_3)_4]$ (96%). At 90°C the product consisted of butadiene (66%), cyclooctadiene (22%) and vinylcyclohexene (15%). Reaction with tricyclohexylphosphine of an ethereal solution at -15°C led to phosphine exchange and $[\text{Ni}(\text{PCy}_3)(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ (**1a**) was isolated. Treatment of an ethereal solution with gaseous HCl at -30°C led to the formation of a red solution from which yellow crystals of $[\text{NiCl}(\text{PPh}_3)(\eta^3\text{-1-C}_5\text{H}_9\text{C}_3\text{H}_4)]$ (**4**) (78%) were isolated. Found: Ni, 12.6; P, 6.7; Cl, 7.6. Calcd.: Ni, 12.62; P, 6.67; Cl, 7.63%.

η^3, η^3 -Octadienediylnickel *o*-tolylphosphite

This complex was prepared as a red oil by reaction of $[\text{Ni}(\text{COD})_2]$ and *o*-tolylphosphite with butadiene in ether at -35°C . ^{31}P and ^{13}C NMR spectra showed the product to consist mainly of the desired product as well as $[\text{Ni}(\text{COD})_2]$ and $[\text{Ni}\{\text{P}(\text{O-}o\text{-tolyl})_3\}_2(\text{COD})]$ (**3**).

η^1, η^3 -Dimethyloctadienediylnickeltricyclohexylphosphine (**8-10**) (from isoprene)

This yellow solid, having a citrus odour, was prepared by reaction of 3.05 g (6.08 mmol) $[\text{Ni}(\text{PCy}_3)(\text{CDT})]$ with 1.3 ml isoprene in 40 ml ether at -10°C . The original yellow solid dissolved slowly to give a red solution from which the product was isolated by the addition of pentane to the concentrated solution. Yield 2.29 g (79%).

Found: Ni, 12.4; P, 6.6. $\text{C}_{28}\text{H}_{49}\text{PNi}$ (475) calcd.: Ni, 12.35; P, 6.53%. Mol wt. (cryoscopic) 456, 480.

The same compound could also be prepared by treating equimolar amounts of $[\text{Ni}(\text{COD})_2]$ and PCy_3 in ether or toluene with isoprene at -30°C or (in somewhat reduced yield) from reactions involving $[\text{Ni}(\text{PCy}_3)_2]$ and $[\text{Ni}(\text{PCy}_3)(\text{MeCH}:\text{CH}_2)_2]$ (**13**). The rearrangement of the various isomers was followed by NMR spectroscopy (see relevant section).

Reaction of a sample prepared at room temperature with CO in toluene at -30°C led to the formation of dipentene (89%). The main product of the reaction with excess triphenylphosphine at 90°C was isoprene while the reaction with $[\text{Ni}(\text{PCy}_3)_2]$ (**11**) and PCy_3 in toluene led to the formation of $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-CH}_2:\text{CHCMe}:\text{CH}_2)]$ (**12**) as a yellow solid. Found: Ni, 8.5; P, 9.0. Calcd.: Ni, 8.55; P, 9.02%.

η^1, η^3 -Dimethyloctadienediylnickeltrimethylphosphine (from isoprene)

This complex formed as a low-melting, red solid from the reaction of $[\text{Ni}(\text{PMe}_3)(\text{CDT})]$, $[\text{Ni}(\text{CH}_2:\text{CH}_2)_3]/\text{PMe}_3$ or $[\text{Ni}(\text{bicycloheptene})_3]/\text{PMe}_3$ with isoprene at -30°C . The isomerization of the initial product, in which the methyl groups occupy 3,6-positions, into the 2,6- and 2,7-substituted isomers was monitored by ^{13}C NMR spectroscopy.

η^1, η^3 -Dimethyloctadienediylnickeltriisopropylphosphine (from isoprene)

Orange crystals of this complex were prepared by treating equimolar amounts of $[\text{Ni}(\text{COD})_2]$ and PPr_3 in an ether/toluene solution at -40°C . Yield ca. 75%. Found: Ni, 16.5; Calcd.: Ni, 16.55%.

The ^{13}C NMR spectrum showed that at low temperature the methyl groups occupy exclusively 3,6-positions; at room temperature, rearrangement occurs to give a mixture of isomers whose ^{13}C NMR spectral parameters suggest that the main component has 2,6-substitution.

η^1, η^3 -Dimethyloctadienediylnickeltriphenylphosphine (from isoprene)

This yellow complex was prepared by reaction of $[\text{Ni}(\text{PPh}_3)(\text{CDT})]$ with excess isoprene in ether at -20°C for 20 h. Yield ca. 80%. Found: Ni, 13.0. Calcd.: Ni, 12.8%.

The same complex was also formed by reaction of equimolar amounts of $[\text{Ni}(\text{COD})_2]$ and PPh_3 with isoprene at -10°C . The ^{13}C NMR spectrum indicated that the methyl groups occupy 2,6-positions.

*η^1, η^3 -Dimethyloctadienediylnickeltricyclohexylphosphine (**14**) (from piperylene)*

1.2 g (2.84 mmol) $[\text{Ni}(\text{PCy}_3(\text{MeCH}:\text{CH}_2)_2)]$ (**13**) was suspended in 30 ml ether, cooled to -10°C , and 0.85 ml *cis*-piperylene added. After several hours, a clear and red solution developed from which, after 3 d at -30°C , yellow-brown crystals of the product deposited. Yield 1.08 g (80%).

Found: Ni, 12.3; P, 6.5. $\text{C}_{28}\text{H}_{49}\text{PNi}$ (475) Calcd.: Ni, 12.35; P, 6.53%.

The ^{13}C NMR spectrum and a partial X-ray structural investigation indicated that the methyl groups are bonded to C(4) and C(5) of the C_8 unit. Treatment of the complex with excess triphenylphosphine at 100°C led to liberation of a ca. 2/1 mixture of *cis*- and *trans*-piperylene in a 77% yield, in addition to traces of dimethylcyclooctadiene.

A red-orange complex having the same composition was prepared by treating

[Ni(PCy₃)(CDT)] or [Ni(PCy₃)(MeCH:CH₂)₂] with *trans*-piperylene in ether at -10°C for 5 h. Yield ca. 60%. Found: Ni, 12.5; P, 6.6. Calcd.: Ni, 12.35; P, 6.53%.

Treatment of this complex with excess triphenylphosphine at 100°C led to liberation of *trans*-piperylene (66%) as well as dimethylcyclooctadiene (10%).

η^3, η^3 -Dimethyloctadienediylnickeltrimethylphosphine (from piperylene)

A yellow-brown, low-melting solid was formed by treating [Ni(PMe₃)(CDT)] with *trans*-piperylene in ether at 0°C for 3 d. Yield ca. 80%. ¹H and ¹³C NMR spectra indicated that this material (Found: Ni, 17.8. calcd.: Ni, 21.7%) consisted of the desired complex, having methyl groups on C(4) and C(5) of the C₈ unit, contaminated with CDT and [Ni(PMe₃)(CDT)].

An analogous reaction carried out with *cis*-piperylene gave a dark red, low-melting solid (Found: Ni, 19.7. calcd.: Ni, 21.7%) whose ¹³C NMR spectrum was consistent with the formation of a complex having an unsymmetrical η^3, η^3 -Me₂C₈H₈ unit different, however, from that obtained in the reaction with *trans*-piperylene. The spectrum also showed the presence of minor amounts of a complex containing an η^1, η^3 -Me₂C₈H₈ moiety.

η^3, η^3 -Dimethyloctadienediylnickeltriphenylphosphine (from piperylene)

This complex was isolated as an orange crystalline solid from the reaction between [Ni(PPh₃)(CDT)] and *trans*-piperylene in ether at -12°C for 48 h. Yield ca. 80%. Found: Ni, 12.8. Calcd.: Ni, 12.9%.

The ¹³C NMR spectrum showed the methyl groups to be bonded to the C(4) and C(5) atoms of the C₈ unit.

A similar experiment with *cis*-piperylene led to the isolation of an orange solid whose NMR spectra indicated it to be a mixture (2/1) of the above complex and a new system having a symmetrical η^3, η^3 -Me₂C₈H₈ unit.

η^1, η^3 -Tetramethyloctadienediylnickeltricyclohexylphosphine (18a)

2.66 g (5.32 mmol) [Ni(PCy₃)(CDT)] was suspended in ether at -20°C , 1.5 ml of 2,3-dimethylbutadiene was added and the reaction mixture was allowed to reach room temperature slowly. The resulting orange-red solution was concentrated and a yellow solid deposited which was washed with ether at -20°C and dried under high vacuum. Yield 2.41 g (90%). Found: Ni, 11.8. P, 6.1. C₃₀H₅₃PNi (503) Calcd.: Ni, 11.68; P, 6.17%.

The same complex could also be prepared by treating bis(η^4 -2,3-dimethylbutadiene)nickel with tricyclohexylphosphine in ether at -30°C [13]. The ¹³C NMR spectrum indicated that the methyl groups are bonded to C(2), C(3), C(6) and C(7) of the C₈ fragment. Reaction with CO at room temperature led to displacement of 2,4-dimethyldipentene (65%) as well as 2,3-dimethylbutadiene (12.6%). Reaction with excess triphenylphosphine at 100°C caused 2,3-dimethylbutadiene (90.3%) to be liberated.

η^1, η^3 -Tetramethyloctadienediylnickeltrimethylphosphine (18b)

Orange crystals of this complex were prepared by treating [Ni(PMe₃)(CDT)] with excess 2,3-dimethylbutadiene in ether/pentane at room temperature for 24 h. Yield ca. 85%. Found, Ni, 19.5. Calcd.: Ni, 19.65%.

The ¹³C NMR spectrum confirmed the presence of methyl groups at C(2), C(3), C(6) and C(7) of the C₈ fragment.

References

- 1 (a) G. Wilke, *Angew. Chem.*, 75 (1963) 10; *Angew. Chem. Int. Ed. Engl.*, 2 (1963) 105; (b) See P.W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Vol. II, Chapter III, Academic Press, New York, 1975, and *Comprehensive Organometallic Chemistry*, Chapter 37.4, 37.6 and 65.4, Pergamon Press, Oxford, 1982 for a summary of earlier literature.
- 2 P.W. Jolly, I. Tkatchenko and G. Wilke, *Angew. Chem.*, 83 (1971) 328; *Angew. Chem. Int. Ed. Engl.*, 10 (1971) 328.
- 3 P.W. Jolly, I. Tkatchenko and G. Wilke, *Angew. Chem.*, 83 (1971) 329; *Angew. Chem. Int. Ed. Engl.*, 10 (1971) 329.
- 4 B. Barnett, B. Bussemeier, P. Heimbach, P.W. Jolly, C. Krüger, I. Tkatchenko and G. Wilke, *Tetrahedron Lett.*, (1972) 1457.
- 5 B. Bussemeier, P.W. Jolly and G. Wilke, *J. Am. Chem. Soc.*, 96 (1974) 4726.
- 6 B. Bussemeier, P.W. Jolly and R. Salz, Abstract 184 Seventh Int. Conf. Organomet. Chem. Venice, 1975.
- 7 B. Bussemeier, Doctoral Thesis, Univ. Bochum, 1973.
- 8 R. Baker and A.H. Copeland, *Tetrahedron. Lett.*, (1976) 4535; *J. Chem. Soc., Perkin Trans. I*, (1977) 2560.
- 9 R. Baker, M.S. Nobbs and D.T. Robinson, *Chem. Commun.*, (1976) 723; *J. Chem. Soc., Perkin Trans. I*, (1978) 543.
- 10 B. Henc, P.W. Jolly, R. Salz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard and C. Krüger, *J. Organomet. Chem.*, 191 (1980) 449.
- 11 H.B.R. Krische, Doctoral Thesis, Universität Essen-Gesamthochschule, 1980.
- 12 P.W. Jolly, K. Jonas, C. Krüger and Y.-H. Tsay, *J. Organomet. Chem.*, 33 (1971) 109.
- 13 P.W. Jolly, R. Mynott and R. Salz, *J. Organomet. Chem.*, 184 (1980) C49.
- 14 See for example P. Heimbach and H. Schenkluhn, *Top. Curr. Chem.*, 92 (1980) 45.
- 15 R. Huisgen, A. Dahmen and H. Huber, *J. Am. Chem. Soc.*, 89 (1967) 7130.
- 16 P. Heimbach, *Angew. Chem.*, 85 (1973) 1035; *Angew. Chem. Int. Ed. Engl.*, 12 (1973) 975.
- 17 H. Buchholz, P. Heimbach, H.J. Hey, H. Selbeck and W. Wiese, *Coord. Chem. Rev.*, 8 (1972) 129.
- 18 R. Benn and G. Schroth, *Org. Magn. Res.*, 14 (1981) 435.
- 19 R. Benn, J. Klein, A. Ruffńska and G. Schroth, *Z. Naturforsch. B*, 36 (1981) 1595.
- 20 P.W. Jolly and R. Mynott, *Adv. Organomet. Chem.*, 19 (1981) 257.
- 21 R. Mynott, unpublished results.
- 22 H. Brandes, R. Goddard, P.W. Jolly, C. Krüger, R. Mynott and G. Wilke, *Z. Naturforsch. B*, 39 (1984) 1139.