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HOMOGENEOUS CATALYSIS. IV†. HYDROSILYLATION OF CYCLIC OR LINEAR DIENES USING LOW-VALENT NICKEL COMPLEXES AND RELATED EXPERIMENTS**

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Summary

The hydrosilylation of cyclohexadienes using $Ni(acac)_2$-$Al(OEt)Et_2$ gives only the allylic cyclohexenylsilane with both 1,3- or 1,4-(in presence of a phosphine)cyclohexadienes. The reactions with the isomeric cis- or trans-1,3-pentadienes (giving 1:1 adducts), using the $Ni(acac)_2$-$AlEt_3$ catalyst, are compared. 2,3-Dimethyl-1,3-butadiene readily gives mainly the product of 1,4- rather than 1,2-addition, but the proportion of the latter is increased by incorporating PPh_3 into the catalyst. $Ni(acac)_2$ with other reducing agents as cocatalysts are also effective. Other less reactive catalysts for linear 1,3-dienes include $[NiCl_2(PPh_3)_2]$-Bu^nMgBr, and $[Ni(dipy)(PhCN)_2]$-$AlEt_3$, and for crotonaldehyde $[Ni(dipy)(PhCN)_2]$.

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**No reprints available.

† For Part III, see ref. 1.

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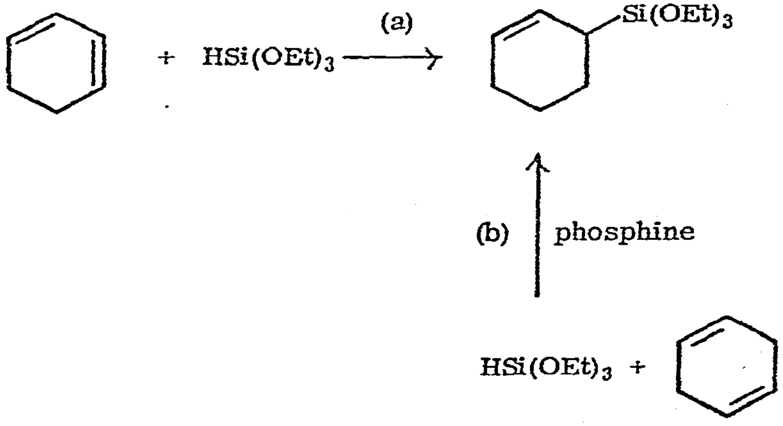
Introduction

We have reported the use of Ziegler systems using metal acetylacetonates in conjunction with various reducing agents for the hydrosilylation of 1-alkynes and linear 1,3-dienes [2]. In this paper we report on further studies of the utility of these and related systems for the catalysis of hydrosilylation.

Cyclic dienes

Nickel acetylacetonate is an active catalyst, in the presence of $Al(OEt)Et_2$ as cocatalyst, for the hydrosilylation using alkoxysilanes of (a) 1,3-dyclohexadiene and (b) in the presence of a tertiary phosphine [1:2 $Ni(acac)_2$:phosphine], for 1,4-cyclohexadiene. No reaction is observed with alkyl- or siloxy-silanes, $HSiEt_3$ or $HSi(OSiMe_3)_2Me$; and with $AlEt_3$ as cocatalyst rapid reduction of the $Ni(acac)_2$ occurs resulting in precipitation of metal. No reaction is observed for either system when attempting to hydrosilylate 1,3-cyclo-octadiene, 1,5-cyclo-octadiene, or norbornadiene (Table 1).

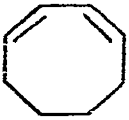
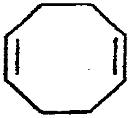
Addition of triethoxysilane to 1,3-cyclohexadiene and catalyst results [equation (1a)] in the formation of 1,4-adduct (97%).



(1)

TABLE 1

HYDROSILYLATION OF CYCLIC DIENES AT 20° C [a]

Diene (mmol)		Silane (mmol)	Reducing agent[b]	Yield[d] (%)
	(15)	$HSi(OEt)_2$ (5.4)	$Al(OEt)Et_2$	97
	(18)	$HSiEt_3$ (6.3)	$Al(OEt)Et_2$	0
	(15)	$HSi(OEt)_3$ (5.4)	$AlEt_3$	0[e]
	(15)	$HSi(OSiMe_3)_2Me$ (5.0)	$Al(OEt)Et_2$	0
	(18)	$HSiEt_3$ (6.3)	$AlEt_3$	0[e]
 [c]	(15)	$HSi(OEt)_2$ (5.4)	$Al(OEt)Et_2$	52
 [c]	(18)	$HSiEt_3$ (6.3)	$Al(OEt)Et_2$	0
	(15)	$HSi(OEt)_2$ (5.4)	$Al(OEt)Et_2$	0
 [c]	(15)	$HSi(OEt)_3$ (5.4)	$Al(OEt)Et_2$	0[f]

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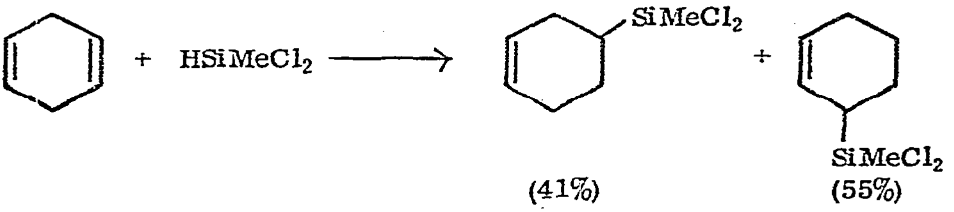
[a] $Ni(acac)_2$ 0.1 mmol. [b] 0.2 mmol added as solution in benzene. [c] PPh_3, 0.2 mmol added. [d] Based on silane; calculated by quantitative GLC. [e] Rapid catalyst decomposition. [f] Catalyst reacted to form $[Ni(PPh_3)_2(1,5\text{-}COD)]$.

Addition of triethoxysilane to 1,4-cyclohexadiene is envisaged to be by an isomerisation as the first step, followed by hydrosilylation, with the products being identified by ^{1}H NMR by comparison with spectra of similar compounds [7a] (Table 5).

Previous studies with $[NiCl_2(PPh_3)_2]$ [7] and 1,4-cyclohexadiene resulted in both possible isomers [equation (2)] [7a], and that chloroplatinic acid H_2PtCl_6 catalyses addition of trimethylsilane to 1,3- and 1,5-cyclo-octadienes [7b].



(2)

Reduction of $Ni(acac)_2$ in 1,5-cyclo-octadiene by the aluminium reagent in the presence of phosphine is a rapid reaction yielding a yellow solution of 1,5-cyclo-octadienebis(triphenylphosphine)nickel(0), which did not catalyse hydrosilylation under ambient reaction conditions.

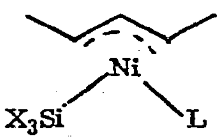
cis- <u>or</u> trans-1,3-<u>Pentadiene</u> We have previously reported that use of a $Ni(acac)_2$–$AlEt_3$ system at room temperature yields the adducts (I) and (II) from the hydrosilylation of commercial 1,3-pentadiene (present in excess) by triethoxysilane [2] [equation (2)]. Thus we obtained a high

$$CH_3CH{=}CH\text{-}CH{=}CH_2 + HSi(OEt)_3 \longrightarrow \underset{(I)}{CH_3CH_2CH{=}CHCH_2Si(OEt)_3} \qquad (2)$$

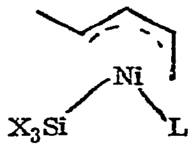
$$+ \underset{(II)}{CH_3CH{=}CH\text{-}CH[Si(OEt)_3]CH_3}$$

yield of adducts, the ratio of (I):(II) being 70:30. We now find that the hydrosilylation of pure *trans*-1,3-pentadiene by triethoxysilane yields 85% (based on silane) of the 1:1 adducts, with a ratio of (I):(II) of 70:30. The previously-used commercial sample of 1,3-pentadiene contained approximately 60% *trans*-1,3-pentadiene, 20% *cis*-1,3-pentadiene, and 20% cyclopentene. However, when pure *cis*-1,3-pentadiene is hydrosilylated by triethoxysilane, using the same catalyst system, the yield of 1:1 adducts is only 56%; with a (I):(II) ratio of 85:15. In both cases the major isomer is isolated, and identified by comparison of its NMR spectra with those of an authentic sample. As a 3:1 molar ratio of 1,3-pentadiene:silane is used during these and other experiments, the adducts from the commercial sample are probably those formed by preferential hydrosilylation of the *trans*-1,3-pentadiene, the reaction with *cis*-1,3-pentadiene appearing to be slower. Thus the (I):(II) ratio is similar whether using an excess of commercial sample or the pure *trans*-1,3-pentadiene. In chloroplatinic acid-catalysed hydrosilylations, competition experiments indicated that *cis*-1,3-pentadiene reacts more slowly than *trans*-1,3-pentadiene [3].

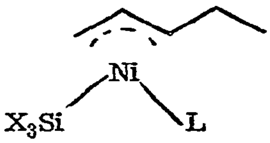
In our mechanism for the hydrosilylation of 1,3-dienes [2], we proposed that a hydridonickel species, formed by oxidative addition of the silane to a Ni^0 intermediate, reacted with the diene to form the π-allyls (III) and (IV), which could rearrange through a σ-butenyl intermediate to the π-allyl (V).



(III)



(IV)

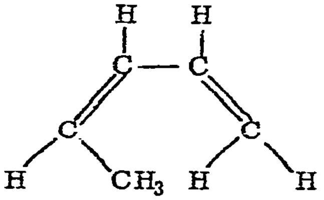


(V)

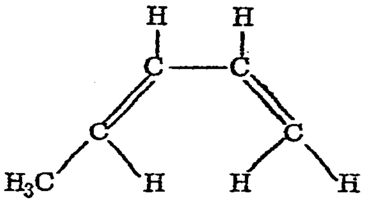
(L represents all other ligands)

Carbon-silicon bond formation from (III) or (IV) leads to (II), whereas bond formation from (V) leads to (I).

The differences in the hydrosilylation of cis- and trans-1, 3-pendadiene may be rationalised in terms of this proposed mechanism. cis-1,3-Pentadiene, (VI), is expected to react more slowly in the s-cisoid configuration with a nickel hydride than trans-1,3-pentadiene, (VII), due to steric hindrance of the methyl group. Thus the formation of the catalytic intermediates, (III) and (IV), would be slowed down, and the rate of catalyst deactivation could become comparable to the rate of hydrosilylation. This would lead to lower yields. The greater proportion of (II) formed from cis-1,3-pentadiene could be due to the formation of (V) directly from the diene, as the formation of (III) and (IV) becomes slower. A mechanism involving π-allyls, similar to (III), (IV), and (V), has been proposed for the reaction of 1,3-pentadienes with amines, catalysed by a $[Ni\{P(OEt)_3\}_4]$-CF_3CO_2H system [4]. cis- And trans-1,3-pentadiene react differently [equations (3) and (4)].



(VI)



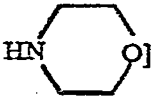
(VII)

$$\underline{trans}\text{-}CH_3CH{=}CHCH{=}CH_2 + HNR_2 \xrightarrow{80^{0}\,C,\ 6\ h} \underline{trans}\text{-}CH_3CH{=}CHCH(NR_2)CH_3$$

(VIII) 100% (3)

$$\underline{cis}\text{-}CH_3CH{=}CHCH{=}CH_2 + HNR_2 \xrightarrow{80^{0}\,C,\ 6\ h} \underline{trans}\text{-}CH_3CH{=}CHCH(NR_2)CH_3$$

(IX) 15% (4)

$[HNR_2$ + ]

$+\ \underline{trans}\text{-}CH_3CH_2CH{=}CHCH_2NR_2$

(X) 20%

Compounds (VIII) and (IX) are the analogues of (II) and (I); with trans-1,3-pentadiene a high overall yield is obtained in both cases, whereas with cis-1,3-pentadiene far lower yields are obtained; the proportion of (VIII), or its analogue (II), is lower in the reaction with cis-1,3-pentadiene. The hydroamination thus shows qualitative similarities to the $Ni(acac)_2$-$AlEt_3$ catalysed hydrosilylation of cis- and trans-1,3-pentadienes [equation (2)], which is consistent with the similar mechanisms proposed.

Other linear dienes The hydrosilylation of a 2,3-dimethyl-1,3-butadiene using the $Ni(acac)_2$-$AlEt_3$ catalyst system gives essentially quantitative yields of the 1,4 adduct, a 2,3-dimethyl-2-butenylsilane, (XI), [equation (5)], at room temperature. The 1,2 adducts, 2,3-dimethyl-3-butenylsilanes, are also formed in very low yield (ca. 1-2%). These were identified by comparison of their GLC characteristics with authentic samples. However, if triphenylphosphine is added to the catalyst system ($Ni:PPh_3$, 1:1) the ratio of 1,4 adduct:1,2 adduct becomes 85:15, although the yield drops to 46% [$X_3 = (OSiMe_3)_2Me$]. The interpretation is as follows. The hydrosilylation of 2,3-dimethyl-1,3-butadiene by bis-(trimethylsiloxy)methylsilane involves a diene, which according to the proposed mechanism [2], should give rise to a sterically hindered π-allyl intermediate, and a bulky silane. Hence simultaneous π-allyl formation and oxidative addition of the silane to nickel should become more difficult if triphenylphosphine is also co-ordinated to the nickel.

$$CH_2{=}C(CH_3){=}CH_2 + HSiX_3 \longrightarrow \underset{(XI)}{(CH_3)_2C{=}C(CH_3)CH_2SiX_3} \qquad (5)$$

[(XIa), X = OEt; (XIb), $X_3 = (OSiMe_3)_2Me$; (XIc), $X_3 = Et_2Me$]

Sodium bis(2-methoxy-ethoxy)aluminium hydride in place of triethylaluminium has been noted before in the hydrosilylation of 1-alkynes [5] and 1,3-butadiene [6]. Sodium borohydride in conjunction with $Ni(acac)_2$

TABLE 2

HYDROSILYLATION OF 2,3-DIMETHYL-1,3-BUTADIENE AT 20° C [a]

Silane (mmol)	Reducing agent (mmol)	Solvent [b]	Yield of (XI) [c] (%)
$HSi(OEt)_3$ (5.4)	$AlEt_3$ [d] (0.2)	None	94
$HSiEt_2Me$ (3.5)	$AlEt_3$ [d] (0.2)	None	96
$HSi(OSiMe_3)_2Me$	$AlEt_3$ [d] (0.2)	None	97
$HSi(OSiMe_3)_2Me$ [e]	$Al(OEt)Et_2$ [d]	None	46 [f]
$HSi(OSiMe_3)_2Me$	$Na[AlH_2(OCH_2CH_2OCH_3)_2]$ [d]	None	72
$HSi(OSiMe_3)_2Me$	$NaBH_4$	Diglyme	0
$HSi(OSiMe_3)_2Me$ [g]	$NaBH_4$	Diglyme	37

[a] $Ni(acac)_2$, 0.1 mmol; 2,3-dimethyl-1,3-butadiene, 8.8 mmol; at 20° C for 4 h

[b] Solvent 2 cm^3

[c] Based on silane; calculated by quantitative GLC; contains small amount of an isomer.

[d] Added as a solution in benzene

[e] PPh_3, 0.1 mmol, added

[f] Contains 15% of $CH_2{=}C(CH_3)C(CH_3)CH_2SiX_3$

[g] 60° C for 3 h

also gives a catalyst system which is only weakly active at elevated temperatures (60° C). The results are summarised in Table 2.

Attempts to hydrosilylate 2,5-dimethyl-2,4-hexadiene with triethoxysilane using the $Ni(acac)_2$-$AlEt_3$ catalyst system resulted in catalyst decomposition and no hydrosilylation. This result is not surprising, as this diene is very sterically-hindered, and addition across the Ni-H bond postulated as a step in the catalytic cycle [2], would be very difficult.

The use of dichlorobisphosphinenickel(II) complexes Dichlorobisphosphinenickel(II) complexes, in conjunction with butylmagnesium bromide, form active catalysts for the hydrosilylation of dienes at room temperature (Table 3).

The activity of these catalyst systems is lower than that of the nickel(II) acetylacetonate system. The results resemble those obtained by using dichlorobisphosphinenickel(II) complexes without added reducing agent at 105° C, e.g., equation (6) [7]. The use of an added reducing agent obviates the need for higher temperatures, which were necessary for reduction of the Ni^{II}

$$CH_2{=}C(CH_3)CH{=}CH_2 + HSiMeCl_2 \xrightarrow[105^\circ C,\ 8\ days]{[NiCl_2(dmpf)]} \underset{33\%}{(CH_3)_2C{=}CHCH_2SiMeCl_2} \qquad (6)\ [7,8]$$

$$+ \underset{44\%}{CH_3CH{=}C(CH_3)CH_2SiMeCl_2}$$

[dmpf = 1,1'-bis(dimethylphosphino)ferrocene]

complexes by silane to a catalytically-active Ni^0 species [8]. More basic phosphines increase the yield of the 1:1 adducts. This trend was also observed for the dichlorobisphosphinenickel(II) catalysts [7]. The products formed and their proportions resemble those obtained with the $Ni(acac)_2$-$AlEt_3$ system to which the appropriate phosphine has been added [2]. The

(Continued on p. 144)

TABLE 3

HYDROSILYLATION OF 1,3-DIENES USING DICHLOROBISPHOSPHINENICKEL(II) COMPLEXES[a]

Catalyst	Diene	Silane	Yield of 1:1-adduct[b] (%)	Products (ratio)
$[NiCl_2(PPh_3)_2]$	1,3-pentadiene	$HSi(OEt)_3$	45	$CH_3CH_2CH{=}CHCH_2SiX_3$, $CH_3CH{=}CH(SiX_3)CH_3$; 90:10
$[NiCl_2diphos]$	1,3-pentadiene	$HSi(OEt)_3$	60	$CH_3CH_2CH{=}CHCH_2SiX_3$, $CH_3CH{=}CH(SiX_3)CH_3$; 70:30
$[NiCl_2(PMe_2Ph)_2]$	1,3-pentadiene	$HSi(OEt)_3$	77	$CH_3CH_2CH{=}CHCH_2SiX_3$, $CH_3CH{=}CH(SiX_3)CH_3$; 65:35
$[NiCl_2(PMe_2Ph)_2]$	2,3-dimethyl-1,3-butadiene	$HSi(OSiMe_3)_2Me$	23[c]	$(CH_3)_2C{=}C(CH_3)CH_2SiX_3$, $CH_2{=}C(CH_3)CH(CH_3)CH_2SiX_3$, 80:20
$[NiCl_2(PMe_2Ph)_2]$[d]	1,3-pentadiene	$HSi(OEt)_3$	0	

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[a] Ni complex, 0.2 mmol; toluene 1 cm^3; and diene (1,3-pentadiene, 15 mmol; or 2,3-dimethyl-1,3-butadiene, 9 mmol); BuMgBr in Et_2O (0.5 mmol) added at -60° C; allowed to warm slowly to 0°; silane added [$HSi(OEt)_3$, 5.4 mmol; or $HSi(OSiMe_3)_2Me$, 4.4 mmol]; stirred at ambient temperature for 4 h.

[b] Based on silane; calculated by GLC

[c] Also heated at 60° C for 3 h

[d] Reductant $LiAlH_4$, 0.8 mmol, or $AlEt_3$, 0.4 mmol

TABLE 4

DIPYRIDYL(BENZONITRILE)NICKEL(0) AS A HYDROSILYLATION CATALYST[a]

Unsaturate (mmol)	Silane (mmol)	Conditions (°C, h)	Yield (%)[b]	Products (ratio)
1,3-pentadiene (15)	$HSi(OEt)_3$ (5.4)	20^0, 4	74	$CH_3CH_2CH{=}CHCH_2SiX_3$, $CH_3CH{=}CHCH(SiX_3)CH_3$ (70:30)
2,3-dimethyl-1,3-butadiene (8.8)	$HSi(OSiMe_3)_2Me$ (4.4)	20^0, 6	75	$CH_3)_2C{=}C(CH_3)CH_2SiX_3$, $CH_2{=}C(CH_3)CH(CH_3)CH_2SiX_3$ (80:20)
1-pentyne (15)	$HSi(OEt)_3$ (5.4)	20^0, 6	12	$CH_2{=}C(R)C(R){=}CHSiX_3$, $RCH{=}CHC(R){=}CHSiX_3$ (80:20) [$R = n\text{-}C_3H_7$]
crotonaldehyde[c] (20)	$HSi(OEt)_3$ (11)	20^0, 4 then 100^0, 3	75	$CH_3CH{=}CHCH_2OSiX_3$

[a] Dipy(PhCN)Ni(0) (0.1 mmol) and unsaturate mixed at 0^0 C; $AlEt_3$ (0.2 mmol) added; stirred at 0^0 C for 10 min; silane added

[b] Based on silane; calculated by quantitative GLC

[c] No $AlEt_3$ added

lack of catalytic reaction using lithium aluminium hydride or triethylaluminium is, however, surprising.

The use of dipyridyl(benzonitrile)nickel(0) as a hydrosilylation catalyst

Dipyridyl(benzonitrile)nickel(0) is an air-stable compound and catalyst for the polymerisation of acrylonitrile in air [9]. However, attempts to use it as a hydrosilylation catalyst were only moderately successful.

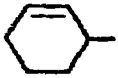
Without a co-catalyst, it is inactive for the hydrosilylation of dienes or acetylenes, but upon addition of triethylaluminium, the reaction mixtures become homogeneous, and moderate yields of adducts are obtained (Table 4). The effect of the triethylaluminium may be to cause alkylation yielding diethyl(dipyridyl)nickel(II), which is known to be a modest hydrosilylation catalyst [10]. Alternatively, ligand abstraction (for which there is precedent [11])may occur, leaving a catalytic nickel species.

Dipyridyl(benzonitrile)nickel reacts with crotonaldehyde to give a homogeneous solution at 20° C, and this is an active catalyst at higher temperatures for the hydrosilylation of crotonaldehyde by triethoxysilane (Table 3).

Experimental

All reactions were carried out under pure argon, using freshly distilled, dry, degassed solvents.

^{1}H NMR spectra were recorded on a Varian Associates A60 or T60 spectrometer. IR spectra were obtained with a Perkin-Elmer 457 grating spectrophotometer as thin films. Mass spectrum - GLC analyses were carried out on a machine constructed from an Edwards E606 Fast Scanning Mass Spectrometer and a Pye-Unicam Model 204 Series 64 gas chromatograph. Preparative GLC separations were carried out using a Pye-Unicam Model 105 instrument. The GLC analysis of the reaction products was carried out on a Pye Series 104 Gas Chromatograph, using a 6 ft column of 10% SE30 on 100-120 mesh Chromasorb G, using the following conditions:

Compound	Temperature (°C)	Internal ref.
$CH_3CH{=}CHCH_2OSi(OEt)_3$	140	Indane
$CH_3CH_2CH{=}CHCH_2Si(OEt)_3$	155	Indane
$CH_3CH{=}CHCH[Si(OEt)_3]CH_3$	155	Indane
$(CH_3)_2CH{=}C(CH_3)CH_2SiEt_2Me$	160	Indane
$(CH_3)_2CH{=}C(CH_3)CH_2Si(OEt)_3$	160	Indane
$(CH_3)_2CH{=}C(CH_3)CH_2Si(OSiMe_3)_2Me$	165	Indane
$H_2C{=}C(Pr^{\underline{n}})C(Pr^{\underline{n}}){=}CHSi(OEt)_3$	195	n-Dodecane
$Pr^{\underline{n}}CH{=}CHC(Pr^{\underline{n}}){=}CHSi(OEt)_3$	195	n-Dodecane
 $-Si(OEt)_3$	165	Indane

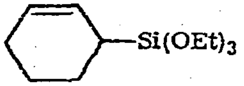
All the unsaturated organic compounds were commercial products, dried over molecular sieves and distilled in an inert atmosphere prior to use, with the exception of 2,3-dimethyl-1,3-butadiene, which was prepared by the literature method [12]. Triethoxy- [13], diethylmethyl- [14], bis-(trimethylsiloxy)methyl- [15] silanes were prepared by standard methods. Nickel acetylacetonate was a commercial sample dried by heating under vacuum for 6 h at 110° C. The dichlorobisphosphinenickel(II) complexes were prepared by standard methods [15, 16], as was the dipyridyl(benzonitrile)nickel(0) [9]. Other details are in Tables 1-5.

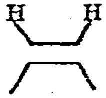
A typical hydrosilylation is as follows.

$Al(OEt)Et_2$ (0.4 mmol) (as M solution in benzene) was added to a solution of $Ni(acac)_2$ (52 mg, 0.2 mmol) in 1,3-cyclohexadiene (5.0 g, 62.5 mmol) at 0° C, and the mixture stirred until a dark brown colour was formed. Triethoxysilane (3.63 g, 22 mmol) was added and the mixture allowed to warm to room temperature and stirred for 8 h.

Volatiles were removed under reduced pressure (~ 2 mmHg) and the residue distilled under reduced pressure through a Vigreux column to give

TABLE 5

^{1}H NMR DATA FOR  [a]

Chemical shift (τ) (integration, description)		Assignment
4.25 - 4.40	(2H, multiplet)	
6.2	(6H, quartet)	O-Si-CH_2-
7.95 - 8.45	(7H, broad multiplet)	Ring protons
9.55	(9H, triplet)	OSi-C-CH_3

[a] 100 MHz spectra; CD_2Cl_2 solution, $CHCl_3$ reference.

2-cyclohexenyltriethoxysilane (3.04 g, 64%), b.p. 122°C/10 mmHg: (Found: C, 59.0; H, 9.92. $C_{12}H_{24}SiO_3$ requires C, 59.0; H, 9.84%). GLC showed this to contain one adduct identified by ^{1}H NMR on a Varian 100 MH_2 NMR spectrometer (Table 5).

To obtain 1:2 (diene:silane) adducts, which acyclic dienes, the proportion of silane was increased (from 3:1, diene:silane to 3:2), and in the hydrosilylation using Ni^0 complexes the silane was added to a solution of the complex in the unsaturate.

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TABLE 6

^{1}H NMR DATA FOR $(CH_3)_2C=C(CH_3)CH_2SiX_3$ [a]

Compound	$(C\underline{H}_3)_2C=C(C\underline{H}_3)$-C Chemical shift ($\tau$) [b]	$C=C-C\underline{H}_2-Si$ Chemical shift (τ) [c]	SiX_3 Chemical shift (τ)
(XIa)	8.33	8.43	6.25 (6H, quartet) ($\underline{J}$ = 7Hz, $Si-O-CH_2-$) 8.88 (9H, triplet) ($\underline{J}$ = 7Hz, $Si-O-C-CH_3$)
(XIb)	8.45	8.62	10.00 (18$\underline{H}$, singlet) ($-Si-O-SiCH_3$) 10.11 (3H, singlet) ($Si-CH_3$)
(XIc)	8.40	8.50	9.0 - 9.6 (10H, $Si-CH_2-CH_3$) 10.03 (3H, singlet) ($SiCH_3$)

[a] 60 MHz spectra, CCl_4 solution; benzene or TMS reference.

[b] 9H, singlet

[c] 2H, singlet

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