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HOMOGENEOUS CATALYSIS

II*. ZIEGLER SYSTEMS AS CATALYSTS FOR HYDROSILYLATION

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Summary

Ziegler type systems, e.g., $M(acac)_n$—$AlEt_3$ (M = Ni, Co, or Fe) catalyse the hydrosilylation of 1,3-dienes or terminal acetylenes. With isoprene or 1,3-pentadiene the 1,4-adducts $CH_3CH{=}C(CH_3)CH_2SiX_3$ or $CH_3CH_2CH{=}CHCH_2SiX_3$ are the major products, and Ni salts [$NiCl_2$ or $Ni(acac)_2$] provide the best catalysts. For 1,3-pentadiene and $HSi(OR)_3$ a significant by-product is $CH_3CH{=}CHCH(SiX_3)CH_3$, the formation of which is suppressed by addition of phosphines. A chain-reaction mechanism consistent with these results involves the formation successively of a Ni^0 complex, its oxidative adduct L(diene)Ni(H)-SiX_3, a π-allyl complex L(π-allyl)$NiSiX_3$, isomeric σ-pentenyl derivatives, and (I)-(III) + the Ni^0 complex. Terminal acetylenes RC≡CH yield the products in which linear dimerisation accompanies hydrosilylation. The head-to-head adduct $H_2C{=}C(R)C(R){=}CH(SiX_3)$ preponderates over the head-to-tail isomer $R(H)C{=}C(H)C(R){=}CH(SiX_3)$; structures of the former were established by IR and NMR studies and examination of the Diels—Alder adducts with tetracyanoethylene, including comparisons with results on RC≡CD. The catalytic cycle is believed to be similar to that proposed for 1,3-dienes; the linear dimerisation arising from successive insertion of RC≡CH into the Ni—H and Ni—C [in Ni—C(R)=CH_2] bond. Competition experiments demonstrate that hydrosilylation is favoured by electronegative substituents X at Si, and that terminal acetylenes are more reactive than 1,3-dienes. Bis(π-1,5-cyclooctadiene)nickel(0) is also shown to be an effective hydrosilylation catalyst for 1,3-pentadiene.

Introduction

Hydrosilylation, the addition of silicon hydrides, $HSiX_3$, to unsaturated hydrocarbons, was first reported by Sommer in 1947 (e.g., 1-octene → $C_8H_{17}SiX_3$). The reaction is of considerable interest and commercial importance.

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* For Part I see ref. 27. A preliminary report of this paper has appeared (ref. 1).

The use of transition metal catalysts has recently been reviewed [2]. The preferred catalyst for industrial use is chloroplatinic acid, Speier's catalyst. It is evident that, in this and the many other homogeneous hydrosilylation catalyst systems, the mechanism involves the oxidative addition of the silane at a low oxidation state metal centre [2]. Such oxidative addition is also a key step for numerous other transition metal-promoted reactions, such as olefin hydrogenation [3]. The two component Ziegler catalyst systems, involving a transition metal salt and a Main Group metal reducing agent [3], are effective for many of these reactions; it is believed that a low oxidation state transition metal complex intermediate is formed. Such complexes may be stabilised by suitable ligands, such as dienes or acetylenes [3]. We now report on the use of Ziegler systems in hydrosilylation of 1,3-dienes and acetylenes. For both classes of hydrocarbons there are distinctive features which may prove to be of value.

Results and discussion

The activity of Ziegler type systems such as $M(acac)_n{-}AlEt_3$; (M = Cr, Mn, Fe, Co, or Ni) was first examined for α-olefins such as 1-octene with triethyl- or triethoxy-silanes under various conditions. However, the systems containing nickel and cobalt showed only low activity because of competing olefin isomerisation and reduction to the metal, although they were reported to show activity for the hydrogenation of 1-octene [4]. This study is being continued in the hope of suitably modifying the catalyst system. For the present, we restrict this report to results on dienes and acetylenes. Because silanes may react independently with either the transition metal component or $AlEt_3$, the order of addition in these reactions is critical. The preferred procedure is to add the silane as the last component in the reaction mixture [see footnotes *a* for Tables 1 or 2].

Dienes

The hydrosilylation of 1,3-dienes such as isoprene (eqn. 1) or 1,3-pentadiene (eqn. 2) by Ziegler systems gave mainly the 1,4-adducts. Isoprene gave the same products, 2-methyl-2-butenylsilane derivatives (I), as Speier's catalyst [5]. By contrast, 1,3-pentadiene gave principally 2-pentenylsilane derivatives (II), whereas the Speier system [6] affords 1-methyl-2-butenylsilane derivatives

$$CH_2{=}CH{-}C(CH_3){=}CH_2 + HSiX_3 \rightarrow CH_3CH{=}C(CH_3)CH_2SiX_3 \qquad (1)$$

(Ia), $X = OCH_3$

(I)

$$CH_3CH{=}CH{-}CH{=}CH_2 + HSiX_3 \rightarrow \qquad (2)$$

$$CH_3CH_2CH{=}CHCH_2SiX_3 + CH_3CH{=}CH{-}CH(SiX_3)CH_3$$

(II) (III)

(IIa), $X = OC_2H_5$ (IIIa), $X = OC_2H_5$
(IIb), $X = C_2H_5$
(IIc), $X_3 = Cl_2CH_3$
(IId), $X = CH_3$

TABLE 1

HYDROSILYLATION OF DIENES AT 20°

$M(acac)_n$ [a]	Diene	Silane	Solvent	Time	Yield of 1,1-adduct [b]
$Ni(acac)_2$	Isoprene	$HSi(OEt)_3$	None	2	94
$NI(acac)_2$	Isoprene	$HSi(OMe)_3$	None	2	92
$Ni(acac)_2$	Isoprene	$HSiEt_3$	Benzene	4	97
$Ni(acac)_2$	Isoprene	$HSiEt_3$	THF	4	96
$Ni(acac)_2$	Isoprene	$HSiEt_3$	n-Hexane	4	90
$Ni(acac)_2$	Isoprene	$HSiEt_3$ [e]	Benzene	4	93
$NiCl_2$ [c]	Isoprene	$HSiEt_3$	THF	6	95
$Ni(acac)_2$ [d]	Isoprene	$HSiEt_3$	THF	5	87
$Co(acac)_3$	Isoprene	$HSi(OEt)_3$	None	6	44
$Fe(acac)_3$	1,3-Pentadiene	$HSiEt_3$	None	2	41
$Ni(acac)_2$	1,3-Pentadiene	$HSiEt_3$	None	3	99
$Ni(acac)_2$	1,3-Pentadiene	$HSiMeCl_2$	None	3	96
$Ni(acac)_2$	1,3-Pentadiene	$HSi(OEt)_3$	None	3	96 [f]
$Ni(acac)_2$ [g]	1,3-Pentadiene	$HSi(OEt)_3$	None	3	96 [f]
$Ni(acac)_2$ [h]	1,3-Pentadiene	$HSi(OEt)_3$	None	2	91 [f]
$Co(acac)_3$	1,3-Pentadiene	$HSi(OEt)_3$	None	4	48

[a] $M(acac)_n$, 0.1 mmol; $AlEt_3$, 0.2 mmol (Ni) or 0.3 mmol (Fe or Co); diene, 15 mmol; $HSi(OEt)_3$, 5.4 mmol or $HSiEt_3$, 6.3 mmol or $HSiMeCl_2$, 9.6 mmol; and solvent 2 ml. [b] Based on silane; containing a small amount of isomer(s). [c] $AlEt_3/Ni^{2+} = 3$. [d] Reductant: $LiAlH_4$, 0.4 mmol. [e] 10 mmol. [f] Containing approximately 30% of $MeCH=CH[Si(OEt)_3]Me$. [g] Reductant: BuMgBr, 0.2 mmol. [h] Reductant: Et_2AlOEt, 0.2 mmol.

(III). Only for the case of triethoxysilane was this isomer, (IIIa) also formed. It was isolated by preparative GLC and identified by its NMR and IR spectra (see experimental section). Compounds (III) may arise from 1,2-addition to the diene, but it is more probable that they, like (II), derive from 1,4-addition but in the reverse sense. Labelling experiments may resolve these alternatives.

Only the systems with M = Fe, Ni, or Co show any activity; however, the Co and Fe systems give lower yields of the hydrosilylated products, and many more side-products. The nickel catalyst is thus the reagent of choice in terms both of reactivity and selectivity and is more active than Speier's catalyst. The results are summarised in Table 1.

The preponderance of 1,4-addition products suggests that hydrosilylation proceeds through a π-allylic intermediate, as is also proposed for many catalytic reactions of dienes [7, 8]. A possible mechanism for the hydrosilylation of 1,3-pentadiene is shown in Fig. 1. This involves the formation of a zerovalent nickel species, stabilised by diene or other ligands, followed by oxidative addition of silane and subsequent formation of a π-allylic intermediate. The next step is the formation of a secondary alkyl—nickel complex. The rearrangement of secondary nickel alkyls to primary alkyls has been proposed by Kumada [9] to occur during the coupling of secondary alkyl Grignard reagents to alkyl halides catalysed by bis(phosphine)nickel dihalides. Using trialkylsilanes, the rearrangement must occur faster than the silicon—carbon bond forming step; with trialkoxysilanes, which react faster with dienes (see competition experiments), appreciable amounts of (III) are formed before rearrangement occurs. Kumada et al. [9] found the rearrangement of secondary nickel alkyls was accelerated by the addition of more electron-donating ligands on nickel, due to the stabilisation of the π-intermediate (the so-called β-effect [10]). Addition of

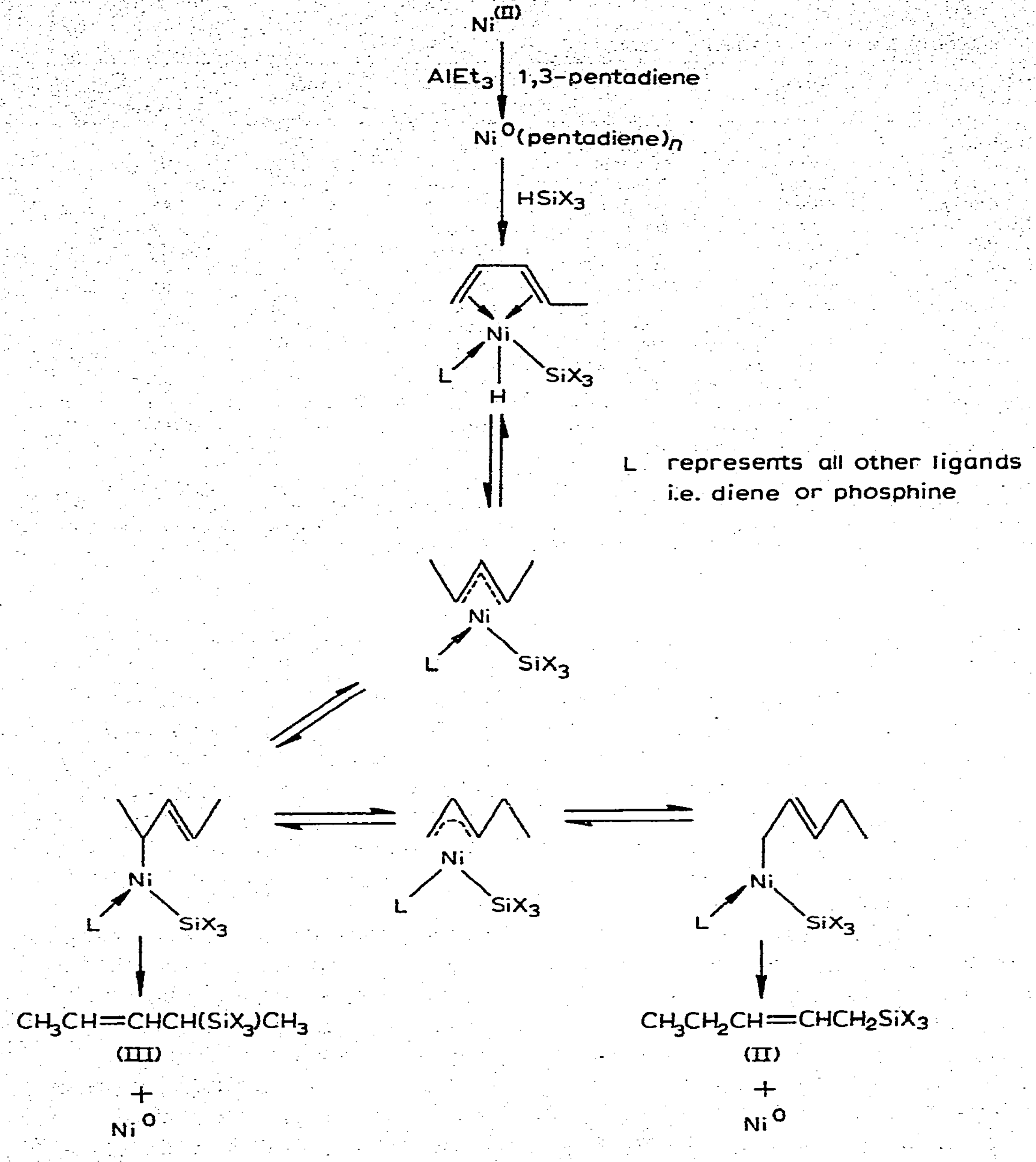


Fig. 1. Proposed mechanism for hydrosilylation of 1,3-pentadiene.

various ratios of phosphines, which are better electron donors than dienes, was, in fact, found to lessen the amounts of (IIIa) formed; the results are summarised in Table 2. Diphos ($Ph_2PCH_2CH_2PPh_2$) gives higher yields of (IIIa), in keeping with its low activity in rearranging secondary alkyls [9].

Nickel(0) and palladium catalysts have been reported [7] to give with butadiene the coupled adducts, octadienylsilane derivatives. We find no coupled

TABLE 2

LIGAND EFFECTS ON THE HYDROSILYLATION OF 1,3-PENTADIENE [a]

Ligand (L)	Ratio of L/Ni^{2+}	Yield of 1/1-adduct (%) [b]	Ratio of (IIa)/(IIIa)
None [c]		96	70/30
None		91	70/30
PPh_3	1	97	97/3
PPh_3	2	94	93/7
PPh_3	3	98	94/6
Diphos [d]	1	96	75/25
bipy [e]	1	97	85/15
$P(OPh)_3$	1	73	90/10

[a] *(i)* $Ni(acac)_2$, 0.1 mmol; 1,3-pentadiene, 15 mmol and L mixed at 20°; *(ii)* $AlEt_2(OEt)$, 0.2 mmol in benzene added at 0°; *(iii)* $HSi(OEt)_3$, 5.4 mmol added at 0°; stirred at 20° for 3 h. [b] Based on silane. [c] 0.2 mmol $AlEt_3$ as reductant. [d] 1,2-bis(diphenylphosphino)ethane. [e] 2,2'-bipyridine.

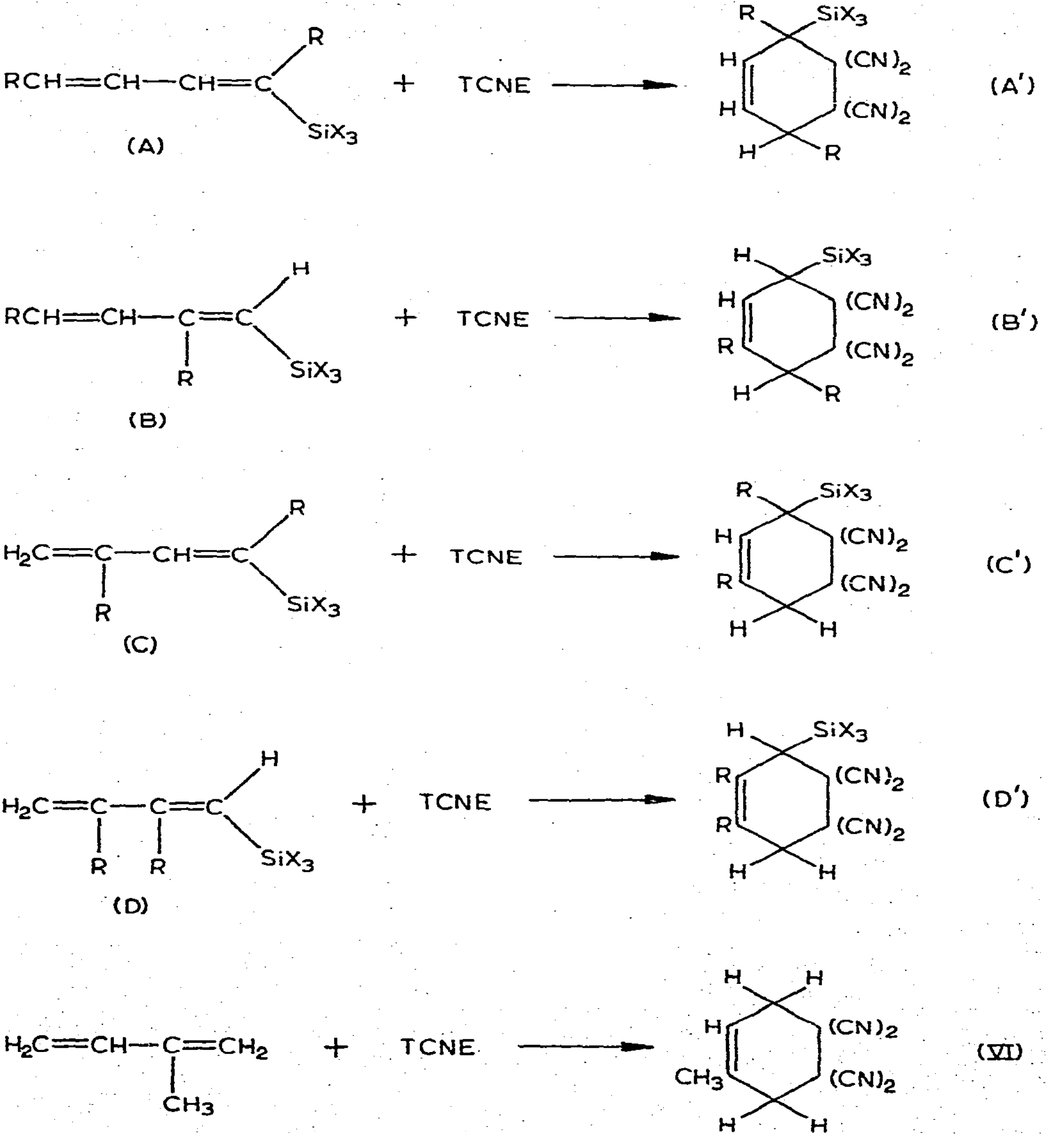


Fig. 2. Possible structures and Diels—Alder adducts.

adducts, octadienylsilane derivatives. We find no coupled products for the case of isoprene or 1,3-pentadiene with the Ziegler systems.

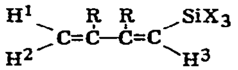
These Ziegler catalysts are inactive for the hydrosilylation of cyclic dienes such as cyclopentadiene, *cis,cis*-1,5-cyclooctadiene, or norbornadiene.

Acetylenes

Terminal acetylenes, RC≡CH, are known to react with silicon hydrides to give 1/1-[$RCH{=}CH(SiX_3)$] or 1/2-[$RCH_2CH(SiX_3)_2$] adducts in the presence of peroxides, bases, or platinum catalysts [11]; the last-named give exclusively the *trans*-isomers [12]. With Ziegler systems containing nickel, terminal acetylenes have been found to give coupled adducts, 1,3-butadienylsilane derivatives (eqn. 3). Thus nickel acetylacetonate was reduced in 1-pentyne with triethylaluminium to give a dark-green solution. Addition of triethoxysilane at 0° was highly exothermic; distillation gave a colourless liquid in high yield. GLC analysis showed the presence of two components [(IVa), 80%; (Va), 20%], from which pure specimens of (IVa) and (Va) were obtained by preparative GLC. The mass spectra (P^+ = 300) and elemental analyses revealed both of them to be 2/1 pentyne—silane adducts. There are four possible structures (Fig. 2, A—D) for these, even without considering geometrical isomers. The IR spectrum of the major product, (IVa), showed the presence of a conjugated double bond at 1600 cm^{-1} and a terminal methylene group (3080 and 902 cm^{-1}) (Table 3), which suggests structures C or D. In the olefinic region of the NMR spectrum three peaks appeared at τ 4.96 (triplet), τ 5.10 (multiplet), and τ 5.21 (multiplet), in integrated ratio of 1/1/1. The fine structure was confirmed as arising from coupling with the methylene protons adjacent to the carbon—carbon double bonds, as this changed to a first-order spectrum consisting of a singlet and two doublets when the methylene proton resonance at τ 7.85 was irradiated. The peak at τ 4.96 is therefore assigned to the proton of the group $=CH(SiX_3)$, and the others to the terminal methylene protons; it is curious that in vinylsilanes $H_2C{=}CH(SiX_3)$, the olefinic proton adjacent to the

TABLE 3

SPECTROSCOPIC DATA



$$H^1H^2C{=}C(R){-}C(R){=}C(SiX_3)H^3$$

R	SiX_3	NMR [a] Chemical shifts (τ)		IR [b] (cm^{-1})		
		H^3	H^1 and H^2	C—H asym. stretch	C—H out of plane def.	Conj. double bond
n-C_3H_7	$Si(OC_2H_5)_3$	4.96	5.10 [c], 5.21 [c]	3080	902	1600
n-C_3H_7	$Si(C_2H_5)_3$	4.88	5.23 [e]	3080	902	1598
n-C_3H_7	$SiCl_2(CH_3)$	4.61	4.99 [c], 5.08 [c]	3080	915	1594
n-C_3H_7	$Si(CH_3)_3$	4.85	5.25 [e]	3080	904	1598
n-C_3H_7	$Si(CH_3)_3$ [d]		5.28 [e]			1587
n-C_3H_7	$Si(OCH_3)_3$	5.00	5.15 [e]	3080	906	1595
n-C_4H_9	$Si(C_2H_5)_3$	4.83	5.18 [e]	3080	902	1595
$(CH_3)_2CHCH_2$-CH_2	$Si(CH_3)$-$(C_2H_5)_2$	4.80	5.19 [e]	3075	903	1595
C_6H_5	$Si(CH_3)_3$	3.59	4.03 [c], 4.56 [c]	[f]	908	1565
$CH_2{=}C(CH_3)$	$Si(OC_2H_5)_3$	4.86	[g]	[f]	890	1598

[a] CCl_4 solution; benzene or TMS reference. [b] Liquid film. [c] Centre of multiplet. [d] $H(D)C{=}C(R){-}C(R){=}CD[Si(OC_2H_5)_3]$. [e] Two protons. [f] Unassignable due to overlapping bands. [g] $RCH_A{=}CH_B{-}C(R){=}CH(SiX_3)$; AB quartet, τ_{HA} 3.62; τ_{HB} 3.43; J_{AB} 16 Hz.

silyl group is described [13, 14] as being at the lowest field of the three olefinic protons. The spectroscopic data are summarised in Table 3, and show that the terminal methylene protons are equivalent in the case of trialkylsilyl derivatives, but non-equivalent for trialkoxy- and methyldichloro-silyl derivatives.

$$2RC{\equiv}CH + HSiX_3 \rightarrow \underset{(IV)}{H_2C{=}C(R)C(R){=}CH(SiX_3)} + \underset{(V)}{R(H)C{=}C(H){-}C(R){=}CH(SiX_3)} \qquad (3)$$

(IVa), $R = n\text{-}C_3H_7$, $X = OC_2H_5$
(IVb), $R = n\text{-}C_3H_7$, $X = C_2H_5$
(IVc), $R = n\text{-}C_3H_7$, $X_3 = CH_3Cl_2$
(IVd), $R = n\text{-}C_3H_7$, $X = CH_3$
(IVe), $R = n\text{-}C_3H_7$, $X = OCH_3$
(IVf), $R = n\text{-}C_4H_9$, $X = C_2H_5$
(IVg), $R = (CH_3)_2CHCH_2CH_2$, $X_3 = (C_2H_5)_2CH_3$
(IVh), $R = C_6H_5$, $X = CH_3$.

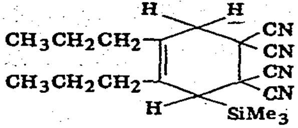
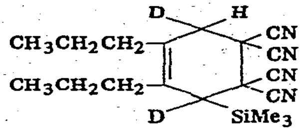
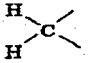
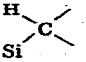
(Va), $R = CH_2{=}C(Me)$, $X = OC_2H_5$

We sought further to distinguish structures C and D by means of a Diels—Alder reaction; an adduct having no olefinic protons would be derived only from structure D (Fig. 2). The reactions of compounds (IVa), (IVb), or (IVd) with maleic anhydride in benzene or xylene under reflux gave colourless viscous oils. The IR and NMR spectra indicated the formation of a Diels—Alder adduct having a structure similar to D′. However, the products were not isolated pure, due to difficulty of crystallisation. Pure crystals were obtained, however, from the reaction of the trimethylsilyl derivative (IVd) with tetracyanoethylene [15]. The NMR spectrum showed complete absence of olefinic protons, whereas the adduct (VI) derived from isoprene showed an olefinic proton at τ 4.42.

In order to confirm the proposed structure, and particularly to establish position of addition of the silane hydrogen atom, the reaction was re-examined in deuterated 1-pentyne-d_1, $C_3H_7C{\equiv}CD$ (purity > 95%) and trimethylsilane. The mass spectrum of the product (VII) showed a parent ion ($P^+ = 212$) which corresponded to a 2/1 adduct, $[(C_3H_7C{\equiv}CD)_2 \cdot HSi(CH_3)_3]$. The IR spectrum, on the basis of comparison with (IVd), showed the disappearance of absorption bands attributed to the terminal methylene group ($=CH_2$), and the appearance of new bands at 3045, 2260, and 2175 cm^{-1}, assigned to C—H and C—D stretches in the groups $=CHD$ and $=C(R)D$; e.g., for the compound $DHC{=}C(D)C_4H_9$ these bands occur at 3030, 2275, and 2230 cm^{-1} [16]. Comparison of NMR spectra (Table 3) of (IVd) and (VII) indicated that the latter was 2,3-di-n-propyl-1-trimethylsilyl-1,3-butadiene-d_1,d_4, which was confirmed by the formation of the Diels—Alder adduct (IX) (Table 4). This suggests that the major product of hydrosilylation of terminal acetylenes is derived from 1,4-addition of silane to

TABLE 4

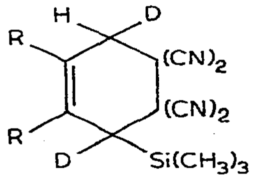
^1H NMR DATA FOR TCNE ADDUCTS (VIII) AND (IX) [a]

Assignment	Chemical shifts (τ) for  (VII)	Chemical shifts (τ) for  (IX)
	6.83—7.15 (2H, multiplet)	6.96 (1H, broad singlet)
	7.25 (1H, broad singlet)	None
$—CH_2—C=$	7.2—8.3 (4H, multiplet)	7.2—8.3 (4H, multiplet)
$CH_3CH_2—$	8.2—9.3 (10H, multiplet)	8.2—9.3 (10H, multiplet)
$CH_3—Si$	9.57 (9H, singlet)	9.57 (9H, singlet)

[a] $CDCl_3$ solution; benzene as internal reference.

the head-to-head coupled dimer of the acetylene, the formation of which is unusual in the dimerisation of terminal acetylene [17].

$$2RC{\equiv}CD + HSi(CH_3)_3 \rightarrow H(D)C{=}C(R){-}C(R){=}C(D)Si(CH_3)_3 \xrightarrow{TCNE}$$

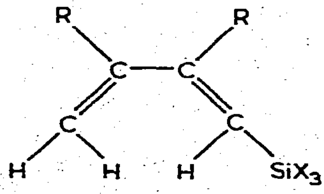


(4)

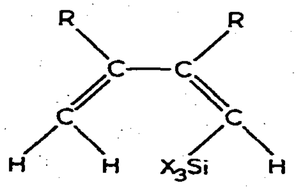
(VIII)

The minor product [(V), X = CH_3] may have structure A or B, because the absence of a terminal methylene group is indicated by the IR spectrum. The NMR spectrum showed a broad singlet at τ 4.92 and about eight peaks from τ 3.30 to τ 4.43 in a ratio of 1/2. The latter peaks are assigned to the protons of the group —CH=CH—, and the former to the proton of the group $—C{=}CH{-}SiX_3$, on the basis of similarity of shifts and hyperfine splitting to those in (IVa). The structure of the minor product is thus believed to be B, formed by the 1,4-addition of the silane to the head-to-tail coupled dimer of the acetylene.

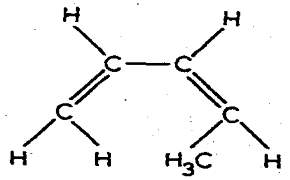
Although for (IV), two geometric isomers, (IV) or (IV′), are possible, the GLC and NMR indicate that only one isomer is formed.



(IV)



(IV′)



(X)

The fact that Diels—Alder adducts are accessible from these 1,3-butadienes suggests that structure (IV) is appropriate, as (IV′) is seen from molecular models to be prevented from forming adducts due to the steric hindrance of the silyl group, [as is *cis*-1,3-pentadiene (X), by the methyl group, whereas *trans*-1,3-pentadiene readily forms adducts [18]].

The Ziegler system was found to be active with other alkylacetylenes, the 2/1 adducts [(IV) f—g] being formed in comparable yields and with similar ratios of (IV)/(V) (i.e., 80/20). The reaction of 2-methyl-1-buten-3-yne (isoprenylacetylene), however, leads to the isolation of the 2/1 adduct in 50% yield with the major isomer (≈ 80%) being (Va) identified by its NMR spectrum (see Table 3). The hydrosilylation of phenylacetylene was carried out in benzene with methyldichlorosilane giving a low yield (36%) of (IVh) after methylation with methyllithium and subsequent work-up. The lower yield in this case was presumably due to concomitant formation of phenylacetylene oligomers (15%) and purification difficulties. The system was inactive for all internal acetylenes, which are also not oligomerised by Ni^0 catalysts [17], perhaps due to lack of an active hydrogen to form a nickel—hydrogen bond or steric hindrance to insertion. $HOCH_2C{\equiv}CH$ or $ClCH_2C{\equiv}CH$ did not hydrosilylate forming polymers, whereas $Me_3SiC{\equiv}CH$ did not react, presumably for steric reasons. Ziegler systems containing Cr^{III}, Mn^{II}, Fe^{III}, Co^{III}, Mo^{III}, or Cu^{II} acetylacetonates were inactive for the hydrosilylation of terminal acetylenes, giving acetylene polymers or oligomers.

Various catalysts and solvent systems were used for the hydrosilylation of pentyne with silanes, as summarised in Table 5.

A possible mechanism for the reaction is outlined in Fig. 3. Again it involves formation of a Ni^0 species stabilised by acetylene ligands, oxidative addition of the silane, followed by insertion of acetylene molecules into first a Ni—H bond and then into a Ni—C bond. Finally the carbon—silicon bond is formed regenerating the acetylene-stabilised nickel(0) species. The successive insertion of the acetylene first into a nickel—hydrogen bond and then into a nickel—carbon bond may explain the unusual preponderance [17] of the head-to-head dimerised product. The formation of a Ni—H bond may alternatively occur by oxidative addition of the acetylene, as is proposed in nickel-catalysed acetylene oligomerisation [17], thus explaining the inactivity of internal acetylens in hydrosilylation.

Relative reactivities of (a) silanes and (b) unsaturated hydrocarbons

In hydrosilylation the reactivity of silanes is known to depend on the nature of the unsaturated substrate and the catalyst employed. For example, with Speier's catalyst, the activity of silanes has been shown to increase with increasing electronegativity of the substituents on silicon [19]. The competition of silanes for a deficiency of unsaturated substrates showed that $HSi(CH_3)Cl_2$ and $HSi(OC_2H_5)_3$ were each more active than $HSi(C_2H_5)_3$ towards isoprene or 1-pentyne using the $Ni(acac)_2$—$Al(C_2H_5)_3$ system, see Table 6. Unfortunately, competition experiments between chloro- and alkoxy-silanes proved impracticable due to the occurrence of exchange of substituents on silicon. Competition between 1-pentyne and a diene for a deficiency of silane similarly showed that acetylenes are more reactive than dienes, because of the formation of only the pentyne—silane 2/1 adduct.

TABLE 5

HYDROSILYLATION OF 1-PENTYNE AT 20°

Catalyst [a]	Molar ratio [b]	Pentyne (mmol)	Silane	(mmol)	Solvent	Time (h)	Yield (%) [c]	Isomer Ratio	
								(I)	(II)
$Ni(acac)_2$—Et_3Al	2	15	$HSi(OEt)_3$	(5.4)	None	3	89	81	19
$Ni(acac)_2$—Et_3Al	2	15	$HSi(OEt)_3$	(7.5)	None	5	74	81	19
$Ni(acac)_2$—Et_3Al	2	10.8	$HSi(OEt)_3$	(10.8)	None	5	61 [d]	84	16
$Ni(acac)_2$—Et_3Al	2	15	$HSi(OEt)_3$	(5.4)	Benzene	6	81	79	21
$Ni(acac)_2$—Et_3Al	2	15	$HSi(OEt)_3$	(5.4)	THF	6	88	84	16
$Ni(acac)_2$—Et_3Al	2	15	$HSiEt_3$	(6.3)	None	6	90	74	26
$Ni(acac)_2$—Et_3Al	2	15	$HSi(OMe)_3$	(7.5)	None	3	72	89	11
$Ni(acac)_2$—$LiAlH_4$	4	15	$HSiEt_3$	(6.3)	THF	6	87	74	26
$NiCl_2$—Et_3Al	2	15	$HSi(OEt)_3$	(5.4)	None	6	80	85	15
$Ni(acac)_2$—BuMgBr	2	15	$HSi(OEt)_3$	(5.4)	Et_2O	4	45	89	11
$Ni(acac)_2$—CH_3Li	5	15	$HSiEt_3$	(6.3)	Et_2O	12	20	72	28
$NiCl_2$—$NaBH_4$	4	15	$HSi(OEt)_3$	(5.4)	EtOH	6	21 [e]	83	17
$Ni(acac)_2$—$AlEt_3$ [f]	2	15	$HSi(OEt)_3$	(5.4)	Benzene	12	0 [g]		
$Ni(acac)_2$—$AlEt_3$ [h]	2	15	$HSiEt_3$	(6.3)	Benzene	12	0		

[a] Ni^{2+}, 0.1 mmol. [b] Molar ratio of reductant: Ni^{2+}. [c] Based on silane. [d] Based on pentyne. [e] Also 40% $Si(OEt)_4$ formed. [f] PPh_3, 0.2 mmol. [g] Pentyne oligomers formed. [h] $P(OPh)_3$, 0.2 mmol.

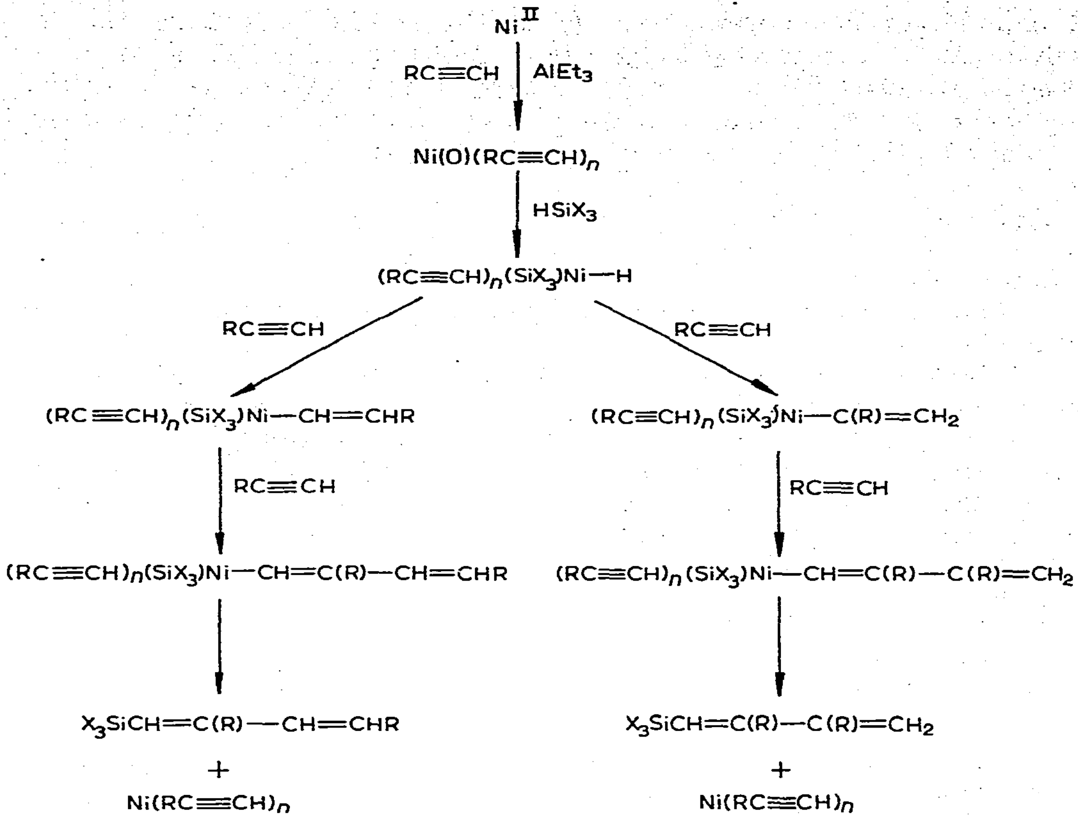


Fig. 3. Proposed mechanism for hydrosilylation of terminal acetylenes.

Use of bis(π-1,5-cyclooctadiene)nickel(0)

The Ziegler system often utilises Et_3Al as the reducing agent. This limits the scope of the reaction if Et_3Al reacts more rapidly with a functionalised acetylene. An alternative zerovalent nickel catalyst, bis(π-1,5-cyclooctadiene)-nickel(0), was therefore investigated. With 1,3-pentadiene, a 90% yield of the

TABLE 6

COMPETITION EXPERIMENTS AT 20° [a]

Hydrocarbon (mmol)	Silanes (mmol)	(mmol)	Conversion of silane (%)	Yield of adduct [b] (%)
Isoprene (10)	$HSi(OEt)_3$	(6.3)	100	97
	$HSiEt_3$	(6.3)	58	49
Isoprene (10)	$HSiMeCl_2$	(6.3)	100	79
	$HSiEt_3$	(6.3)	61	47
Pentyne (15)	$HSi(OEt)_3$	(6.3)	84	81
	$HSiEt_3$	(6.3)	36	36
Pentyne (15)	$HSiMeCl_2$	(6.3)	60	57 [c]
	$HSiEt_3$	(6.3)	3	0
Pentyne (20) Isoprene (20)	$HSiEt_3$	(6.3)	100	90 0

[a] $Ni(acac)_2$, 0.1 mmol; Et_3Al, 0.2 mmol; 3 h at 20°. [b] Based on silane. [c] Some acetylene oligomer also formed.

1/1 adduct was isolated, with a ratio of (IIa)/(IIIa) of 70/30. Although this catalyst with 1,3-butadiene at a higher temperature and trialkylsilanes is reported [7] to give 38% of the coupled adduct, octadienylsilane derivatives, no coupled products were found in this case. With 1-pentyne, relatively low yields (43%) of the 2/1 pentyne/silane adducts were formed.

Experimental

General procedures

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

^{1}H NMR spectra were recorded on Varian Associates A60 or T60 spectrometers. Mass spectra were obtained on a Hitachi—Perkin—Elmer RMU6 instrument. IR spectra were taken with a Perkin—Elmer 457 grating spectrophotometer as thin films. 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	Temp. (°C)	Internal ref.
$CH_3CH{=}C(CH_3)CH_2SiX_3$	150	Indane
$CH_3CH_2CH{=}CHCH_2SiX_3$	150	Indane
$CH_2{=}C(C_3H_7){-}C(C_3H_7){=}CHSiX_3$	180	Naphthalene

All the unsaturated organic compounds were commercial products, dried over molecular sieves and distilled prior to use, with the exception of 1-pentyne which was prepared by the literature method [20]. Triethoxy- [21], trimethoxy- [21], trimethyl- [22], triethyl- [23], diethylmethyl- [24] silanes and bis(π-1,5-cyclooctadiene)nickel [25] were prepared by standard methods. 1-Pentyne-d_1, n-$C_3H_7C{\equiv}CD$, was prepared in a purity of more than 95% from the reaction [26] of D_2O (purity 99.7%) and n-$C_3H_7C{\equiv}CNa$. The metal acetylacetonates were commercial samples dried by heating under vacuum for 6 h at 110°.

The hydrosilylation of isoprene or 1,3-pentadiene

A typical procedure for the hydrosilylation of 1,3-dienes is as follows. The reduction of Ni(acac)$_2$ (78 mg, 0.3 mmol) in 1,3-pentadiene (6.8 g, 100 mmol) with AlEt$_3$ (0.6 mmol in 0.6 ml of benzene) was carried out anaerobically, using ice-bath cooling. This afforded an orange-yellow solution. After addition of triethylsilane (3.6 g, 31 mmol) the mixture was set aside (6 h) at room temperature. The reaction proceeded exothermically. After removal of volatile materials under reduced pressure at room temperature, distillation gave impure triethyl-(2-pentenyl)silane (IIb) (4.2 g, 82% based on the silane), b.p. 88°/11 mm. GLC analysis at 140° showed it to contain a small amount of an isomer. [The reaction with triethoxysilane gave a product containing much more (ca. 30%) of the isomer (III).] Isomer (III) was isolated by preparative GLC and the structure was deduced from IR and ^{1}H NMR spectra, details of which follow.

(a). $CH_3CH[Si(OEt)_3]CH{=}CHCH_3$. IR: ν(CH) of the =CH, 3015; ν(C=C) 1648 cm^{-1}. NMR: τ 4.5-5.1 (2H, CH=CH), 6.25 (6H, quartet, J 7 Hz, O—CH$_2$–

TABLE 7

ANALYTICAL AND PHYSICAL [a] DATA

		B.p. (°C/mm)	n_D^{21}	Analysis found (calcd.) (%)			Mol. wt. found [b] (calcd.)
				C	H	N	
(Ia)	$C_8H_{18}SiO_3$	87/29		50.4 (50.5)	9.92 (9.55)		
(IIa)	$C_{11}H_{24}SiO_3$	97—99/15	1.4183	56.9 (56.9)	10.6 (10.4)		232 (232)
(IIb)	$C_{11}H_{24}Si$	88/1	1.4538	71.8 (71.7)	13.2 (13.1)		184 (184)
(IIc)	$C_6H_{12}Cl_2Si$	[illegible]	1.4502	[illegible] (39.4)	[illegible] (6.61)		
(IId)	$C_8H_{18}Si$ [c]	55/58	1.4236	67.3 (67.5)	12.7 (12.8)		
(III)	$C_{11}H_{24}SiO_3$		1.4168				
(IVa)	$C_{16}H_{32}SiO_3$	138/14	1.4431	64.3 (64.0)	10.8 (10.7)		300 (300)
(IVb)	$C_{16}H_{32}Si$	123—125/5	1.4712	75.8 (76.1)	12.5 (12.8)		252 (252)
(IVc)	$C_{11}H_{20}Cl_2Si$	101—102/5					
(IVd)	$C_{13}H_{26}Si$	92/1	1.4562	74.4 (74.2)	12.6 (12.5)		210 (210)
(IVe)	$C_{13}H_{26}SiO_3$	108—110/8		60.0 (60.4)	9.92 (10.1)		
(IVf)	$C_{18}H_{36}Si$	123/1	1.4700	77.4 (77.1)	13.3 (12.9)		
(IVg)	$C_{19}H_{38}Si$	82/0.2		77.6 (77.5)	12.9 (13.0)		
(IVh)	$C_{19}H_{22}Si$	65—67 [d]		82.1 (82.0)	7.97 (7.97)		
(V)	$C_{16}H_{28}SiO_3$	71/0.05		65.3 (64.8)	9.40 (9.52)		296 (296)
(VIII)	$C_9H_{26}N_4Si$	95—96 [d]		67.7 (67.4)	7.75 (7.74)	16.7 (16.6)	338 (338)
(IX)	$C_{19}H_{24}D_2N_4Si$			66.7 (67.0)	8.19 (8.29)	16.8 (16.5)	

[a] Containing a small amount of isomer. [b] Mass spectra P^+. [c] Obtained from the reaction of (II) with CH_3Li. [d] Melting point (°C).

—C), 7.8-8.6 (4H, CH_3—C=C—CH—Si), 8.85 (9H, triplet, *J* 7 Hz, O—C—CH_3), and 8.97 (3H, broad doublet, *J* 7.5 Hz, $\geqslant$C—CH_3).

(b). CH_3CH_2CH=$CHCH_2Si(OC_2H_5)_3$. IR: ν(CH) of the =CH, 3015; ν(C=C) 1649 cm^{-1}. NMR: τ4.5-4.9 (2H, CH=CH), 6.25 [6H, quartet, *J* 7 Hz, O—CH_2—C], 7.8-8.3 (2H, C—CH_2—C=), 8.4-8.7 (2H, Si—CH_2—C=), 8.85 (9H, triplet, *J* 7 Hz, O—C—CH_3), and 9.07 (3H, triplet, *J* 8 Hz, CH_3).

Some data for 1,3-pentadiene—silane adducts are summarised in Table 7.

The hydrosilylation of acetylenes

(a). Alkylacetylenes. A typical procedure is as follows. The reduction of $Ni(acac)_2$ (130 mg, 0.5 mmol) with $AlEt_3$ (1 mmol in 1 ml of benzene) in 6.2 g (90 mmol) of 1-pentyne at 0° under nitrogen gave immediately a dark-green solution. Triethoxysilane (7.4 g, 45 mmol) was added; after a few minutes, an exothermic reaction took place with gentle refluxing of pentyne. The mixture was set aside (12 h, with stirring) at 20°. Distillation gave the pentyne/silane 2/1 adduct (9.0 g, 67%), b.p. 100-102°/2.5 mm, which consisted of two isomers (20/80). Careful fractional redistillation gave H_2C=$C(n\text{-}C_3H_7)$—$C(n\text{-}C_3H_7)$=$CHSi(OC_2H_5)_3$, (IVa), (in purity greater than 90%), b.p., 138°/14 mm. The

isomer, n-$C_3H_7CH{=}CH{-}C(n\text{-}C_3H_7){=}CHSi(OC_2H_5)_3$, (V), was isolated by preparative GLC. The assignments of NMR spectra for compounds (IVa) and (V) follows.

(IVa): τ 4.96 (1H, triplet, J 1 Hz, $=CH{-}Si$), 5.10 and 5.21 (2H, $H_2C{=}$), 6.25 (6H, quartet, J 7 Hz, $O{-}CH_2$), 7.3-8.2 (4H, $CH_2{-}C{=}$), 8.2-9.4 (10H, $CH_3CH_2{-}$), 8.84 (9H, triplet, J 7 Hz, $O{-}C{-}CH_3$).

(V): τ 3.3-4.5 (2H, $CH{=}CH$), 4.92 (1H, broad singlet, $=CH{-}Si$), 6.21 (6H, quartet, J 7 Hz, $O{-}CH_2$), 7.5-8.1 (4H, $CH_2{-}C{=}$), 8.2-9.3 (10H, CH_3CH_2), 8.75 (9H, triplet, J 7 Hz, $O{-}C{-}CH_3$).

Reactions with trimethylsilane and methyldichlorosilane were carried out using a solvent such as benzene, in a flask fitted with a dry-ice condenser.

The physical properties of the adducts are summarised in Table 7.

(b). Phenylacetylene. $Ni(acac)_2$ (78 mg, 0.3 mmol) in phenylacetylene (5.1 g, 50 mmol) and benzene (10 ml) was reduced at 0° by $AlEt_3$ (0.6 mmol). Methyldichlorosilane (5.0 ml) was added at 0°, and the mixture allowed to warm to room temperature. After the exothermic reaction had ceased, stirring at 20° was continued (6 h). Volatile material was removed under vacuum, and the viscous yellow-brown residue dissolved in ether (90 ml). This was treated in turn with CH_3Li (57 mmol) solution and water, and the non-aqueous portion was dried (Na_2SO_4). After removal of solvent, the 2/1 adduct was extracted with petroleum ether (80 ml), the solvent removed, and the solid adduct recrystallised ($MeOH/C_5H_{12}$) to afford the adduct (2.5 g, 36% based on $PhC{\equiv}CH$).

The Diels—Alder reaction with tetracyanoethylene

$H_2C{=}C(C_3H_7){-}C(C_3H_7){=}CHSi(CH_3)_3$ (IId), (748 mg, 3.56 mmol) was added to tetracyanoethylene (450 mg, 3.52 mmol) in tetrahydrofuran (8 ml). The orange-yellow solution was heated (5 h) under reflux. After removal of the solvent, the residue was recrystallised (C_6H_6/C_5H_{12}) to give white crystals of the adduct, (60% based on tetracyanoethylene), m.p. 95—96°. NMR assignments are in Table 4.

Use of bis(π-1,5-cyclooctadiene)nickel(0) as catalyst

1,3-Pentadiene (3.4 g, 50 mmol) was added to bis(π-cyclooctadiene)nickel (0.28 g, 1.0 mmol) and the golden solution cooled to 0°. Triethoxysilane (4.0 ml, 3.5 g, 22 mmol) was added, and the reaction mixture allowed to warm to room temperature, when an exothermic reaction began. After 4 h at 20°, the volatiles were removed under vacuum and the residue distilled giving the 1/1 pentadiene—silane adduct (4.6 g, 90%), b.p. 96°/10 mm, identified by comparison of its NMR, IR, and GLC characteristics with that of an authentic sample.

The hydrosilylation of 1-pentyne was carried out in the same manner (yield 43%).

Analytical and physical data for the new compounds are summarised in Table 7.

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