Journal of Organometallic Chemistry, 76 (1974) 95—103
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SILICON HYDRIDES AND NICKEL COMPLEXES

IV*. PREPARATION OF SILICON—NICKEL COMPLEXES BY THE REACTION OF SILICON HYDRIDES WITH σ-ALKYL—NICKEL COMPLEXES

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(Received February 6th, 1974)

Summary

Three silicon—nickel complexes, $Ni(bipy)(SiX_3)_2$ (Ia: $X_3 = Cl_3$, Ib: $X_3 = MeCl_2$) and $Ni(h^5\text{-}C_5H_5)(PPh_3)(SiCl_3)$ (II), were prepared by treatment of silicon hydrides with appropriate alkyl—nickel complexes, $Ni(bipy)R_2$ (IIIa: R = Me, IIIb: R = Et) and $Ni(h^5\text{-}C_5H_5)(PPh_3)Et$ (IV), respectively. Both complexes Ia and Ib reacted with hydrogen (or deuterium) chloride to give the corresponding chlorosilane $HSiX_3$ (or $DSiX_3$) and $Ni(bipy)Cl_2$, in good yields. Ib reacted with tetracyanoethylene to afford $MeCl_2SiSiCl_2Me$, but in low yield. II reacted with methyl iodide to form $MeSiCl_3$ (23.5% yield). The silicon—nickel complex Ia was inactive as catalyst for hydrosilylation of olefins, whereas the alkyl complexes IIIb and IV were active.

Introduction

Silicon—transition metal complexes have been identified as key intermediates in hydrosilylation of olefins catalyzed by transition metal complexes [2]. In the course of studies on the hydrosilylation of olefins catalyzed by phosphine—nickel(II) and —nickel(0) complexes [3], we felt a considerable interest in the isolation of new silicon—nickel complexes. Compared with the significant amount of recent research on the chemistry of silicon—platinum complexes [4] much less interest has been shown in the chemistry of silicon—nickel compounds. This may be due in part to a lack of suitable preparative methods or, more likely, a supposed instability of nickel complexes. When we began this study, only three complexes containing a silicon—nickel bond, $Cl_3SiNi(CO)(h^5\text{-}C_5H_5)$ [5], $Li[(CO)_3NiSiPh_3]\cdot 2THF$ [6], and $[Me_4N][(CO)_3NiSiPh_3]$ [6], had been reported. In the meantime bipyridyl and h^5-cyclopentadienyl groups have been

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* For a preliminary communication of this work see ref. 1; for part III of this series see ref. 3c.

used as strongly stabilizing ligands for organo—transition metal complexes. Indeed, $Ni(bipy)R_2$ [7] and $Ni(h^5\text{-}C_5H_5)(PPh_3)R$ [8] (where R = alkyl) are among the most stable σ-alkyl—nickel complexes, but the alkyl—nickel bond(s) involved in these complexes are susceptible to the attack of organic halides [9] and/or olefins [10]. These properties suggest the possibility of preparing some silicon—nickel complexes.

This paper is mainly concerned with the preparation of three silicon—nickel complexes with bipyridyl or h^5-cyclopentadienyl ligands, Ia, Ib and II, by the treatment of the appropriate alkyl complexes with silicon hydrides. During the course of this study a very brief description of compound II, prepared by a different method, has appeared [11].

$Ni(bipy)(SiX_3)_2$ (Ia: $X_3 = Cl_3$, Ib: $X_3 = MeCl_2$)

$Ni(h^5\text{-}C_5H_5)(PPh_3)(SiCl_3)$ (II)

A study of the catalytic activity of complexes Ia, Ib and II and related nickel complexes in the hydrosilylation of olefins will also be reported here.

Results and discussion

Reaction of a silicon hydride with a dialkyl(bipyridyl)nickel(II)

When dimethyl(bipyridyl)nickel(II) (IIIa) was treated with six equivalents of trichlorosilane in ether at —35° for 1.5 h under argon, an immediate color change of the reaction mixture from deep green to brown occurred with evolution of approximately two equivalents of a gas consisting of methane and hydrogen. Filtration of the reaction mixture at ca. —70° gave bis(trichlorosilyl)bipyridylnickel(II) (Ia) as an insoluble yellow-brown powder in 88% yield. GLC analysis of the filtrate showed the formation of methyltrichlorosilane (73% yield). Similar treatment of trichlorosilane with diethyl(bipyridyl)nickel(II) (IIIb) at ca. —55° gave Ia in 85% yield, along with ethyltrichlorosilane (64% yield) and hydrogen (87% yield). An analogous reaction of methyldichlorosilane with IIIb but at a slightly elevated temperature (—35°) and a higher ratio of silane to nickel (12/1) gave bis(methyldichlorosilyl)bipyridylnickel(II) (Ib) in 84% yield, along with ethylmethyldichlorosilane (96% yield) and hydrogen (ca. 100% yield). The principal process of the reaction is represented by eqn. 1.

$$\underset{\substack{\text{(IIIa: R = Me,}\\ \text{IIIb: R = Et)}}}{Ni(bipy)R_2} + 3HSiX_3 \longrightarrow \underset{\substack{\text{(Ia: } X_3 = Cl_3\text{,}\\ \text{Ib: } X_3 = MeCl_2\text{)}}}{Ni(bipy)(SiX_3)_2} + RSiX_3 + H_2 + RH \qquad (1)$$

The complexes Ia and Ib were characterized by elemental analysis, IR spectra (Table 1), and some reactions described below. Both these new complexes are stable in an inert atmosphere but they fume and decompose spontaneously in air leaving a light green substance which is possibly dichloro(bipyridyl)nickel(II). Complex Ia is insoluble in most organic solvents and decomposes immediately in protic solvents, while Ib is slightly soluble in benzene giving a reddish solution. Complex Ia is more thermally stable than Ib (see Table 1) and this can be ascribed to a greater extent of p_π—d_π bonding between the trichlorosilyl group and the nickel atom [12].

TABLE 1

SOME PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR SILICON—NICKEL COMPLEXES

Compound	Color	M.p. (dec.) [a] (°C)	Analysis found (calcd.) (%)			
			C	H	Cl	N
Ia [b]	Yellow-brown	185-190	24.97 (24.83)	2.16 (1.67)		5.96 (5.79)
Ib [c]	Violet-brown	95-100	33.30 (32.54)	3.37 (3.19)		6.55 (6.32)
II [d]	Light brown	171-175	53.91 (53.07)	3.99 (3.87)	19.89 (20.43)	

[a] *In an evacuated sealed tube.*

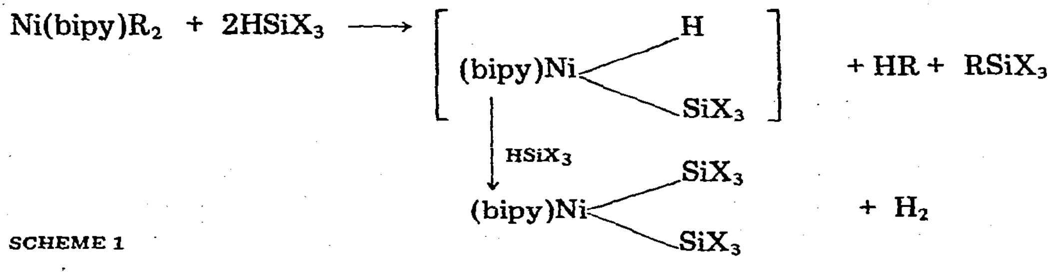
[b] IR (cm^{-1}, KBr): 3075 w, 1600 s, 1565 m, 1490 m, 1470 m, 1440 s, 1320 m, 1235 w, 1100 s (br), 825 m, 800 w, 763 s, 730 m, 655 w, 635 w, 610 w, 590 w, 548 s, 516 s, 500 (sh), 477 s.

[c] IR (cm^{-1}, KBr): 3060 w, 2960 w, 2170 m, 1596 s, 1560 m, 1484 m, 1463 m, 1439 s, 1310 m, 1260 s, 1100 s (br), 900 s (br), 803 m, 760 s, 731 m, 721 w, 703 w, 650 m, 630 w, 464 m, 431 m, 410 w.

[d] IR (cm^{-1}, KBr): 3040 w, 1586 w, 1570 w, 1477 m, 1435 s, 1400 w, 1345 w, 1310 w, 1260 w, 1182 w, 1160 w, 1097 (sh), 1093 s, 1070 w, 1043 w, 1025 w, 1015 w, 998 m, 905 w, 835 m, 807 m, 797 s, 757 (sh), 752 m, 745 s, 700 (sh), 695 (sh), 692 s, 617 w, 545 (sh), 538 s, 525 s, 510 m, 483 s, 460 m, 435 w, 420 w.

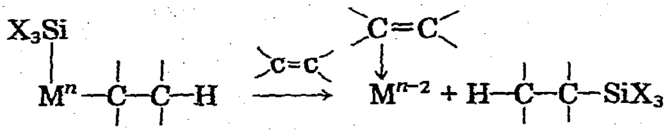
Although the reaction of IIIb with other silicon hydrides, such as $HSiPhCl_2$, $HSiPh_2Me$, $HSi(m\text{-}CF_3C_6H_4)_2Me$, and $HSi(OEt)_3$, gave no stable silicon—nickel complexes, the interaction of some of them with the nickel complex was demonstrated by the formation of an alkylated silane. Thus, phenyldichlorosilane reacted with IIIb at —35° to give ethylphenyldichlorosilane (75% yield based on IIIb) and black precipitates. While neither diphenylmethylsilane nor triethoxysilane reacted with IIIb in ether even at reflux temperature, bis(*m*-trifluoromethylphenyl)methylsilane gave bis(*m*-trifluoromethylphenyl)ethylmethylsilane (38% yield) under the same conditions. These results demonstrate that the reactivity of silicon hydrides towards the nickel complex decreases in the order: $HSiCl_3 > HSiMeCl_2 > HSiPhCl_2 > HSi(m\text{-}CF_3C_6H_4)_2Me \gg HSiPh_2Me, HSi(OEt)_3$. Similar effects of substituents were observed with the reactions of other transition metal complexes and silicon hydrides [13].

The reaction represented by eqn. 1 can be considered to occur through a mechanism involving sequential processes of oxidative addition followed by reductive elimination, as illustrated in Scheme 1. Hydrogen is presumably produced in the final step from the interaction of the silicon hydride with the hydridonickel(II) intermediate, even if it is not detected. Non-evolution of hydrogen when a lower molar ratio of silicon hydride to nickel ($HSiCl_3$/Ni = 1/2) is used would seem to be consistent with this scheme.



SCHEME 1

The formation of ethylsilane derivatives in high yields may be of interest in the light of a suggested mechanism for transition metal complex-catalyzed hydrosilylation of an olefin (eqn. 2). This involves a possible intermediate with a silyl and an alkyl group attached to a transition metal atom [2].



(2)

Reactions of Ia and Ib

Compounds Ia and Ib reacted with excess dry hydrogen chloride in benzene at room temperature to give trichlorosilane (35% yield) and methyldichlorosilane (61% yield), respectively, along with dichloro(bipyridyl)nickel(II) in good yield. With deuterium chloride, trichlorodeuterosilane was obtained from Ia and methyldichlorodeuterosilane from Ib. The results clearly demonstrate the presence of silicon—nickel bonds in these compounds (eqn. 3).

$$\mathrm{Ni(bipy)(SiX_3)_2} + \mathrm{2H(D)Cl} \longrightarrow \mathrm{Ni(bipy)Cl_2} + \mathrm{2H(D)SiX_3} \qquad (3)$$

Compound Ib reacted with tetracyanoethylene (TCNE) in refluxing benzene to give *sym*-dimethyltetrachlorodisilane in low yield (9%). In the absence of TCNE, the disilane was not formed. Analogous treatment of Ia produced no disilane compound, probably owing to the stronger silicon—nickel bond. Methyl iodide could not cleave the silicon—nickel bond in Ia.

Reaction of trichlorosilane with ethyl(h^5-cyclopentadienyl)(triphenylphosphine)-nickel(II)

Ethyl(h^5-cyclopentadienyl)(triphenylphosphine) nickel(II) (IV) reacted with trichlorosilane in ether at room temperature for many hours to give trichlorosilyl(h^5-cyclopentadienyl)(triphenylphosphine) nickel(II) (II) (eqn. 4), as light brown powder (49% yield), together with ethyltrichlorosilane (21% yield). Since gaseous products could not be detected the complete stoichiometry remains uncertain.

$$\underset{\text{(IV)}}{\mathrm{Ni}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})\mathrm{Et}} + n\,\mathrm{HSiCl_3} \rightarrow \underset{\text{(II)}}{\mathrm{Ni}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})(\mathrm{SiCl_3})} + \mathrm{EtSiCl_3} \qquad (4)$$

Compound II is hygroscopic but when exposed in air it showed no noticeable color change. The silicon—nickel bond was cleaved upon treatment with methyl iodide; methyldichlorosilane was formed in 23.5% yield, along with a brown-violet solid, possibly $\mathrm{Ni}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})\mathrm{I}$. The attempted cleavage of the silicon—nickel bond by hydrogen chloride resulted in complicated reactions.

Hydrosilylation of olefins catalyzed by nickel complexes bearing a bipyridyl or h^5-cyclopentadienyl ligand

The reactions of silicon hydrides with alkylnickel complexes containing bipyridyl or h^5-cyclopentadienyl as an additional ligand suggested the catalytic activity of these nickel complexes in hydrosilylation reactions. Therefore, the

TABLE 2

HYDROSILYLATION OF OLEFINS CATALYZED BY NICKEL COMPLEXES[a]

Catalyst[b]	Catalyst/ olefin ratio	Olefin	Silane	Temp. (°C)	Product (yield, %)[c]
$Ni(bipy)Et_2$	2×10^{-3}	1-Octene	$HSiCl_3$	120	$n\text{-}C_8H_{17}SiCl_3$ (19)
$Ni(bipy)Et_2$	3×10^{-2}	Butadiene	$HSiMeCl_2$	120	$CH_3CH{=}CHCH_2SiMeCl_2$ (89) *cis* / *trans* 76/24
$Ni(bipy)(SiCl_3)_2$	2×10^{-3}	1-Octene	$HSiCl_3$	120	No reaction
$Ni(bipy)Cl_2$	2×10^{-3}	1-Octene	$HSiCl_3$	120	No reaction
$Ni(Cp)(PPh_3)Et$	2×10^{-2}	1-Octene	$HSiMeCl_2$	90	$n\text{-}C_8H_{17}SiMeCl_2$ (18)
$Ni(Cp)(PPh_3)Cl$	2×10^{-2}	1-Octene	$HSiMeCl_2$	90	$n\text{-}C_8H_{17}SiMeCl_2$ (21)
$Ni(Cp)_2$	5×10^{-2}	1-Octene	$HSiCl_3$	90	$n\text{-}C_8H_{17}SiCl_3$ (58)
$Ni(Cp)_2$	5×10^{-2}	1-Octene	$HSiMeCl_2$	90	$n\text{-}C_8H_{17}SiMeCl_2$ (56)
$Ni(Cp)_2$	2×10^{-2}	$PhCH{=}CH_2$	$HSiMeCl_2$	90	$PhCH(CH_3)SiMeCl_2$ (88)
$Ni(Cp)_2$	1×10^{-2}	Butadiene	$HSiMeCl_2$	90	$CH_3CH{=}CHCH_2SiMeCl_2$ (78) *cis* / *trans* 85/15

[a] A mixture of an olefin and a silane in a 1/2 ratio was heated with a catalyst in a sealed glass tube for 20 h. [b] Cp = h^5-cyclopentadienyl. [c] Yields, based on olefin used, were determined by GLC.

addition of silicon hydrides to olefins was examined in the presence of such complexes as catalysts. The results are summarized in Table 2. Of the catalysts containing a bipyridyl ligand, only $Ni(bipy)Et_2$ was effective. Dichloro(bipyridyl)nickel(II) and the silicon—nickel complex Ia were inactive. The inactivity of the latter may be due in part to its ready conversion to the former by hydrogen chloride dissolved in trichlorosilane (as evidenced by color change of the reaction mixture upon heating). All the complexes with h^5-cyclopentadienyl group were effective catalysts, nickelocene being the most effective. Introduction of a triphenylphosphine ligand onto the nickel producing $Ni(h^5\text{-}C_5H_5)(PPh_3)R$ (R = Cl, Et) reduced the catalytic activity. Addition of methyldichlorosilane to butadiene in the presence of $Ni(bipy)Et_2$ or nickelocene as catalyst gave a mixture of *cis* and *trans* isomers of the 1,4-adduct enriched in the *cis* isomer. Similar results have been reported for the palladium-catalyzed hydrosilylation [14]. It is interesting to note that nickelocene has been reported not to catalyze the addition of trimethylsilane to butadiene [15], whereas it did catalyze the addition of methyldichlorosilane as reported here.

Experimental

All stoichiometric reactions were carried out under nitrogen or argon, in a 50 ml two-necked flask, equipped with a three-way tap. A Varian Aerograph Model 90P, equipped with a 20-ft column packed with Apiezon-L (30% on Celite) or Silicone DC550 (30% on Celite), was used for isolation and purification of volatile products. Microanalyses were carried out in the Microanalytical Center of Pharmaceutical Department of Kyoto University. Infrared spectra were measured on a Hitachi EPI G3 grating spectrophotometer. The KBr "sandwich" discs for air-sensitive complexes were prepared in a glove box under argon. NMR spectra were obtained on a Varian T-60 spectrometer.

Starting materials were prepared as described in the literature: Ni(bipy)Me_2 (IIIa) [10], Ni(bipy)Et_2 (IIIb) [7], Ni(bipy)Cl_2 [16], Ni(h^5-C_5H_5)(PPh_3)Et (IV) [8], Ni(h^5-C_5H_5)(PPh_3)Cl [17], Ni(h^5-C_5H_5)$_2$ [18]. All solvents were distilled under nitrogen. Trichlorosilane and methyldichlorosilane were distilled from quinoline under nitrogen before use. Deuterium chloride was prepared by the reaction of deuterium oxide with tetrachlorosilane and dissolved in dry benzene, the concentration of which was determined by titration.

Bis(trichlorosilyl)bipyridylnickel(II) (Ia)

(a). In a 50-ml two-necked flask, equipped with a serum cap and a three-way tap connected to a gas buret, were placed IIIa (0.602 g, 2.46 mmol) and dry ether (25 ml). To the solution was added trichlorosilane (1.5 ml, 14 mmol) by means of a syringe, with stirring and cooling at —35° in a dry ice—methanol bath. After 10 min, rapid evolution of gas began and the color of the reaction mixture changed from deep green to brown. Stirring was continued at ca. —35° for 1.5 h. 106 ml (at 22°) of gas (4.38 mmol, 1.78 equivalents of IIIa used) evolved. The mass spectrum of the gas showed peaks of methane (*m/e* 16) and hydrogen (*m/e* 2). The reaction mixture was filtered, washed with 6 ml of dry ether at ca. —70°, and dried *in vacuo* at room temperature to give 1.046 g (88% yield) of a yellow-brown powder Ia. GLC analysis of the filtrate showed the formation of $MeSiCl_3$ (74% yield) which was characterized by comparison of its GLC retention time and IR spectrum with those of an authentic sample.

(b). Similarly, IIIb (0.740 g, 2.71 mmol) in 30 ml of ether was treated with trichlorosilane (1.5 ml, 14 mmol) at —55° to —50° for 2h to yield 1.108 g (85% yield) of Ia, along with hydrogen (57 ml at 22°, 2.36 mmol, 87% yield) and ethyltrichlorosilane (64% yield). Ethane which might be formed could not be detected in the gas, probably because it remained dissolved in the reaction mixture.

Bis(methyldichlorosilyl)bipyridylnickel(II) (Ib)

Diethyl(bipyridyl)nickel (IIIb) (0.897 g, 3.28 mmol) in 30 ml of ether was treated with methyldichlorosilane (4.405 g, 38.3 mmol) at —35° for 2h to give 1.216 g (84%) of a violet-brown powder (Ib), along with hydrogen (86 ml at 25°, 3.52 mmol, 107% yield based on IIIb used) and ethylmethyldichlorosilane (96% yield).

Reaction of phenyldichlorosilane with IIIb

To IIIb (0.286 g, 1.05 mmol) in 20 ml of ether was added phenyldichlorosilane (1.286 g, 7.26 mmol) at —35°. The color of the reaction mixture changed from deep green to dark brown with evolution of hydrogen. After 2 h stirring at —35°, 0.56 equivalent of hydrogen had been evolved. Filtration of the reaction mixture gave black precipitates which were too unstable to be characterized. GLC analysis of the filtrate showed the formation of ethylphenyldichlorosilane in 75% yield.

Reaction of bis(m-trifluoromethylphenyl)methylsilane with IIIb

To IIIb (0.255 g, 0.934 mmol) in 15 ml of ether was added bis(*m*-trifluoromethylphenyl)methylsilane (1.138 g, 3.402 mmol) at room temperature with stirring. The reaction mixture was refluxed for 6 h with stirring and then hydrolyzed to give bis(*m*-trifluoromethylphenyl)ethylmethylsilane (38% yield). (Mol. wt. found: *m/e* 362. $C_{17}H_{16}F_6Si$ calcd.: 362.40.) NMR (CCl_4): δ 0.49 (s, 3H, $SiCH_3$), 0.96 (m, 5H, $SiCH_2CH_3$), 7.50 ppm (m, 8H, $CF_3C_6H_4$).

Attempted reaction of methyldiphenylsilane and triethoxysilane with IIIb

A mixture of methyldiphenylsilane (0.688 g, 3.48 mmol) and IIIb (0.242 g, 0.887 mmol) in 10 ml of ether was refluxed for 6 h with stirring. No product was detected by GLC analysis.

A mixture of triethoxysilane (0.819 g, 4.98 mmol) and IIIb (0.218 g, 0.799 mmol) in 10 ml of ether was refluxed for 3 h with no product formation.

Reaction of hydrogen chloride with Ia and Ib

To Ia (0.257 g, 0.531 mmol) in 10 ml of benzene was added a solution of dry hydrogen chloride (1.92 mmol) in benzene (4 ml) at room temperature with stirring. The color of the reaction mixture changed gradually from brown to light green. No evolution of gas was observed. After stirring at room temperature for 1.5 h, the reaction mixture was filtered. Washing the solid product with benzene, and drying it *in vacuo* gave 0.109 g (72% yield) of $Ni(bipy)Cl_2$, which was identified by comparison of its IR spectrum with that of an authentic sample. The IR spectrum of the filtrate in a solution cell coincided with that of trichlorosilane, ν(Si—H) 2260 cm^{-1}. The yield (35%) was estimated from the intensity of the ν(Si—H) peak. Reaction of hydrogen chloride (2.0 mmol) with Ib (0.190 g, 0.428 mmol) gave $Ni(bipy)Cl_2$ (0.115 g, 94% yield) and methyldichlorosilane (61% yield), ν(Si—H) 2210 cm^{-1}. Reaction of deuterium chloride with Ia or Ib was carried out in the same manner as above. IR: $DSiCl_3$, ν(Si—D) 1645 cm^{-1}; $DSiMeCl_2$, ν(Si—D) 1600 cm^{-1}.

Reaction of TCNE with Ib

A mixture of Ib (0.441 g, 0.994 mmol) and TCNE (0.128 g, 1.00 mmol) in 5 ml of benzene was heated under reflux for 1.5 h. The color of the reaction mixture changed from brown to dark brown. The reaction mixture was filtered to give brown precipitates of unknown structure. GLC analysis of the filtrate showed the formation of *sym*-dimethyltetrachlorodisilane (9% yield) [19]. The filtrate was phenylated with phenylmagnesium bromide to form *sym*-dimethyltetraphenyldisilane which was characterized by comparison of its GLC retention time and IR spectrum with those of an authentic sample [20].

Reaction of trichlorosilane with IV

To a solution of IV (0.414 g, 1.0 mmol) in 10 ml of ether was added 1.5 ml of trichlorosilane, and the resultant green-brown clear solution was stirred at room temperature for 85 h. Brown crystals which deposited were filtered under nitrogen pressure, washed with 10 ml of ether and then dried *in vacuo*. The product, trichlorosilyl (*pentahapto*-cyclopentadienyl)(triphenylphosphine)-nickel(II) (II), weighed 0.255 g (47% yield). Its IR spectrum (KBr sandwich disc) showed the absence of aliphatic and siloxane groups and the appearance of Si—Cl bonds. GLC analysis of the filtrate showed the formation of ethyltrichlorosilane in 21% yield based on the nickel complex.

Reaction of methyl iodide with II

To II (0.149 g, 0.285 mmol) was added methyl iodide (0.7 ml). The mixture was stirred magnetically at room temperature for 1 h. Volatile material was evaporated under reduced pressure and collected at −78° to leave a brown-violet solid. The NMR spectrum of the volatile condensate revealed that methyltrichlorosilane was the sole product (23.5% yield by GLC analysis). The brown violet solid was believed to be $Ni(h^5\text{-}C_5H_5)(PPh_3)I$ but showed no satisfactory analytical data.

Hydrosilylation

The hydrosilylation reactions were carried out in the same manner as described in the previous paper [3].

Analytical data and IR and NMR spectra of *cis*- and *trans*-$CH_3CH{=}CHCH_2\text{-}SiMeCl_2$ are as follows.

Analysis (mixture of *cis* and *trans* isomers) found: Cl, 41.54. $C_5H_{10}Cl_2Si$ calcd.: Cl, 41.93%.

cis-$CH_3CH{=}CHCH_2SiMeCl_2$. IR (cm^{-1}, neat): $\nu(CH{=}CH)$ 3025, $\nu(Si{-}CH_3)$ 1265, δ (CH=CH) 663. NMR(CCl_4): δ 0.76 (s, 3H, $Si{-}CH_3$), 1.66 (m, 3H, $C{-}CH_3$), 2.09 (m, 2H, $CH_2{-}Si$), 5.60 ppm (m, 2H, CH=).

trans-$CH_3CH{=}CHCH_2SiMeCl_2$: IR (cm^{-1}, neat): $\nu(CH{=}CH)$ 3025, $\nu(Si{-}CH_3)$ 1265, δ (CH=CH) 970. NMR(CCl_4): δ 0.76 (s, 3H, $Si{-}CH_3$), 1.70 (m, 3H, $C{-}CH_3$), 2.00 (m, 2H, $CH_2{-}Si$), 5.45 ppm (m, 2H, CH=).

Acknowledgments

The authors thank Toshiba Silicone Co., Ltd. and Nitto Electric Industrial Co., Ltd. for support of this work.

References

1 Y. Kiso, K. Tamao and M. Kumada, Chem. Commun., (1972) 105.
2 (a) C. Eaborn and R.W. Bott, in A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 1, Part 1, Marcel Dekker, New York, 1968, pp. 213 - 278.
(b) A.J. Chalk, Trans. New York Acad. Sci., Ser. II, 32 (1972) 481.
3 (a) Y. Kiso, M. Kumada, K. Tamao and M. Umeno, J. Organometal. Chem., 50 (1973) 297.
(b) Y. Kiso, M. Kumada, K. Maeda, K. Sumitani and K. Tamao, J. Organometal. Chem., 50 (1973) 311.
(c) M. Kumada, K. Sumitani, Y. Kiso and K. Tamao, J. Organometal. Chem., 50 (1973) 319.
4 (a) U. Belluco, G. Deganello, R. Pietropaolo and P. Uguagliati, Inorg. Chim. Acta Rev., 4 (1970) 7.
(b) E.H. Brooks and R.J. Cross, Organometal. Chem. Rev. Sect. A, 6 (1971) 227.
(c) C.S. Cundy, B.M. Kingston and M.F. Lappert, Advan. Organometal. Chem., 11 (1973) 253.
5 W. Jetz and W.A.G. Graham, J. Amer. Chem. Soc., 89 (1967) 2773.
6 Th. Kruck, E. Job and U. Klose, Angew. Chem., 80 (1968) 360.
7 T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji and S. Ikeda, J. Amer. Chem. Soc., 88 (1966) 5198.
8 H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida and N. Hagihara, J. Organometal. Chem., 6 (1966) 86.
9 M. Uchino, A. Yamamoto and S. Ikeda, J. Organometal. Chem., 24 (1970) C63.
10 T. Yamamoto, A. Yamamoto and S. Ikeda, J. Amer. Chem. Soc., 93 (1971) 3350.
11 M.L. Schneider, H.M.M. Sheaver, F. Glockling and A. McGregor, J. Inorg. Nucl. Chem., 32 (1970) 3101.
12 O. Kahn and M. Bigorgne, J. Organometal. Chem., 10 (1967) 137.
13 (a) F. de Charentenay, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1968) 787; R.N. Haszeldine, R.V. Parish and D.J. Parry, J. Chem. Soc. A, (1969) 683.
(b) K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 28 (1971) C37.

14 V. Vaisarová, M. Capka and J. Hetflejs, Synth. Inorg. Metal-org. Chem., 2 (1972) 289.
15 S. Takahashi, T. Shibano, H. Kojima and N. Hagihara, Organometal. Chem. Syn., 1 (1970/1971) 193.
16 J.A. Broomhead and F.P. Dwyer, Aust. J. Chem., 14 (1961) 250.
17 C. Beermann and H. Bestian, Angew. Chem., 71 (1959) 618.
18 J.F. Cordes, Chem. Ber., 95 (1962) 3084.
19 H. Sakurai, T. Watanabe and M. Kumada, J. Organometal. Chem., 7 (1967) P15.
20 H. Gilman, R.K. Ingham and A.G. Smith, J. Org. Chem., 18 (1953) 1743.