Journal of Organometallic Chemistry, 76 (1974) 105—115
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REACTION OF BIS(SUBSTITUTED-SILYL)BIPYRIDYLNICKEL(II) WITH ACETYLENES

STEREOCHEMISTRY OF DISILYLATION*

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(Received February 6th, 1974)

Summary

A violet complex, [*trans*-α,α'-bis(trichlorosilyl)stilbene]bipyridylnickel(0) (II), was obtained from the reaction of Ni(bipy)($SiCl_3$)$_2$ (Ia) with diphenylacetylene. Treatment of II with methylmagnesium bromide, followed by hydrolysis, produced free *trans*-α,α'-bis(trimethylsilyl)stilbene. The same *trans*-stilbene was formed as the sole product of the reaction of Ni(bipy)($SiMeCl_2$)$_2$ with diphenylacetylene followed by methylation, although here the nickel(0) complex analogous to II could only be isolated in an impure state. The reaction of both Ia and Ib with other acetylenes such as PhC≡CH, PhC≡CMe and n-BuC≡C-n-Bu, in general gave after similar treatment a mixture of *cis*- and *trans*-1,2-bis(trimethylsilyl)olefins. The *cis/trans* isomer ratio decreased in the order: PhC≡CMe > PhC≡CH > PhC≡CPh. A study of solvent effects on the reaction of Ia with PhC≡CH showed that the *cis/trans* isomer ratio decreased as follows: benzene > diethyl ether > tetrahydrofuran.

Introduction

The reactions of transition metal hydrides [2] and alkyls [3] with acetylenic compounds have been investigated extensively, and in general they give rise either to σ-alkenyl— or to acetylene—transition metal complexes. Few reactions leading to the formation of π-olefin—transition metal complexes are known [2d].

Addition of metal hydrides across the triple bond occurs in general in a *cis* fashion [2] although *trans* addition has been reported in several examples [2d, 4] involving acetylenic compounds substituted by electron-accepting groups such as CF_3 and $COOCH_3$. To our knowledge, only *cis* stereochemistry has been observed in the reaction of metal alkyls with acetylenic compounds [3].

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* For a preliminary communication see ref. 1.

Compounds containing covalent silicon—transition metal bonds have been studied extensively in recent years [5]. While many studies have been carried out on the cleavage of such bonds [6], the addition reaction across a triple bond has been less extensively investigated. Only a few reactions under UV irradiation conditions have been reported by Clark and coworkers [7], who observed that while *cis* addition occurs in the reaction of $Me_3SiFe(CO)_2(\pi\text{-}C_5H_5)$ with $CF_3C\equiv CH$, *trans* addition takes place in the reaction of $Me_3SiMn(CO)_5$ with $CF_3C\equiv CCF_3$ and $CF_3C\equiv CH$. Mechanistic details have not been described.

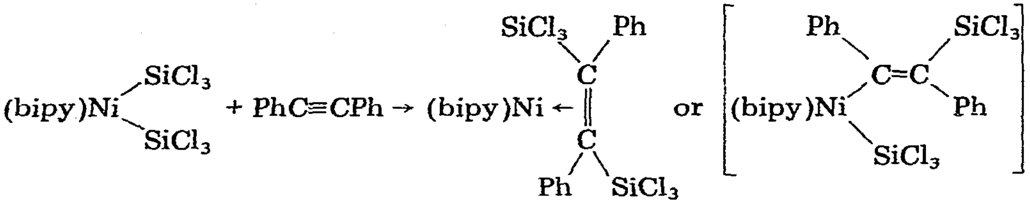
In the preceding paper [8] we reported the preparation and some reactions of $Ni(bipy)(SiX_3)_2$ (Ia $X_3 = Cl_3$, Ib $X_3 = MeCl_2$; bipy = bipyridyl). During further investigations on the reactivity of these covalent silicon—nickel complexes we found that compounds Ia and Ib react with various substituted acetylenes very easily at or below room temperature to give, after methylation, 1,2-bis(trimethylsilyl)olefins, generally as a *cis/trans* isomer mixture. Furthermore, from the reaction of Ia and diphenylacetylene, we have succeeded in isolating [*trans*-α,α'-bis(trichlorosilyl)stilbene] bipyridylnickel(0) (II) as an interesting intermediate. This paper deals with these new reactions.

Results and discussion

Reaction of Ni(bipy)(SiX₃)₂ with diphenylacetylene

Bis(trichlorosilyl)bipyridylnickel(II) (Ia) reacted very easily with diphenylacetylene in benzene at room temperature with a color change from brown to purple to give a violet colored powdery product (II) (65% yield). The IR spectrum (KBr) showed no peaks over the range of 1500—1650 cm^{-1} other than those displayed by the starting material Ia.

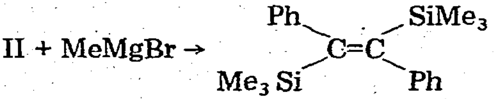
Although an alternative structure II' would be possible, the chemical behavior of this product supports the proposed structure.



(1)

(Ia) (II) (II')

First, treatment of the above reaction product with methylmagnesium bromide, followed by hydrolysis with dilute hydrochloric acid, gave the known *trans*-α,α'-bis(trimethylsilyl)stilbene (III) [9] as the sole product (55% yield). No *cis* isomer [10] was detected at all. This is consistent with the *trans* configuration of the olefin ligand bonded to the nickel atom (eqn. 2).



(2)

(III)

Second, the action of dry hydrogen chloride on the product of reaction 1 gave, after filtration of the reaction mixture, dichloro(bipyridyl)nickel(II) in quantitative yield. Careful examination of the filtrate by IR spectroscopy revealed the complete absence of trichlorosilane which is expected to be formed from structure II′. Methylation of the filtrate afforded 1,2-bis(trimethylsilyl)-1,2-diphenylethane [9] (18% yield). No traces of α-trimethylsilylstilbene which would arise from structure II′ were produced.

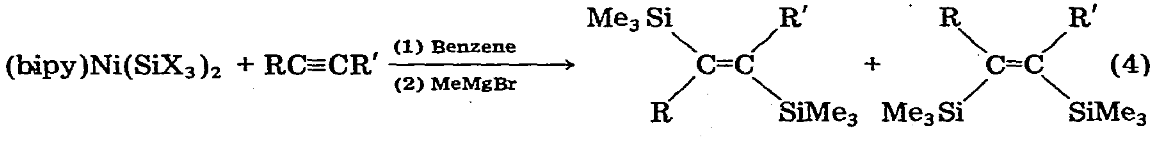
$$\mathrm{II} + 2\,\mathrm{HCl} \rightarrow \mathrm{Ni(bipy)Cl_2} + \mathrm{(Cl_3Si)PhHC{-}CHPh(SiCl_3)}$$
$$\mathrm{(Cl_3Si)PhHC{-}CHPh(SiCl_3)} + 6\,\mathrm{MeMgBr} \rightarrow \mathrm{(Me_3Si)PhHC{-}CHPh(SiMe_3)} \qquad (3)$$

The olefin—nickel complex II is slightly soluble in benzene but insoluble in ether; it is air-sensitive, especially in solution. II is almost inert to the action of excess triphenylphosphine or trichlorosilane in ether or benzene even under reflux conditions. Such a strong nickel—olefin bond may be attributed to the presence of the electron-accepting trichlorosilyl groups and phenyl groups on both the olefinic carbons.

An analogous reaction between bis(methyldichlorosilyl)bipyridylnickel(II) (Ib) and PhC≡CPh occurred in benzene solution at room temperature within 1 min, as evidenced by a color change from violet-brown to blue. Although attempts to isolate the nickel complex resulted in decomposition, α,α′-bis(trimethylsilyl)stilbene (III) could again be obtained in 52% yield by methylation of the product of reaction of equal amounts of Ib and PhC≡CPh in benzene at room temperature. In an effort to isolate the nickel—olefin complex, we treated Ib with PhC≡CPh in toluene at a lower temperature (—25 to —10°) for 3 h. Filtration of the reaction mixture at —40° gave a blue-green precipitate. This is believed to be (bipy)Ni[*trans*-Ph(MeCl$_2$Si)C=C(SiMeCl$_2$)Ph], although the complex did not show satisfactory analytical data. Methylation of this nickel complex gave III in 14% yield.

Reaction of Ni(bipy)(SiX$_3$)$_2$ (I) with other acetylenes

Reactions of I with three other substituted acetylenes, PhC≡CH, PhC≡CMe and n-BuC≡C-n-Bu, in benzene were examined. After a given reaction time the mixture was treated directly with methylmagnesium bromide and then hydrolyzed. GLC analysis of the hydrolyzate showed that disilylation of acetylenes had occurred in all cases, and monosilylation had taken place to a lesser extent (eqn. 4). The results are summarized in Table 1. This table also contains the results of similar reactions with PhC≡CPh.



$$\mathrm{(bipy)Ni(SiX_3)_2} + \mathrm{RC{\equiv}CR'} \xrightarrow[\text{(2) MeMgBr}]{\text{(1) Benzene}} \qquad (4)$$

(*trans*-IV) (*cis*-IV)

IVa: R = Ph, R′ = Me; IVb: R = Ph, R′ = H; IVc: R = R′ = n-Bu.

In marked contrast to the case where PhC≡CPh was used, the reactions with at least two other acetylenes, (PhC≡CH and PhC≡CMe) gave *cis* isomers as main products. Determination of the stereochemistry of these products was based

(continued on p. 110)

TABLE 1

REACTION OF $\mathrm{Ni(bipy)(SiX_3)_2}$ WITH ACETYLENES; FOLLOWED BY METHYLATION

$\mathrm{SiX_3}$ (mmol)	Acetylene (mmol)	Benzene (ml)	Product	Yield [a] (%)	*cis/trans* [a]
$\mathrm{SiCl_3}$ (0.70)	$\mathrm{PhC{\equiv}CPh}$ (1.74)	5	$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)Ph}$	49	0/100 [b]
$\mathrm{SiCl_3}$ (0.61)	$\mathrm{PhC{\equiv}CH}$ (1.42)	5	$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)H}$	47	73/27
$\mathrm{SiCl_3}$ (1.22)	$\mathrm{PhC{\equiv}CMe}$ (2.76)	10	$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)Me}$	38	92/8
$\mathrm{SiCl_3}$ (1.01)	$\mathrm{n\text{-}BuC{\equiv}C\text{-}n\text{-}Bu}$ (3.33)	8	$\mathrm{n\text{-}Bu(Me_3Si)C{=}C(SiMe_3\text{-}n\text{-}Bu}$	44	*c*
$\mathrm{SiMeCl_2}$ (1.11)	$\mathrm{PhC{\equiv}CPh}$ (1.11)	10	$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)Ph}$	52	0/100 [b]
$\mathrm{SiMeCl_2}$ (0.68)	$\mathrm{PhC{\equiv}CH}$ (1.80)	5	$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)H}$	49	67/33
$\mathrm{SiMeCl_2}$ (1.15)	$\mathrm{PhC{\equiv}CMe}$ (2.59)	10	$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)Me}$	45	93/7
$\mathrm{SiMeCl_2}$ (0.72)	$\mathrm{n\text{-}BuC{\equiv}C\text{-}n\text{-}Bu}$ (1.75)	5	$\mathrm{n\text{-}Bu(Me_3Si)C{=}C(SiMe_3)\text{-}n\text{-}Bu}$	52	*c*

[a] Determined by GLC unless otherwise indicated. [b] Determined by NMR. [c] Not determined.

TABLE 2

IR, ^{1}H NMR AND ANALYTICAL DATA FOR DISILYLOLEFINS

$R(Me_3Si)C{=}C(SiMe_3)R'$	ν(Si—Me) (cm^{-1})[a,b]	Chemical shift (δ ppm)[c]				Analysis found (calcd.) (%)	
		R	$(Me_3Si)C$	$C(SiMe_3)$	R′	C	H
trans-$Ph(Me_3Si)C{=}C(SiMe_3)Ph$[d]	1245 [1257(sh)]	7.10(m)	−0.38(w)	−0.38(s)	7.10(m)		
cis-$Ph(Me_3Si)C{=}C(SiMe_3)Ph$[e]		6.70(m)	0.13(s)	0.13(s)	6.70(m)		
trans-$Ph(Me_3Si)C{=}C(SiMe_3)H$	1247 [1258(sh)]	7.03(m)	0.05(s)	−0.20(s)	6.26(s)	67.96 (67.66)	9.93 (9.73)
cis-$Ph(Me_3Si)C{=}C(SiMe_3)H$	1250 [1263(sh)]	7.00(m)	0.22(s)	0.14(s)	6.33(s)	67.36 (67.66)	10.00 (9.73)
trans-$Ph(Me_3Si)C{=}C(SiMe_3)Me$[f]	1247 [1261(sh)]	6.99(m)	0.02(s)	−0.29(s)	2.00(s)	69.32 (68.62)	10.19 (9.96)
cis-$Ph(Me_3Si)C{=}C(SiMe_3)Me$	1244 [1261(sh)]	6.96(m)	0.25(s)	0.02(s)	1.54(s)	68.73 (68.62)	10.24 (9.96)
n-Bu$(Me_3Si)C{=}C(SiMe_3)$-n-Bu[f,g]	1246 [1260(sh)] [1254(sh)]	*h*	0.15(s)	0.15(s)	*h*	67.19 (67.49)	12.79 (12.74)

[a] Neat. [b] sh Shoulder. [c] Carbon tetrachloride solution containing cyclohexane as an internal standard (60 MHz) unless otherwise indicated. [d] See ref. 9. [e] Ref. 10. [f] On a 100-MHz NMR spectrometer. [g] Benzene was used as an internal standard for NMR. [h] 0.91 (t, CH_3), 1.28 (m, CH_2), 2.18 (m, $=C{-}CH_2$).

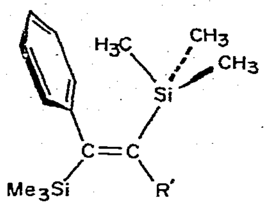
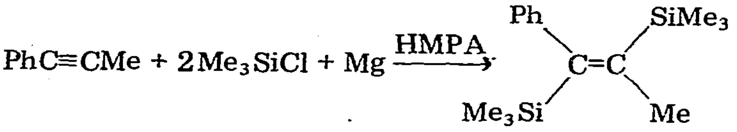


Fig. 1. Shielding of the protons of one of the trimethylsilyl groups in *trans*-IVa and *trans*-IVb.

mainly on ^{1}H NMR spectra (Table 2). The signal for one of the trimethylsilyl groups for each of *trans*-IVa and *trans*-IVb occurs at a higher field than that for the other because of the anisotropic effect of the benzene ring (see Fig. 1). No such effect will be expected for the *cis* isomers.

Pure *trans*-IVa was prepared independently by the reaction of $PhC{\equiv}CMe$, Mg, and Me_3SiCl in hexamethylphosphoramide (HMPA) (eqn. 5) [9]. The NMR spectrum of *trans*-IVa, obtained from reaction 4, showed that it contained some monosilylated olefins [δ −0.07, (s, $SiCH_3$), −0.01 (s, $SiCH_3$), 5.59 (m, =CH), 5.85 ppm (m, =CH)].



$$PhC{\equiv}CMe + 2Me_3SiCl + Mg \xrightarrow{HMPA} (Ph)(Me_3Si)C{=}C(SiMe_3)(Me) \qquad (5)$$

(*trans*-IVa)

Reaction of Ia with n-$BuC{\equiv}C$-n-Bu gave only one isomer of the disilylolefin. GLC analysis in a column packed with Apiezon-L (30% on Celite) or Silicone DC 550 (30% on Celite) showed only one peak and the NMR spectrum (100 MHz) showed only one singlet peak due to the trimethylsilyl group (δ 0.15 ppm). At present, we cannot determine the geometrical configuration of the product, n-$Bu(Me_3Si)C{=}C(SiMe_3)$ n-Bu.

Reactions of Ib with $PhC{\equiv}CH$, $PhC{\equiv}CMe$, and n-$BuC{\equiv}C$-n-Bu were very similar to those of Ia. Ia reacted neither with hexafluoro-2-butyne in toluene nor with acetylene itself in benzene.

We confirmed the absence of *cis/trans* isomerization in the course of methylation by observing that treatment of pure *cis*-IVa,b or a mixture of *cis*- and *trans*-Iva,b with methylmagnesium bromide followed by hydrolysis with dilute hydrochloric acid gave no change in the isomer ratios.

Mechanisms for cis and trans addition of silyl groups on I to acetylenic compounds

In general, a mixture of *cis*- and *trans*-disilylolefins is formed from the reaction of I with acetylenes as described above and the stereochemistry of the products is dependent upon the nature of the acetylenes used. As shown in Table 1, the ratios of *cis* to *trans* addition decrease in the order: $PhC{\equiv}CMe > PhC{\equiv}CH >$ $PhC{\equiv}CPh$. This sequence may suggest that an electronic rather than a steric effect of the substituents governs the stereochemistry of the reaction; electron-donating substituents favor *cis* addition.

On the other hand, it is unlikely that the stereochemistry of the products is dependent upon the nature of silyl groups of I since almost the same ratios of the disilylolefin isomers are observed for Ia and Ib.

The reactivity of the acetylenes toward Ia, examined by a competitive reaction method, decreased in the order: $PhC\equiv CH \gg PhC\equiv CMe \sim n\text{-}BuC\equiv C\text{-}n\text{-}Bu > PhC\equiv CPh$. It should be noted that there is a possibility that the reactivity sequence obtained for various acetylenes by competition experiments is different from that determined in separated experiments because a less reactive acetylene can, by being more strongly complexed, exclude the more reactive from the nickel complex. This situation has been observed in the catalytic hydrogenation of olefins over the platinum black, and other catalytic reactions [11, 12]. Therefore, we are not in a position at present to interpret the differences in reactivity of acetylenic compounds satisfactorily. However, in view of the inertness of $CF_3C\equiv CF_3$, it seems likely that the coordination of an acetylene to nickel is rate-determining. Perfluoroacetylene is known to be a strong π acceptor, but the π-back bonding character of the nickel atom in complex I would be expected to be weak. The differences in reactivity among $PhC\equiv CH$, $PhC\equiv CMe$, $n\text{-}BuC\equiv C\text{-}n\text{-}Bu$, and $PhC\equiv CPh$ may be attributed to steric effects.

Although no simple correlation between the stereochemistry of the reaction and the reactivity of acetylenes was observed, significant information about factors influencing the stereochemistry was obtained from studies on solvent and concentration effects. The reaction of Ia with $PhC\equiv CH$ in three different solvents (benzene, diethyl ether, and tetrahydrofuran) was examined. The results are summarized in Table 3. The *cis/trans* ratios varied significantly with the nature of solvent, decreasing in the order: benzene > diethyl ether > THF. Thus, polar solvents tend to favor *trans* addition. Concentrations of the reaction mixture also influenced the *cis/trans* ratios as shown by runs 2—4 of Table 3. A higher concentration favors the formation of the *trans* isomer.

The *cis* addition can be best understood in terms of a mechanism involving the insertion of an initially coordinated acetylene into the nickel—silicon bond followed by simultaneous occurrence of reductive elimination and coordination of the now-formed disilylolefin. Similar *cis* addition mechanisms have been postulated in many reactions of metal alkyls and hydrides with acetylenic compounds [2, 3].

On the other hand, a mechanism whereby the *trans* addition occurred is not fully understood at the moment. However, in the light of the observed effects of substituents, solvents and concentrations on the ratio of *cis/trans* addition, it seems likely that *trans* addition would proceed through the initial formation

TABLE 3

REACTION OF $Ni(bipy)(SiCl_3)_2$ WITH PHENYLACETYLENE IN VARIOUS SOLVENTS

Run	Solvent (ml)	Nickel complex (mmol)	$PhC\equiv CH$ (mmol)	Yield of product [a,b] (%)	*cis/trans*
1	Benzene (5)	0.61	1.42	47	73/27
2	Ether (3)	0.81	2.04	41	55/45
3	Ether (7)	0.72	1.71	49	63/37
4	Ether (50)	0.46	1.21	29	76/24
5	THF (5)	0.69	1.78	20	4/96

[a] $Ph(Me_3Si)C{=}C(SiMe_3)H$. [b] Determined by GLC.

of a (*trans*-alkenyl)nickel species such as structure II' by a polar, and possibly higher than unimolecular, mechanism. To explain the *trans* addition of transition metal complexes to acetylenes (mostly electronegatively-substituted), pathways involving initial attack of organometallic nucleophiles on acetylenes have often been postulated [4 g, 13].

Experimental

All stoichiometric reactions were carried out in dry, oxygen-free nitrogen. A Varian Aerograph Model 90P, equipped with a 20-ft column packed with Apiezon-L (30% on Celite) or Silicone DC 550 (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. IR spectra were measured on a Hitachi EPI G3 grating spectrophotometer. NMR spectra were obtained on a Varian EM 360 and a Varian HA-100 spectrometer.

All solvents were dried over metallic sodium and $LiAlH_4$ and distilled under nitrogen. Trichlorosilane and methyldichlorosilane were distilled from quinoline under nitrogen before use. The complexes $Ni(bipy)(SiCl_3)_2$ and $Ni(bipy)(SiMeCl_2)_2$ were prepared according to the preceding paper [8]. $PhC{\equiv}CMe$ and $n\text{-}BuC{\equiv}C\text{-}n\text{-}Bu$, were prepared according to the literature [14].

[trans-α,α'-Bis(trichlorosilyl)stilbene] bipyridylnickel(0) (II)

In a 50 ml two-necked flask, equipped with a three-way tap, were placed Ia (0.80 g, 1.65 mmol) and diphenylacetylene (0.70 g, 3.9 mmol). To the mixture was added dry benzene (10 ml) with stirring at room temperature. The color of the reaction mixture changed from brown to purple. After stirring at room temperature for 3 h, the reaction mixture was filtered, and the solid product was washed with 5 ml of dry benzene and dried in vacuo to give 0.705 g (65% yield) of a violet powder (II), m.p. 194—196° (dec. in an evacuated sealed tube). (Found: C, 42.78; H, 2.85. $C_{24}H_{18}Cl_6N_2NiSi_2$ calcd.: C, 43.54; H, 2.74%)

Reaction of II with methylmagnesium bromide

To II (0.257 g, 0.388 mmol) in 6 ml of ether was added 25 mmol of methylmagnesium bromide in ether. After refluxing for 1 h, the reaction mixture was hydrolyzed with dilute hydrochloric acid. GLC analysis of the organic layer showed the formation of *trans*-α,α'-bis(trimethylsilyl)stilbene (III) (55% yield), which was isolated by preparative GLC and recrystallized from ethanol, m.p. 115—116°. Its IR and NMR spectra were identical with those of an authentic sample prepared as reported [9].

Reaction of II with dry hydrogen chloride

To II (0.132 g, 0.196 mmol) in 10 ml of ether was added a solution of dry hydrogen chloride (4.2 mmol) in benzene (7 ml) at room temperature with stirring. The color of the reaction mixture changed gradually from purple to light green. After stirring at the same temperature for 2 h, the mixture was filtered. Washing the solid product with benzene, and drying it in vacuo gave 0.0669 g (100% yield) of $Ni(bipy)Cl_2$, which was identified by comparison of its IR spectrum with that of an authentic sample [15]. The IR spectrum of the filtrate in a solution cell showed no formation of trichlorosilane. The filtrate was methylated and hydrolyzed. GLC analysis showed the formation of 1,2-bis-(trimethylsilyl)-1,2-diphenylethane (18% yield), which was separated and identified by comparison of its m.p. (152—153.5°) and IR spectrum with those of an authentic sample [9].

Attempted reaction of II with trichlorosilane and triphenylphosphine

A mixture of II (0.211 g, 0.319 mmol) and trichlorosilane (2.6 ml) in 10 ml of ether was sitrred at room temperature for 1 h and refluxed for 30 min. No change of color of the reaction mixture was observed. Also, no reaction was observed between II (0.296 g, 0.448 mmol) and triphenylphosphine (0.353 g, 1.35 mmol) in 7.5 ml of benzene under similar conditions.

Reaction of Ib with diphenylacetylene followed by methylation

To Ib (0.492 g, 1.11 mmol) and diphenylacetylene (0.198 g, 1.11 mmol) was added benzene (10 ml) with stirring at room temperature. The color of the reaction mixture changed from brown to blue within 1 min. After stirring at room temperature for 25 min, the reaction mixture was treated with methylmagnesium bromide (7.0 mmol) and hydrolyzed with dilute hydrochloric acid. GLC analysis of the organic layer showed the production of III in 52% yield. No *cis* isomer was observed in its NMR spectrum.

Attempts to isolate $Ni(bipy)[trans\text{-}Ph(MeCl_2Si)C{=}C(SiMeCl_2)Ph]$

To Ib (0.116 g, 1.39 mmol) and diphenylacetylene (0.495 g, 2.78 mmol) was added benzene (15 ml) with stirring at room temperature. After 20 min, the reaction mixture was filtered and dried in vacuo to give a gray nickel complex of unknown structure.

To II (0.367 g, 0.828 mmol) and diphenylacetylene (0.148 g, 0.828 mmol) was added toluene (10 ml) with stirring at —25°. The color of the reaction mixture changed gradually from brown to blue. After 3 h at —10° the reaction mixture was filtrated at —40°, and the solid product was washed with 4 ml of toluene and dried in vacuo to give 0.230 g of blue-gray powder, m.p. 135—137° (dec. in an evacuated sealed tube). (Found: C, 46.67; H, 4.09. $C_{26}H_{24}Cl_4N_2NiSi_2$ calcd.: C, 50.27; H, 3.89%.) Methylation of this nickel complex gave III in 14% yield.

Reaction of I with PhC≡CH, PhC≡CMe, and n-BuC≡C-n-Bu

A typical experiment was as follows. To Ia (0.296 g, 0.611 mmol) in benzene (5 ml) was added PhC≡CH (0.145 g, 1.423 mmol) with stirring at room temperature. The color of the reaction mixture changed from brown to purple within 1 min. After stirring at room temperature for 1 h, the reaction mixture was treated with methylmagnesium bromide (11 mmol) and then hydrolyzed with dilute hydrochloric acid. GLC analysis of the organic layer showed the formation of *cis*- and *trans*-$Ph(Me_3Si)C{=}C(SiMe_3)H$ (*cis/trans* 73/27) in 47% yield. The products were isolated by preparative GLC. See Table 2.

Preparation of trans-$Ph(Me_3Si)C{=}C(SiMe_3)Me$

A mixture of trimethylchlorosilane (5.6 g, 52 mmol) and magnesium (0.46 g, 19 mmol) in HMPA (15 ml) was heated at 120°. Phenylmethylacetylene was added dropwise to the mixture with stirring. After heating at 120—150° for 10 h, the reaction mixture was hydrolyzed, and the organic layer was extracted with n-hexane. GLC analysis showed the formation of *trans*-$Ph(Me_3Si)C{=}C(SiMe_3)Me$ (1% yield) which was isolated by preparative GLC.

Attempted reaction of Ia with $CF_3C\equiv CCF_3$ and $HC\equiv CH$

To Ia (0.513 g, 1.06 mmol) in toluene (20 ml) was added $CF_3C\equiv CCF_3$ (2 ml) with stirring at —35°. Additional stirring at —35 to —30° for 2.5 h and then at 30° for 2 days gave no change of the reaction mixture.

Into Ia (0.135 g, 0.280 mmol) in benzene (10 ml) was bubbled acetylene with stirring at room temperature for 20 min. No change of color of the reaction mixture was observed.

Competitive reactions of Ia with acetylenes

The following was a typical procedure. To Ia (0.306 g, 0.633 mmol) in benzene (7 ml) was added a mixture of $PhC\equiv CMe$ (0.366 g, 3.15 mmol) and $n\text{-}BuC\equiv C\text{-}n\text{-}Bu$ (0.432 g, 3.13 mmol) with stirring at room temperature. After 1 h, the reaction mixture was methylated and then hydrolyzed. The organic layer was analyzed by GLC.

Acknowledgements

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

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