

SILICON HYDRIDES AND NICKEL COMPLEXES

III. HYDROSILYLATION OF OLEFINS WITH DICHLORO[1,2-BIS-(DIMETHYLPHOSPHINO)-1,2-DICARBA-*closo*-DODECABORANE]-NICKEL(II) AS CATALYST

MAKOTO KUMADA, KOJI SUMITANI, YOSHIHISA KISO and KOHEI TAMAO

Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

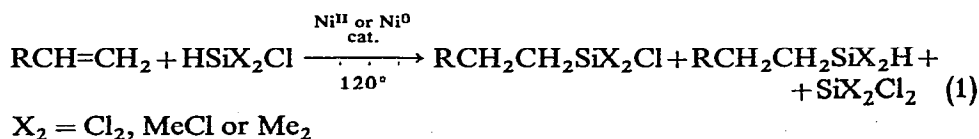
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SUMMARY

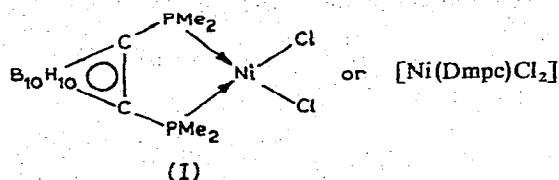
The hydrosilylation of olefins catalyzed by nickel(II) chloride complexed with 1,2-bis(dimethylphosphino)-1,2-dicarba-*closo*-dodecaborane produces terminal and internal adducts in comparable amounts. This unusual feature of the reaction is explained in terms of the electron-accepting nature of the carboranyl group.

INTRODUCTION

The hydrosilylation of olefins catalyzed by Group VIII transition metal complexes has been extensively studied¹. Recently, it has been shown that tertiary phosphine-metal complexes of platinum^{2,3}, palladium⁴⁻⁷ and nickel^{5,8-11} are effective as catalysts, and exhibit individual catalytic characteristics, the results depending upon the nature of the metal and the phosphine ligands. In the previous papers of this series^{10,11} we showed that the hydrosilylation of simple terminal olefins in the presence of a variety of tertiary phosphine-nickel complexes is accompanied by an interchange of hydrogen and chlorine on silicon [see eqn. (1)], and that the electron-donating nature of substituents on phosphorus appears to play an important role in this interchange. In the present paper we describe the rather unusual catalytic features displayed by nickel(II) chloride complexed with 1,2-bis(dimethylphosphino)-



1,2-dicarba-*closo*-dodecaborane [hereafter called bis(dimethylphosphino)-*o*-carborane and abbreviated as Dmpc], (I), in which the carbonyl group is well known to be electron-accepting¹².



RESULTS AND DISCUSSION

Hydrosilylation

The results of the hydrosilylation of olefins catalyzed by the complex (I) are summarized in Tables 1–4. All reactions were carried out essentially as described previously¹⁰. As expected for nickel complex catalysts containing electron-accepting ligands, only traces of the Si–H/Si–Cl interchange products were formed.

The most remarkable feature is the formation of considerable amounts of internal adducts (II) from simple terminal olefins. Such products have not previously been encountered in the hydrosilylation catalysed by transition metal complexes.

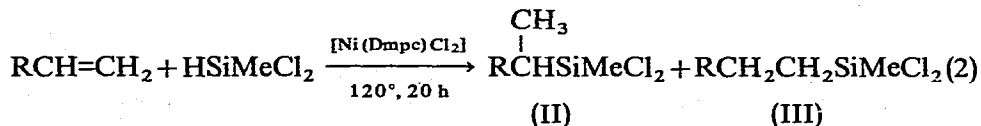


Table 1 indicates that the ratio of the terminal (III) to the internal (II) is virtually constant for hydrosilylation of simple terminal olefins, and that internal olefins also give rise to the terminal adducts. Other silicon hydrides, such as trichlorosilane and phenyldichlorosilane, also add to 1-octene to give a substantial amount of the internal adduct (see Table 2).

Since terminal adducts are formed from the internal olefins, the hydrosilylation must involve olefin isomerization. The isomer ratios in the residual olefins (see Table 3) show that the isomerization competes with the hydrosilylation, but is rather slow.

TABLE 1

ADDITION OF METHYLDICHLOROSILANE TO OLEFINS CATALYZED BY $\text{Ni}(\text{Dmpc})\text{Cl}_2^a$

Olefin	Products	
	Total yield ^b (%)	Internal (II)/terminal (III) ^c ratio
1-Octene	59	38/62
1-Octene ^d	97	36/64
1-Hexene	98	36/64
1-Pentene	84	33/67
Propylene	40	41/59
2-Hexene ^e	38	80/20
2-Pentene ^e	47	51/49

^a Unless otherwise noted, $\text{HSiMeCl}_2/\text{olefin}$ 1, $\text{Ni}(\text{Dmpc})\text{Cl}_2/\text{olefin} \approx 10^{-3}$; 120° , 20 h. ^b Determined by GLC. ^c Area ratio in GLC. ^d $\text{HSiMeCl}_2/\text{octene}$ 2. ^e Heated at 120° for 40 h.

TABLE 2

ADDITION OF SILICON HYDRIDES TO 1-OCTENE^a

Silicon hydride	Products	
	Total yield ^b (%)	Internal (II)/terminal (III) ^c ratio
HSiMeCl ₂	59	38/62
HSiPhCl ₂	100	35/65
HSiCl ₃	100	15/85

^a HSiX₃/1-octene 1, Ni(Dmpc)Cl₂/1-octene $\approx 10^{-3}$; 120°, 20 h. ^b Determined by GLC. ^c Area ratio in GLC.

TABLE 3

ISOMERIZATION OF OLEFINS DURING HYDROSILYLATION^a

Starting olefin	Time (h)	Residual olefin 1-pentene/2-pentene ^b	Adducts	
			Internal (II)/terminal (III) ^b ratio	Total yield ^c (%)
1-Pentene	7	33/67	34/66	78
	12	12/88	34/66	84
	17	14/86	33/67	87
	40	12/88	34/66	84
2-Pentene	20	6/94	50/50	36
	40	5/95	49/51	47
	45	11/89	49/51	54

^a HSiMeCl₂/olefin 1, Ni(Dmpc)Cl₂/olefin $\approx 10^{-3}$; 120°. ^b Area ratio in GLC. ^c Determined by GLC.

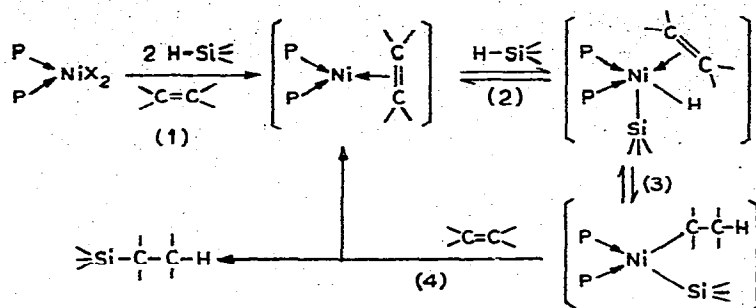
Table 3 indicates that the ratio of the internal to the terminal adduct remains almost constant throughout the reaction.

The internal adduct obtained from a terminal olefin might arise from the preceding isomerization of the terminal to the internal olefin, followed by addition of silicon hydride to the latter. This possibility, however, can be ruled out by the observation that propylene gives the isopropyl derivative, indicating that Markownikoff addition of the silane to the terminal olefin occurs. The formation of the terminal adduct from the internal olefin is inconsistent with a radical mechanism.

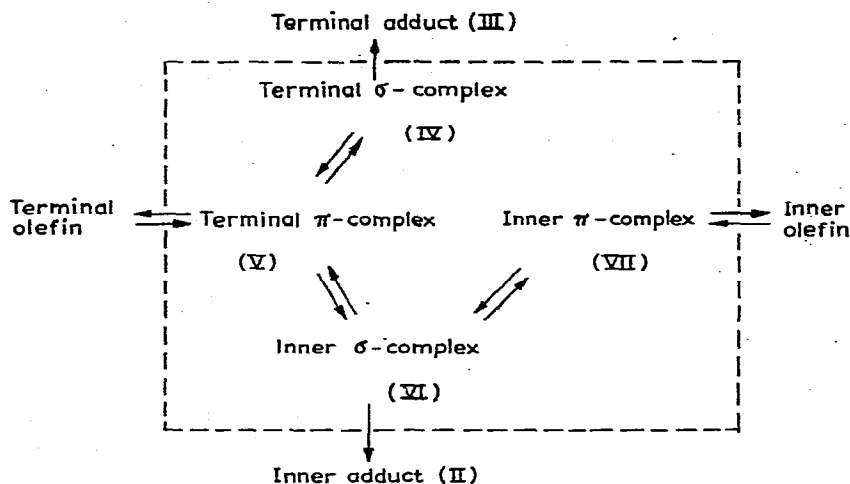
As mentioned briefly in the previous paper¹⁰, there is a general tendency for the nickel-phosphine complexes to give the internal adducts, though in small amounts, from the terminal olefin. Apparently, in the present case, the carboranylphosphine (Dmpc) ligand substantially enhances this tendency, presumably because of the strong electron-accepting properties of the carboranyl group.

In the previous paper¹¹, we proposed a mechanism for hydrosilylations catalyzed by nickel-phosphine complexes (Scheme 1), based upon the Chalk-Harrod mechanism for platinum catalysis¹³, which involves a rapid equilibrium [Step (3)] between a π - and a σ -complex.

SCHEME 1



SCHEME 2



In the present case, we must consider, in the equilibrium step, four possible intermediates, namely, the terminal σ -, terminal π -, internal σ - and internal π -complex. In Scheme 2, these four intermediates are shown inside a rectangle (broken lines) and the products outside. The terminal adduct (III) is formed from the corresponding intermediate (IV), and the internal adduct (II) from (VI). The constancy of the ratio of (II) to (III) throughout the reaction, as mentioned above, suggests that the stabilities of intermediates (IV) and (VI) are comparable, in contrast with the situation in catalysis by other transition metal complexes.

The organic group involved in the intermediate σ -complexes, (IV) and (VI), can be regarded as carbanionic in nature. It seems likely that equalization of stability between the primary and secondary carbanions is brought about by the strongly electron-accepting carbonyl group attached to phosphorus. In other words, the carboranyl group exhibits a leveling effect; the difference in stabilities which would exist originally in the "free" carbanions would be reduced in the intermediates complexed with the Dmpc ligand.

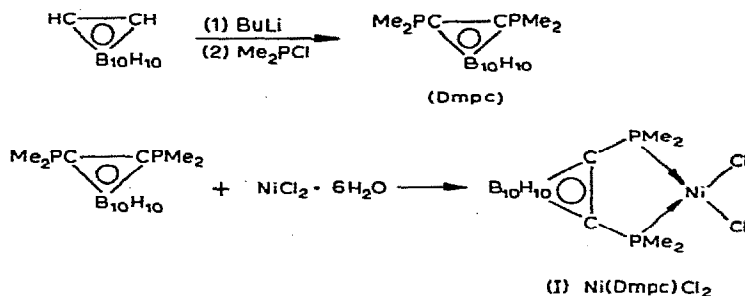
The discussion above for hydroxylation of simple olefins can not be applied to complex olefins, because the substituent effect overcomes the leveling effect (Table

4). Thus, the hydrosilylation of isobutene produced no trace of the internal adduct, *viz.*, the *tert*-butyl derivative, because of steric hindrance. Styrene gave the internal adduct predominantly. In the case of vinylsilane derivatives, the ratio of the terminal to the internal adduct increased in proportion to the inductive effect of the silyl groups.

Finally, with nickel(II) chloride complexed with bis(diphenylphosphino)-*o*-carborane¹⁴, as catalyst, solely the terminal adduct was obtained, and in only 3 to 5% yield, from the addition of methylchlorosilane to 1-octene. This low catalytic activity is comparable to that of dichlorobis(triphenylphosphine)nickel¹⁰.

Preparation of Ni(Dmpc)Cl₂

Dichloro[bis(dimethylphosphino)-*o*-carborane]nickel(II) was prepared by treatment of nickel(II) chloride hexahydrate with bis(dimethylphosphino)-*o*-carborane (Dmpc) in ethyl acetate, essentially as described for the preparation of bis(diphenylphosphino)-*o*-carborane analogs¹⁴. The Dmpc ligand was prepared by standard procedures¹⁵.



The nickel(II) complex of bis(diphenylphosphino)-*o*-carborane was also prepared by a known method¹⁴.

Attempts to prepare the palladium and platinum analogs of these nickel complexes failed; in no case could a single product be isolated.

EXPERIMENTAL

The ¹H NMR spectra were measured on a Varian T-60 spectrometer in carbon tetrachloride solutions containing benzene as an internal standard. IR spectra were recorded with a Hitachi EPI-G3 grating spectrophotometer. A Varian Aero-graph Model 90F, equipped with a 20 ft. column packed with Silicone DC 550 (20% on Celite), was used for isolation and purification of products. *o*-Carborane was prepared by standard procedures¹⁶.

Hydrosilylation

The hydrosilylation reactions were carried out essentially as described in the previous paper¹, except for the use of an equimolar ratio of the silicon hydride to the olefin. The yields and the product ratios (*viz.*, the internal adduct/the terminal adduct, or 1-olefin/2-olefin) were estimated by GLC. The retention times on GLC of the in-

TABLE 4

ADDITION OF METHYLDICHLOROSILANE TO OLEFINS CATALYZED BY Ni(Dmpc)Cl₂^a

(α)

(β)

Olefin	Adducts	
	(α)/(β) ^b	Total yield ^c (%)
$\begin{array}{c} CH_3 \\ \\ CH_3-C=CH_2 \end{array}$	0/100	20
PhCH=CH ₂	94/6	54
Me ₃ SiCH=CH ₂	0/100	100
Cl ₂ MeSiCH=CH ₂	13/87	19

^a HSiMeCl₂/olefin 1, Ni(Dmpc)Cl₂/olefin $\approx 10^{-3}$; 120°, 40 h. ^b Area ratio in GLC. ^c Determined by GLC.

ternal adducts were shorter than those of the terminal ones. The terminal adducts, and all the products listed in Table 4, were identified by comparison of their retention time, IR and ¹H NMR spectra with those of authentic samples obtained by platinum catalyzed hydrosilylation. The internal adducts from trichlorosilane and phenyldichlorosilane could not be fully characterized, since they were isolated only in a rather impure state by GLC. Analytical and/or ¹H NMR spectral data (τ) for other internal adducts are shown below.

CH₃(CH₂)₅CH(CH₃)SiMeCl₂. (Found: C, 48.09; H, 9.13; Cl, 31.75. C₉H₂₀-Cl₂Si calcd.: C, 47.57; H, 8.87; Cl, 32.20%.) NMR: 9.25 (s, SiCH₃), 8.8–9.2 [m, SiCH(CH₃) and terminal CH₃], 8.68 [(br)s, (CH₂)₅].

CH₃(CH₂)₃CH(CH₃)SiMeCl₂. (Found: C, 42.78; H, 8.46; Cl, 35.44. C₇H₁₆-Cl₂Si calcd.: C, 42.21; H, 8.10; Cl, 35.60%.) NMR: 9.30 (s, SiCH₃), 8.7–9.25 [m, SiCH(CH₃) and terminal CH₃], 8.15–8.7 [m, (CH₂)₃].

CH₃(CH₂)₂CH(CH₃)SiMeCl₂. (Found: C, 39.05; H, 7.67; Cl, 38.48. C₆H₁₄-Cl₂Si calcd.: C, 38.92; H, 7.62; Cl, 38.29%.) NMR: 9.28 (s, SiCH₃), 8.8–9.2 [m, SiCH(CH₃) and terminal CH₃], 8.1–8.8 [m, (CH₂)₂].

(CH₃)₂CHSiMeCl₂. NMR: 9.33 (s, SiCH₃), 8.89 [s, (CH₃)₂CH].

Bis(dimethylphosphino)-*o*-carborane: Dmpc

A solution of *o*-carborane (4 g, 27.8 mmol) in 30 ml of ether was added during 10 min, with stirring and under nitrogen, to a solution of *n*-butyllithium (55.6 mmol) in ether at 0°. After 1 h of stirring, a solution of dimethylchlorophosphine¹⁰ (6 g, 62.2 mmol) in ether was added during 10 min, and the resulting mixture was allowed to stand overnight at room temperature with stirring. After 30 min refluxing, the mixture was hydrolyzed. The organic layer and the ether extracts from the aqueous layer were combined, dried over potassium carbonate, and evaporated to dryness. Recrystallization of the residue from heptane, followed by sublimation (ca. 100°/4 mmHg), gave 2.5 g (33.5%) of bis(dimethylphosphino)-*o*-carborane as air-stable,

white crystals, m.p. (in a glass tube sealed under nitrogen) 121.5–122.5°. (Found: C, 27.38; H, 8.13. $C_6H_{22}B_{10}P_2$ calcd.: C, 27.26; H, 8.39%.)

Dichloro[bis(dimethylphosphino)-o-carborane]nickel(II): Ni(Dmpc)Cl₂

A mixture of Dmpc (267.3 mg, 1.0 mmol) and nickel chloride hexahydrate (236.0 mg, 1.0 mmol) in ethyl acetate (20 ml) was stirred at room temperature for 21 h. The orange product which deposited was filtered and dried *in vacuo*. It weighed 322 mg (82% yield). The analytical sample was obtained in the following way. The product (42 mg) was dissolved in a mixture of ethyl acetate (10 ml) and tetrahydrofuran (7 ml) and the solution was filtered. The filtrate was concentrated *in vacuo* to ca. 3 ml. Ethyl acetate (1 ml) was added to give the orange precipitates which were separated by centrifugation and dried *in vacuo*. The product showed no sign of melting or decomposing up to 300° in a sealed glass tube in an atmosphere of nitrogen. (Found: C, 18.39; H, 5.69. $C_6H_{22}B_{10}Cl_2NiP_2$ calcd.: C, 18.29; H, 5.63%.) IR spectrum (cm^{-1} ; KBr): 2990 vw, 2905 w, 2625 vw, 2620 m, 2610 m, 2595 vs, 2550 vs, 1409 vs, 1403 s (sh), 1297 s, 1285 s, 1260 w, 1100 w (sh), 1082 s, 1030 w (br), 983 w, 968 s, 930 vs, 926 vs (sh), 920 vs, 906 m (sh), 870 m, 860 w (sh), 794 m, 756 m, 742 w (sh), 726 w, 711 m, 678 w, 640 vw, 632 w, 626 vw (sh), 570 w, 438 w.

Dichloro[bis(diphenylphosphino)-o-carborane]nickel(II)

To a solution of nickel chloride hexahydrate (78.5 mg, 0.237 mmol) in ethanol (2 ml) were added ethyl acetate (6 ml) and bis(diphenylphosphino)-o-carborane¹⁵ (Dppc) (121.1 mg, 0.237 mmol). The resulting orange-red mixture was stirred at room temperature for 20 h. The orange-red precipitates were filtered off, washed with ethanol, and dried at 50° *in vacuo* (61 mg, 40% yield). The complex decomposed at 238–240° without melting (Found: C, 48.42; H, 5.36. $C_{26}H_{30}B_{10}Cl_2NiP_2$ calcd.: C, 48.65; H, 4.71%.)

Attempted preparation of platinum(II) complexes of Dmpc

(a). As described by Booth and Chatt¹⁷, to a solution of K_2PtCl_4 (116.8 mg, 0.28 mmol) in water (3 ml) was added a solution of Dmpc (68.4 mg, 0.26 mmol) in tetrahydrofuran (2 ml), and the mixture was stirred at room temperature under nitrogen. After 20 min, the precipitates were collected by filtration, and dissolved in dimethylformamide (6 ml) by warming. The solution was then cooled to room temperature, and deposited white-gray powder, which was filtered off, washed with tetrahydrofuran, and dried *in vacuo* (31 mg).

(b). An equimolar mixture of Dmpc and dichlorobis(benzonitrile)platinum(II) in benzene was heated with stirring for 24 h. After filtration and washing with petroleum ether, the white powder was dried *in vacuo*.

These products did not give a satisfactory analysis.

Attempted preparation of palladium(II) complexes of Dmpc and Dppc

Dichlorobis(benzonitrile)palladium(II) was treated with Dmpc or Dppc as described for (b) above. The former gave white powder after reprecipitation from dimethylformamide/water. (Found: C, 16.25; H, 7.73. $C_6H_{22}B_{10}Cl_2P_2Pd$ calcd.: C, 16.32; H, 5.02%.) The latter gave pale yellow crystals after recrystallization from methylene chloride/petroleum ether.

These products did not give satisfactory analyses.

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