

SILICON HYDRIDES AND NICKEL COMPLEXES

II. MECHANISM OF THE HYDROSILYLATION CATALYZED BY NICKEL-PHOSPHINE COMPLEXES

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SUMMARY

Two ethylene-nickel(0) complexes, *viz.*, [1,2-bis(diphenylphosphino)ethane]-(ethylene)nickel(0) and bis(triphenylphosphine)(ethylene)nickel(0) have been used in a comparison of their catalytic activities in hydrosilylation reactions with those of the corresponding nickel(II) complexes, *viz.*, dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) and dichlorobis(triphenylphosphine)nickel(II). The reaction profiles are similar, apart from a significant difference in the induction period; the nickel(II) catalysts requiring a substantially longer time. A mechanism involving a nickel(0) species is proposed for the hydrosilylation.

The interchange of hydrogen and chlorine on silicon accompanying the hydrosilylation is related to a high electron density at the nickel atom bearing the phosphine, olefin, and silicon hydride ligands.

INTRODUCTION

In the preceding paper¹, we described the hydrosilylation of olefins catalyzed by phosphine-nickel(II) complexes. Some of the main features observed are as follows:

(1) Reactions involving nickel(II) catalysts, at least those bearing a bidentate phosphine, scarcely proceed below 90°.

(2). At 120° the reaction proceeds smoothly to form, in many cases, an unexpected "abnormal" adduct, which has arisen from an interchange of hydrogen and chlorine on silicon as well as the expected "normal" adduct.

(3). Both the total yields and the ratios of the abnormal to the normal adduct increase, in general, with increasing electron-donating ability of both the phosphine ligands and the substituents on the olefins.

(4). Isomerization of olefins occurs during the course of hydrosilylation.

(5). *cis*-Addition occurs preferentially.

(6). The reactivity of the silicon hydrides decreases in the order $\text{HSiCl}_3 > \text{HSiMeCl}_2 > \text{HSiMe}_2\text{Cl} \gg \text{HSiMe}_3$.

This paper deals with the mechanism of the nickel complex catalyzed hydrosilylation and that of the H/Cl interchange, in the light of the above observations, with

particular reference to the Chalk-Harrod mechanism² proposed for platinum catalyzed hydrosilylation.

The first step in the Chalk-Harrod mechanism involves the reduction of chloroplatinic acid by a silicon hydride to form a platinum(II) complex. The observation (1) mentioned above suggests that the reduction of nickel(II) to nickel(0) by a silicon hydride may also be a crucial step in the nickel(II) complex catalyzed hydrosilylation. Therefore, it was expected that an olefin-nickel(0) complex would be more effective than the nickel(II) complex. Although this interesting problem was recently discussed by Bennett and Orenski³, we considered it useful to examine the catalytic activities of nickel(II) and nickel(0) complexes in our own systems.

RESULTS AND DISCUSSION

1. Mechanism for the nickel complex catalyzed hydrosilylation

Two ethylene-nickel(0) complexes, *viz.*, [1,2-bis(diphenylphosphino)ethane]-(ethylene)nickel(0) and bis(triphenylphosphine)(ethylene)nickel(0), were used in the comparison of their catalytic activities with those of the corresponding nickel(II) complexes, *viz.*, dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) and dichlorobis(triphenylphosphine)nickel(II). Hitherto unknown [1,2-bis(diphenylphosphino)ethane]-(ethylene)nickel(0), hereafter referred to as Ni(Diphos)(C₂H₄), was prepared essentially by the method described in the literature⁴ for bis(triphenylphosphine)-(ethylene)nickel(0), Ni(PPh₃)₂(C₂H₄).

We also, incidentally, developed an alternative method of preparation of these ethylene-nickel(0) complexes, involving the action of ethyl Grignard reagent on the corresponding dichloronickel(II) complexes, Ni(Diphos)Cl₂ and Ni(PPh₃)₂Cl₂.

TABLE 1

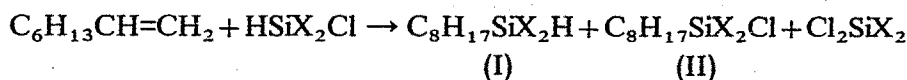
ADDITION OF SILICON HYDRIDES TO 1-OCTENE

Run	Catalyst	Silicon hydride ^a HSiX ₂ Cl	Conditions		Products	
			Temp. (°C)	Time (h)	Total yield (%)	C ₈ H ₁₇ SiX ₂ H/C ₈ H ₁₇ SiX ₂ Cl ratio
Ni ⁰ complex						
1	Ni(PPh ₃) ₂ (CH ₂ =CH ₂)	HSiMeCl ₂	120	20	≈ 5	0/100
2	Ni(Diphos)(CH ₂ =CH ₂)	HSiMeCl ₂	135	40	72	6/94
3		HSiMeCl ₂	120	40	79	7/93
4		HSiMeCl ₂	90	65	84	27/73
5		HSiMeCl ₂ ^b	90	110	82	30/70
6		HSiMeCl ₂	70	264	77	60/40
7		HSiCl ₃	120	20	98	3/97
Ni ^{II} complex						
8	Ni(PPh ₃) ₂ Cl ₂	HSiMeCl ₂	120	20	3 ≈ 5	0/100
9	Ni(Diphos)Cl ₂	HSiMeCl ₂	120	40	75	7/93
10		HSiMeCl ₂	90	120	0	
11		HSiCl ₃	120	20	90	6/94

^a Molar ratio of HSiClX₂/1-octene 2, unless otherwise noted. ^b Molar ratio of HSiMeCl₂/1-octene 6.

The hydrosilylation of 1-octene using these complexes was examined in the manner described in the preceding paper¹. The results obtained are summarized in Table 1. As shown in Table 1, $\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ exhibited as low a catalytic activity as the nickel(II) complex, $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$, and so the subsequent discussion in this paper will be devoted mainly to the catalytic properties of $\text{Ni}(\text{Diphos})(\text{C}_2\text{H}_4)$.

The addition of methyldichlorosilane to 1-octene, in the presence of either $\text{Ni}(\text{Diphos})\text{Cl}_2$ or $\text{Ni}(\text{Diphos})(\text{C}_2\text{H}_4)$ at 120° for 40 h, gave very similar results for the extent of H/Cl interchange and the total yield.



Figures 1 and 2 show the plots for the extent of the reaction at 120° vs. time, with $\text{Ni}(\text{Diphos})(\text{C}_2\text{H}_4)$ and $\text{Ni}(\text{Diphos})\text{Cl}_2$ respectively, as catalysts. The shapes of the curves resemble each other, apart from a significant difference in the induction period; the nickel(II) catalyst requires a substantially longer time. These facts suggest that the same catalytic species may be formed from these two complexes.

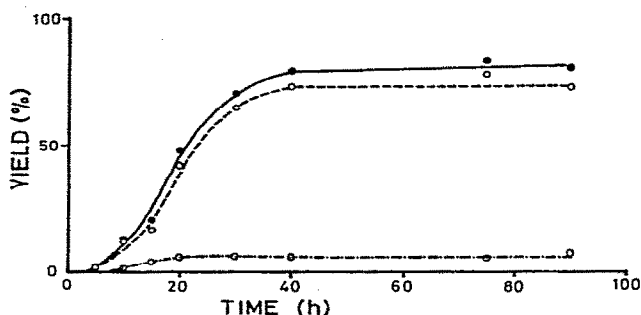


Fig. 1. Plot of the yields of products against time in the reaction of methyldichlorosilane and 1-octene in the presence of $\text{Ni}(\text{Diphos})(\text{CH}_2=\text{CH}_2)$ at 120° : ---○---, $\text{C}_8\text{H}_{17}\text{SiMeCl}_2$; - - -○- - -, $\text{C}_8\text{H}_{17}\text{SiMeClH}$; —●—, total yield.

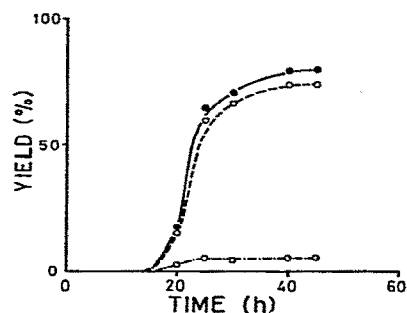


Fig. 2. Plot of the yields of products against time in the reaction of methyldichlorosilane and 1-octene in the presence of $\text{Ni}(\text{Diphos})\text{Cl}_2$ at 120° : ---○---, $\text{C}_8\text{H}_{17}\text{SiMeCl}_2$; - - -○- - -, $\text{C}_8\text{H}_{17}\text{SiMeClH}$; —●—, total yield.

Moreover, as expected, there was a substantial difference in catalytic activity between these two catalysts in the reaction at 90° (Runs 4, 5 and 10). Whereas with the nickel(II) catalyst no reaction occurred even after 120 h, with the corresponding nickel(0) catalyst, hydrosilylation did occur, to give both adducts, (I) and (II), in the same total yield after 65 h as was obtained from the reaction at 120° , but with an enhanced degree of H/Cl interchange. The progress of the reaction at 90° is plotted in Fig. 3. Furthermore, the nickel(0) catalyst caused the reaction to occur even at 70° , to give, after a prolonged reaction time, the same total yield as was obtained at 90° and 120° , with yet further enhancement of the extent of H/Cl interchange (Run 6). These results and the difference in the induction periods mentioned above, indicate that a crucial step may be the reduction of nickel(II) to nickel(0), which appears not to take place

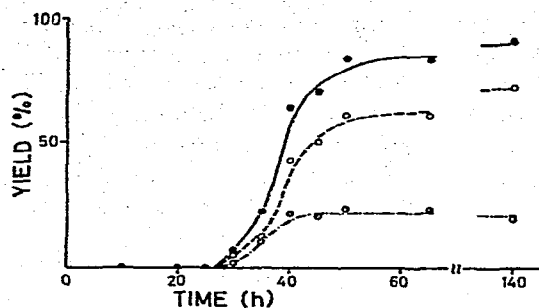
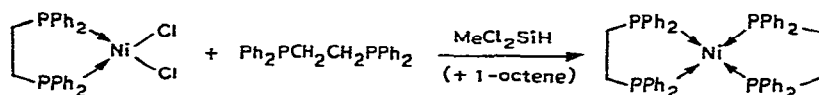


Fig. 3. Plot of the yields of products against time in the reaction of methylchlorosilane and 1-octene in the presence of Ni(Diphos)(CH₂=CH₂) at 90°: ---○---, C₈H₁₇SiMeCl₂; -·-·-○-·-·-, C₈H₁₇SiMeClH; —●—, total yield.

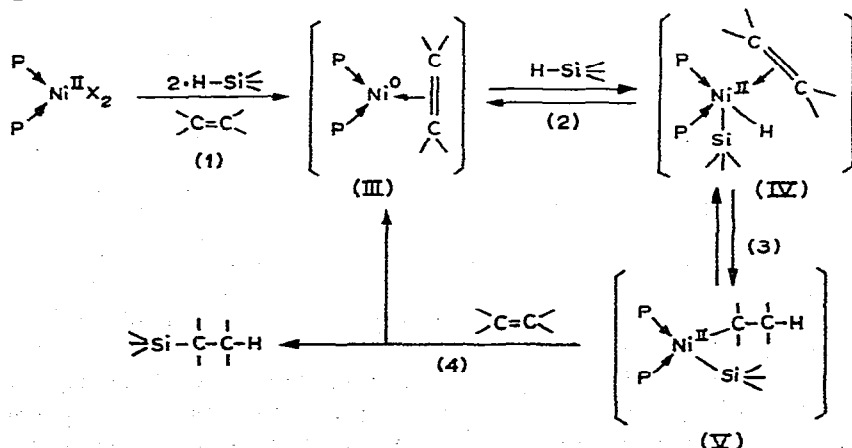
below about 100°. The results with trichlorosilane as the silicon hydride parallel these observations (Runs 7 and 11).

In the light of the above results, it would be expected that the activity of an active nickel(0) species would be reduced by the presence of additional phosphine. The addition of methylchlorosilane to 1-octene in the presence of Ni(Diphos)Cl₂ was in fact, inhibited by adding two equivalents of the Diphos ligand, no reaction occurring, even in 20 h at 135°. Furthermore, bis[bis(diphenylphosphino)ethane]-nickel(0), Ni(Diphos)₂, was isolated when an equimolar mixture of Ni(Diphos)Cl₂ and Diphos was treated with methylchlorosilane, alone or mixed with 1-octene.



A possible mechanism for the hydrosilylation may now be presented, as Scheme 1, based upon the Chalk-Harrod mechanism. In the first step, a bis(phosphine)nickel(II) complex is reduced by two molecules of a silicon hydride in the presence of an

SCHEME 1



olefin to give the corresponding bis(phosphine)(olefin)nickel(0) complex, which, in the second step, undergoes oxidative addition of another molecule of the silicon hydride to produce a nickel(II) intermediate. The third step probably involves an insertion of the olefin into the nickel-hydrogen bond to form a nickel-alkyl complex. This process must be reversible, since the hydrosilylation is always accompanied to some extent by double bond migration in the original olefin. In the final step, coupling of the silyl and alkyl groups on the nickel catalyst occurs, to give the hydrosilylation product, and presumably a second molecule of olefin becomes complexed with the bis(phosphine)-nickel moiety, at the same time, to regenerate the nickel(0) species, thus completing the catalytic cycle.

In this proposed mechanism the reversible step (3) may not be as fast as with the platinum catalysis, but is comparable in rate with the succeeding step (4), since a considerable amount of an internal adduct was obtained from an internal olefin with the nickel catalyst¹, in contrast with the result in presence of platinum catalysts, which leads to formation of only the terminal adducts⁵.

There are some observations suggesting that a nickel(II) intermediate with both hydrogen and silicon bonded to nickel [(IV) in Scheme 1] may be capable of at least a transient existence. Thus, hydrido-nickel complexes with phosphine ligands such as $\text{HNiCl}[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ ⁶ and $[\text{HNi}(\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_{11})_2]_2$ ⁷ are known. Jetz and Graham⁸ prepared a complex containing the silicon-nickel bond, $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})(\text{SiCl}_3)$, under conditions similar to those used for hydrosilylation¹. Furthermore, $\text{M}[\text{Ph}_3\text{SiNi}(\text{CO})_3]$ salts (where $\text{M} = \text{Li}$ or NMe_4) have been characterized by Kruck and coworkers⁹, while we have recently prepared a third type of silicon-nickel complex, *viz.*, $\text{Ni}(\text{SiX}_3)_2(\text{Bipy})$, where $\text{X}_3 = \text{Cl}_3$ or MeCl_2 (ref. 10). A surprisingly stable complex, $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)(\text{SiCl}_3)$, has also been isolated¹¹. Several recent studies of five-coordinate nickel(II) complexes¹² provide results consistent with the existence of a proposed intermediate of type (IV).

Finally, induction periods have been observed even in catalysis by the nickel(0) complex (Figs. 1 and 3). This phenomenon remains rather obscure, but possibly is associated with the initial reaction involving replacement of the ethylene ligand by the other olefin used.

2. Mechanism of the H/Cl interchange process

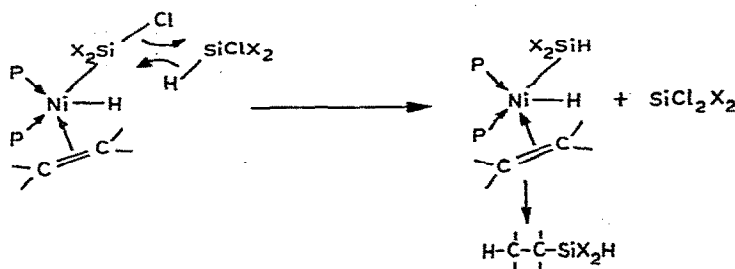
As mentioned in the introduction statement, the H/Cl interchange occurs only in cases in which both the phosphine ligands and the olefins bear electron-donating groups¹. Furthermore, it is influenced by the structure of the silicon hydride and by the ratio of silicon hydride to olefin employed. A large temperature dependence for the interchange has been demonstrated in the present study. Thus, the extent of the H/Cl interchange product increases substantially with a decrease in the reaction temperature, as shown by the following data: 6% at 135°, 30% at 90° and 60% at 70°.

In the light of these facts, it seemed likely that the H/Cl interchange occurs through intermediates which are identical with those involved in the hydrosilylation, and contain at the same time phosphine, olefin, and silicon hydride ligands. To obtain further information supporting this idea, we carried out two experiments using dichloro[1,1'-bis(dimethylphosphino)ferrocene]nickel(II), $\text{Ni}(\text{Dmpf})\text{Cl}_2$, which had been shown to be the most effective catalyst for the H/Cl interchange¹. In one run, methyldichlorosilane was heated at 120° in the presence of $\text{Ni}(\text{Dmpf})\text{Cl}_2$ but in the ab-

sence of olefin. After 36 h, GLC analysis showed the formation of only traces of methyltrichlorosilane; methylchlorosilane could not be detected. In the other run, when a mixture of octylmethylchlorosilane and methylchlorosilane was heated at 120° for 20 h in the presence of $\text{Ni}(\text{Dmpf})\text{Cl}_2$, not even traces of octylmethylchlorosilane were formed. The addition of a small amount of octene to the above system resulted, after 20 h heating, in the formation of only traces of octylmethylchlorosilane.

Particularly in view of the fact that H/Cl interchange occurs only in cases in which both the phosphine ligands and the olefins bear electron-donating substituents we favor a mechanism in which the nickel catalyst behaves like a base such as a tertiary amine, which is well-known to catalyze interchange of hydrogen and chlorine atoms on silicon¹³. In other words, the interchange may take place between chlorine attached to the silicon linked to the nickel(II) intermediate [(IV) in Scheme 1] and a hydrogen atom in the free silicon hydride (Scheme 2).

SCHEME 2



The observed temperature dependence of the H/Cl interchange suggests that a decrease in temperature may retard the last step, (4), in Scheme 1, the rate of the interchange process (Scheme 2) remaining nearly constant.

In connection with the H/Cl interchange, it is of interest to note recent reports concerning disproportionations of organosilicon compounds catalyzed by transition metal complexes. Benkeser and coworkers¹⁴ reported methyl/chlorine interchange between methylsilanes (R_3SiMe) and trichlorosilane in the presence of chloroplatinic acid, and showed that electron-withdrawing substituents in the former retarded the interchange, while Chalk observed a disproportionation of dimethylchlorosilane¹⁵ during hydrosilylation of acrylonitrile catalyzed by rhodium-phosphine complexes.

EXPERIMENTAL

Hydrosilylation was carried out as described in the previous paper¹. The reaction conditions and yields are summarized in Table 1 and Figs. 1-3.

Isolation of bis[1,2-bis(diphenylphosphino)ethane]nickel(0)

A mixture of $\text{Ni}(\text{Diphos})\text{Cl}_2$ (50 mg), Diphos (38 mg) and methylchlorosilane (0.6 g) was placed in a glass tube and degassed. The tube was sealed and then heated at 120° for 20 h. The orange crystals formed were filtered off, washed with dry ether and then methanol in a glove box under nitrogen, and dried *in vacuo* to give 49 mg (60% yield) of $\text{Ni}(\text{Diphos})_2$, m.p. 251-253° (decomp.) (lit.¹⁶ m.p. 253-256°, decomp.) (Found: C, 73.13; H, 5.67. $\text{C}_{52}\text{H}_{48}\text{NiP}_4$ calcd.: C, 73.00; H, 5.66%).

Similar treatment of a mixture of $\text{Ni}(\text{Diphos})\text{Cl}_2$ (50 mg), Diphos (38 mg), HSiMeCl_2 (0.6 g) and 1-octene (0.3 g) gave 58 mg (71 % yield) of orange crystals of $\text{Ni}(\text{Diphos})_2$.

Ethylene[1,2-bis(diphenylphosphino)ethane]nickel(0)

In a 50 ml three-necked flask, equipped with an ethylene inlet tube and a pressure equalizing dropping funnel, was placed a mixture of bis(acetylacetonato)nickel(II) (2.07 g, 8.05 mmol), 1,2-bis(diphenylphosphino)ethane (3.20 g, 8.05 mmol) and 40 ml of dry ether. The slurry was saturated with ethylene at 0° , and 1.3 ml of triethylaluminum dissolved in 15 ml of dry ether was added dropwise at the same temperature over 1 h with magnetic stirring. Stirring was continued at 0° with ethylene bubbling in for a few hours; while being stirred, the mixture underwent a colour change from green-yellow to yellow. It was washed several times with cold ethylene saturated ether (100 ml), and then dried, initially under a rapid stream of ethylene and finally *in vacuo*, to give 2 g (51 % yield) of $\text{Ni}(\text{Diphos})(\text{C}_2\text{H}_4)$, m.p. $235\text{--}245^\circ$ (decomp. in a vacuum sealed tube) (Found: C, 69.40; H, 6.09; P, 11.83. $\text{C}_{28}\text{H}_{28}\text{NiP}_2$ calcd.: C, 69.31; H, 5.82; P, 12.77 %.) The compound appeared to be stable in the air for a few hours, but turned white after 1 day, indicating decomposition. The ethylene ligand in this compound was very readily replaced by tetracyanoethylene. Thus, to a stirred mixture of $\text{Ni}(\text{Diphos})(\text{CH}_2=\text{CH}_2)$ (0.556 g, 1.1 mmol) and tetracyanoethylene (0.147 g, 1.1 mmol) was added dropwise 15 ml of deaerated benzene at room temperature. Rapid evolution of gas (27 ml at STP, ca. 110 % as ethylene) occurred, and the colour darkened. The green-brown precipitates were filtered off, washed with deaerated benzene in a glove-box under nitrogen, and then dried *in vacuo* to give 0.594 g (100 % yield) of (tetracyanoethylene)[1,2-bis(diphenylphosphino)ethane]nickel(0), m.p. 150° (decomp. in a vacuum sealed tube). (Found: C, 65.88; H, 4.39. $\text{C}_{32}\text{H}_{24}\text{N}_4\text{NiP}_2$ calcd.: C, 65.68; H, 4.13 %.) The compound is sensitive to oxygen and turns brown.

Preparation of ethylene complexes by the Grignard method

(a). *Ethylenebis(triphenylphosphine)nickel(0)*. In a 100 ml Schlenk tube, fitted with a side-armed dropping funnel, were placed $\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2$ (1.29 g, 1.92 mmol) and deaerated ether (30 ml) under a slow stream of ethylene. To the suspension ethylmagnesium bromide (13 mmol) in ether was added in one portion, with stirring and cooling in an ice-bath. The mixture became yellow, and after several seconds a brown clear solution was formed, from which a large quantity of bright yellow crystals deposited immediately. After 1 h stirring at 0° , the mixture was hydrolyzed with water (20 ml) and saturated aqueous ammonium chloride (50 ml). The aqueous layer and the supernatant organic solvent were removed by means of a syringe and the remaining yellow solid was dissolved in 15 ml of benzene. The solution was then filtered under ethylene pressure. The filtrate was added to 70 ml of ethylene saturated methanol. After 10 min, the resulting yellow crystals were collected by filtration. The recrystallization was repeated twice, to give 581 mg (50 % yield) of product. (Found: C, 74.38; H, 5.67. $\text{C}_{38}\text{H}_{34}\text{NiP}_2$ calcd.: C, 74.66; H, 5.61 %.) The IR spectrum was superimposable on that of an authentic sample made from $\text{Ni}(\text{Acac})_2$, triphenylphosphine, and triethylaluminum by Maitlis' method^{4b}. Upon treatment with tetracyanoethylene, almost one equivalent of ethylene was evolved.

(b). *Ethylene*[1,2-bis(diphenylphosphino)ethane]nickel(0). Similarly, Ni(Diphos)-Cl₂ (981 mg, 1.86 mmol) in 35 ml of ether was treated with the ethyl Grignard reagent (15 mmol) to yield 291 mg (32 % yield) of the ethylene complex, as light yellow crystals. (Found: C, 69.04; H, 5.88. C₂₈H₂₈NiP₂ calcd.: C, 69.31; H, 5.82 %.)

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REFERENCES

- 1 Y. Kiso, M. Kumada, K. Tamao and M. Umeno, *J. Organometal. Chem.*, 50 (1973) 297.
- 2 a) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 87 (1965) 16.
b) A. J. Chalk, *Trans. N.Y. Acad. Sci., Ser. II*, 32 (1970) 481.
- 3 E. W. Bennett and P. J. Orenski, *J. Organometal. Chem.*, 28 (1971) 137.
- 4 a) G. Wilke and G. Herrmann, *Angew. Chem.*, 74 (1962) 693.
b) E. O. Greaves, C. J. L. Lock and P. M. Maitlis, *Can. J. Chem.*, 46 (1968) 3879.
c) J. Ashley-Smith, M. Green and F. G. A. Stone, *J. Chem. Soc. A*, (1969) 3019.
- 5 For a relevant review, see C. Eaborn and R. W. Bott, in A. G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. I, Part 1, Dekker, New York, 1968, pp. 231-263.
- 6 M. L. H. Green and T. Saito, *Chem. Commun.*, (1969) 208.
- 7 K. Jonas and G. Wilke, *Angew. Chem.*, 82 (1970) 295.
- 8 W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 89 (1967) 2773.
- 9 T. Kruck, E. Job and U. Klobe, *Angew. Chem.*, 80 (1968) 360.
- 10 Y. Kiso, K. Tamao and M. Kumada, *Chem. Commun.*, (1972) 105.
- 11 K. Tamao and M. Kumada, unpublished results.
- 12 P. L. Orioli, *Coord. Chem. Rev.*, 6 (1971) 285, and references cited therein.
- 13 (a) A. D. Petrov and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1960) 519; *Chem. Abstr.*, 54 (1960) 22325;
(b) D. R. Weyenberg, A. E. Bey, H. F. Stewart and W. H. Atwell, *J. Organometal. Chem.*, 6 (1966) 583.
- 14 K. R. Bech and B. A. Benkeser, *J. Organometal. Chem.*, 21 (1970) P 35.
- 15 A. J. Chalk, *J. Organometal. Chem.*, 21 (1970) 207.
- 16 J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).