Journal of Organometallic Chemistry, 85 (1975) 19—33

ASYMMETRIC SYNTHESIS AT SILICON

I. HYDROSILYLATION OF CARBONYL COMPOUNDS CATALYSED BY A CHIRAL PHOSPHINE—RHODIUM COMPLEX: STEREOCHEMISTRY AND MECHANISM*

R.J.P. CORRIU and J.J.E. MOREAU

Laboratoire des Organométalliques, associé au CNRS no. 82, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex (France)

(Received July 17th, 1974)

Summary

Hydrosilylation of carbonyl compounds catalysed by rhodium complexes III accompanied by retention of configuration at the silicon atom.

Optically active alkoxysilanes of up to 46% optical purity are obtained using prochiral silanes and an asymmetric catalyst. The hydrosilylation of prochiral ketones leads to an asymmetric reaction at both the silicon and carbon centres with different optical yields.

A mechanism is proposed to explain the stereochemical results.

Introduction

Elucidation of reaction mechanisms at the Si atom centre has involved stereochemical studies. Since the resolution of 1-NpPhMeSi*H (Np = naphthyl) by Sommer and coworkers [2] several asymmetric monofunctional organosilanes have been obtained [3], but all the syntheses require a resolution stage which restricts the number and variety of the structures. The resolution of bifunctional organosilanes [4] provides a more general route to monofunctional asymmetric organosilanes [5].

Although asymmetric synthesis in carbon chemistry has been widely studied [6], examples of asymmetric induction at heteroatoms are limited [6]. In particular, little work has been carried out in organosilicon chemistry despite the obvious interest it presents.

* For a preliminary communication see ref. 1.

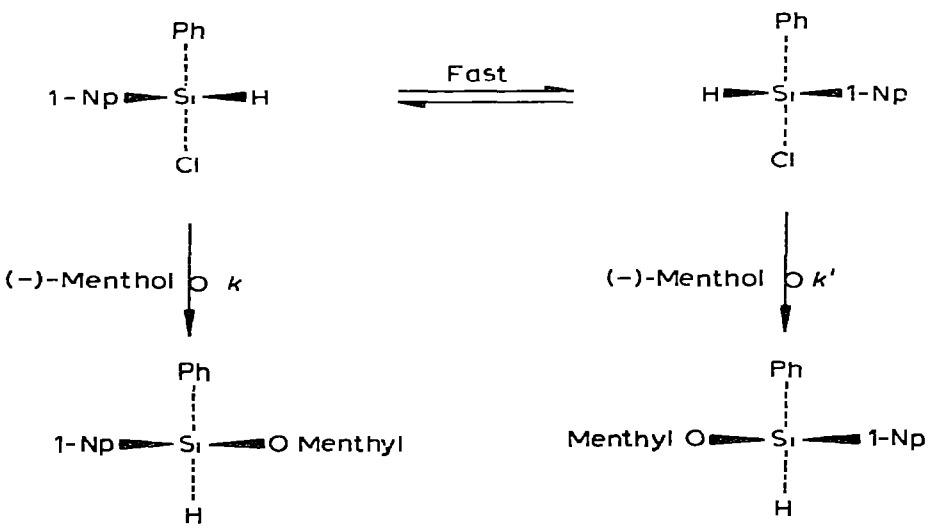
The first example of asymmetric synthesis at a silicon centre was reported by Klebe and Finkbeiner [7], for the reaction of bis(*N*-methylacetamido)methylphenylsilane with optically active amino acids. These authors obtained in unequal amounts the 2-siloxazolidone-5 diastereoisomers, from which alcoholysis leads to an optically active PhMe(MeO)(1-NpO)Si*.

We have attempted to examine some more general cases of asymmetric synthesis at the silicon atom centre. In organic chemistry trigonal carbon constitutes the most important category of prochiral centres which allows asymmetric induction [6]; on the other hand, in silicon chemistry the sp^2 state of the silicon atom does not occur, all four coordinate organosilanes having a tetrahedral structure. Because of this, the possibility of asymmetric synthesis is much more limited.

Starting with a trisubstituted organosilane, R_3SiX, the only possibility of asymmetric synthesis is by a partial substitution of the functional group X by a chiral group. This method of kinetic resolution, which was exploited by Holt et al. [8], gives poor chemical yields for the asymmetric compound.

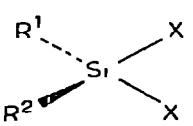
Total chemical transformation of the organosilane starting material can nevertheless be envisaged. We have demonstrated, for menthanolysis of a chlorosilane [4], the validity of the kinetic Scheme 1.

SCHEME 1



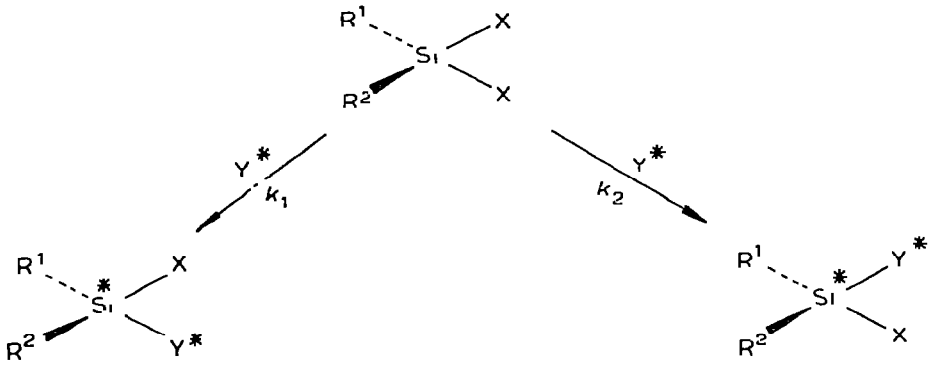
The chlorosilane undergoes rapid racemisation which is faster than alcoholysis. The menthoxysilane diastereoisomers are obtained quantitatively in a ratio close to that of the rate constants: k/k'.

The only possible structure for a prochiral silicon atom is the tetrahedral arrangement shown below, where X is a functional group such as H, halogen or OR.



If we envisage substitution by an asymmetric group Y*, the rates of substitution of the enantiotopic groups X will be different, with unequal rate constants k_1 and k_2, and two diastereoisomers, I and II, of opposite configuration around the silicon atom will be formed in unequal amounts, the more abundant being that whose formation corresponds to the greater rate constant (Scheme 2).

SCHEME 2



(I) (II)

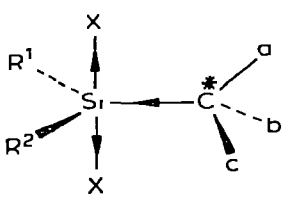
However, the substitution by Y has to satisfy a number of conditions.

(1) Substitution by Y must be selective and must lead to the formation of R^1R^2SiXY, avoiding disubstitution which yields the symmetric product $R^1R^2SiY_2$.

(2) Substitution must be stereospecific. Substitution of the same enantiotopic group, with inversion or retention of configuration at the silicon centre, leads to two opposite configurations for the organosilane. A non-stereoselective substitution will not give an asymmetric synthesis.

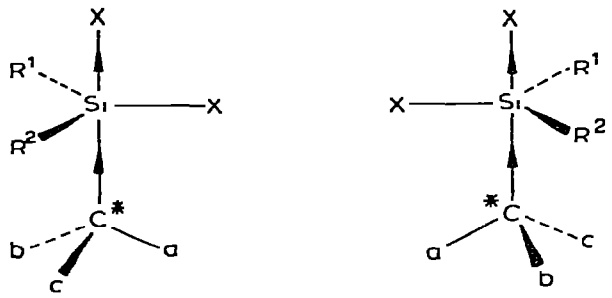
(3) In the case of nucleophilic substitution on silicon, we believe that higher optical yields will be obtained for substitutions carried out with inversion rather than with retention of configuration. We have shown that a nucleophilic substitution proceeds by slow formation of a pentacoordinate intermediate [9]: retention is explained by an equatorial attack of the nucleophile and an axial departure of the leaving group while inversion corresponds to an axial attack followed by an axial departure.

If we consider the substitution of a prochiral organosilane by an asymmetric nucleophile we see that substitution with retention of one or the other enantiotopic groups leads to formation of the same intermediate (A). On the



(A)

other hand, substitution with inversion leads to the formation of two diastereoisomeric intermediates (B_1 and B_2). We have therefore studied asymmetric syn-

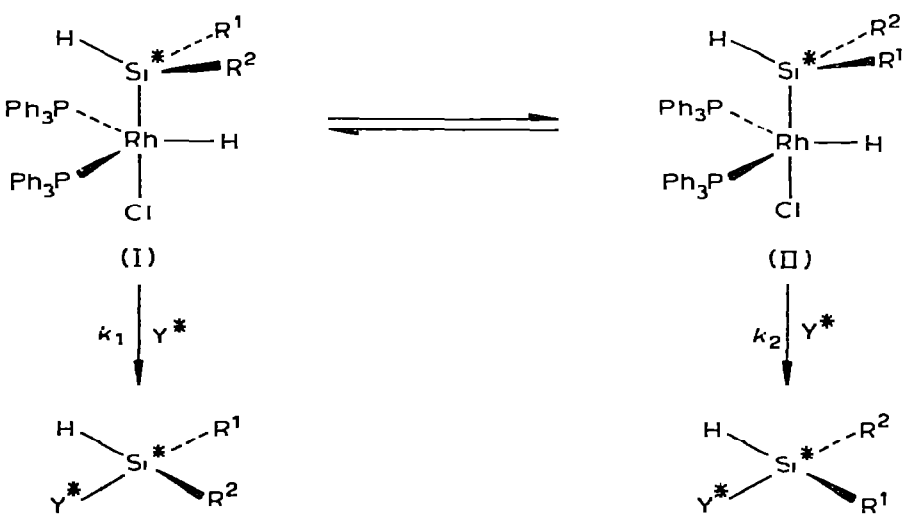


thesis from disubstituted silanes $R^1R^2SiH_2$, initially with reactions catalysed by rhodium complexes. In this case direct substitution at the silicon atom centre does not occur and intervention of the catalysts must be envisaged. The first step will be the oxidative addition of the organosilane (eqn. 1). Such pentacoordinate rhodium complexes have been isolated and are dissociated in solution [10].

$$R^1R^2SiH_2 + (PPh_3)_3RhCl \rightleftharpoons (R^1R^2HSi)(Ph_3P)_2\,Rh(H)(Cl) + PPh_3 \qquad (1)$$

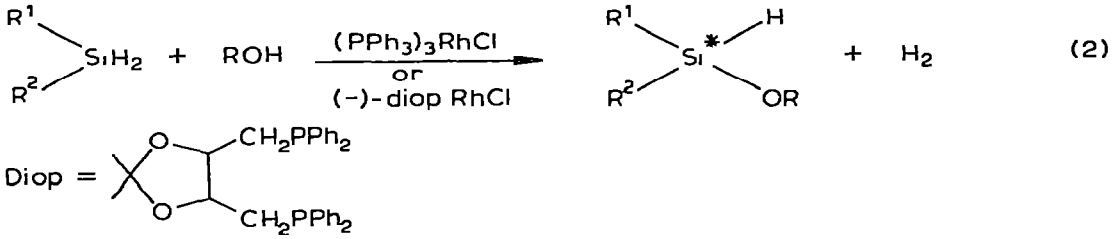
In the case of a prochiral silane we observed the formation of two enantiomeric complexes (I and II), which, owing to dissociation will exist in equilibrium in the solution. Scheme 3 is a kinetic scheme suitable for asymmetric synthesis analogous to that observed for menthanolysis of chlorosilane. The reactions of

SCHEME 3



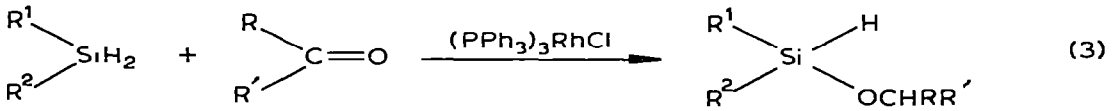
the two complexes with a chiral reagent will lead to the formation of two diastereoisomeric organosilanes in unequal amounts.

We recently studied the alcoholysis of disubstituted organosilanes by an asymmetric alcohol or with chiral rhodium complex catalysts [11] (eqn. 2). Asymmetric alkoxysilanes are obtained with optical yield up to 56%.



We report here the results obtained in the asymmetric hydrosilylation of ketones and aldehydes, and its use in the preparation of optically active organosilanes. Although hydrosilylation is a potentially useful method for asymmetric reduction of ketones [12], the use of prochiral organosilanes has not been reported.

The addition of organosilanes to the carbonyl compounds catalysed by Wilkinson's complex [13, 14] lends itself conveniently to our study (eqn. 3).

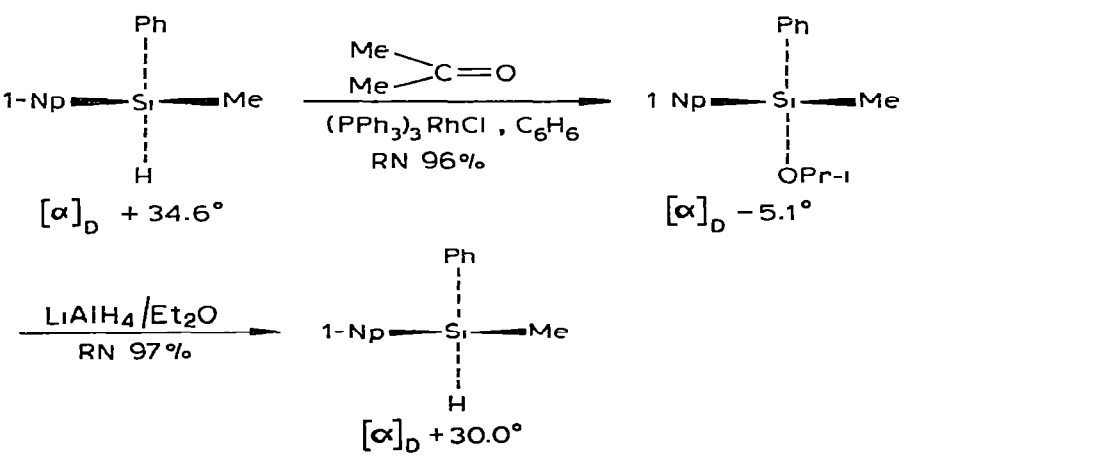


We have, in a preliminary study, verified the selectivity of the prochiral organosilane starting materials [13]. No dialkoxysilanes are detected in the reaction medium and the yield is quantitative. On the other hand the end-products are bifunctional and we have already underlined the theoretical and synthetic importance of such asymmetric compounds [5, 9]. Finally we can envisage the use of a chiral catalyst. Asymmetric catalysis has been used with much success in hydrogenation [15, 16], hydrosilylation [17], hydroformylation [18] and dimerisation [19].

Results

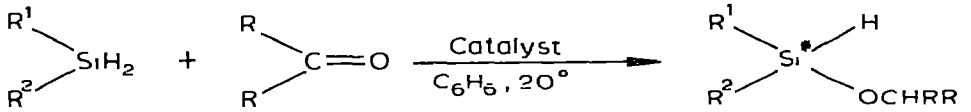
In order to determine the stereochemistry and stereoselectivity of hydrosilylation, we have studied the addition of an asymmetric organosilane *R*(+)-1-NpPhMeSiH to acetone in the presence of $(PPh_3)_3RhCl$. The reactions are summarised in Scheme 4.

SCHEME 4



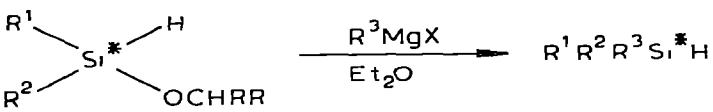
Addition of *R*(+)-1-NpPhMeSiH ($[\alpha]_D$ + 34.6°) to acetone in the presence of Wilkinson's catalyst in benzene leads to *S*(−)-1-NpPhMeSiO-i-Pr ($[\alpha]_D$−5.1°) of the same configuration [20]. The addition reaction therefore takes place with 96% retention of configuration at the silicon centre. We have carried out the reduction of the alkoxysilane obtained by $LiAlH_4$ in ether. This reaction is known to retain the configuration of the silicon atom [21] giving the silane *R*(+) starting material ($[\alpha]_D$ + 30.0°). The hydrosilylation reaction carried out in the absence of solvent takes place with 90% retention of configuration.

Next we studied the asymmetric synthesis from prochiral organosilanes $R^1R^2SiH_2$ with various symmetric ketones using the chiral catalyst described by Kagan and coworkers [15] (eqn. 4). The catalyst used was $[(C_8H_{14})_2RhCl]_2$ + (+) or (−)-diop.



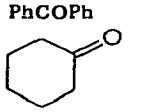
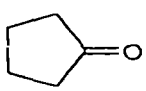
(4)

The addition product, formed quantitatively, was not isolated; its optical purity was measured by conversion to a trisubstituted silane of known maximum specific rotation (eqn. 5). This reaction is both quantitative and stereospecific [5]. The results obtained are presented in Table 1.



(5)

TABLE 1

$R^1R^2SiH_2$	RCOR	Catalyst[a]	$R^1R^2R^3Si^*H$[b]	$[\alpha]_D$ (°)	Configuration	Optical purity (%)
1-NpPhSiH$_2$	MeCOMe	(+)-Cat.	1-NpPhEtSiH	+ 7.5	*R*	30
1-NpPhSiH$_2$	EtCOEt	(+)-Cat.	1-NpPhMeSiH	+16.5	*R*	46
1-NpPhSiH$_2$	EtCOEt	(−)-Cat.	1-NpPhMeSiH	−15.8	*S*	44
1-NpPhSiH$_2$	n-PrCO-n-Pr	(+)-Cat.	1-NpPhMeSiH	+13.9	*R*	39
1-NpPhSiH$_2$	i-BuCO-i-Bu	(+)-Cat.	1-NpPhMeSiH	+12.8	*R*	36
1-NpPhSiH$_2$	PhCOPh	(+)-Cat.	1-NpPhMeSiH	+11.0	*R*	31
1-NpPhSiH$_2$		(+)-Cat.	1-NpPhEtSiH	+ 7.9	*R*	32
1-NpPhSiH$_2$		(+)-Cat.	1-NpPhMeSiH	+12.6	*R*	35
1-NpMeSiH$_2$	EtCOEt	(+)-Cat.	1-NpPhMeSiH	− 4.3	*S*	12
1-NpMeSiH$_2$	PhCOPh	(+)-Cat.	1-NpPhMeSiH	− 2.4	*S*	7
1-NpEtSiH$_2$	EtCOEt	(+)-Cat.	1-NpPhEtSiH	− 5.3	*S*	21
1-NpEtSiH$_2$	PhCOPh	(+)-Cat.	1-NpPhEtSiH	− 8.1	*S*	33

[a] (+)-Cat. = $[(C_8H_{14})_2RhCl]_2$ + (+)-diop; (−)-Cat. = $[(C_8H_{14})_2RhCl]_2$ + (−)-diop. [b] *R*(+)-1-NpPhMeSiH, $[\alpha]_D$ +36.0° (pentane) [20]; *R*(+)-1-NpPhEtSiH, $[\alpha]_D$ + 24.6°(CCl_4) [3].

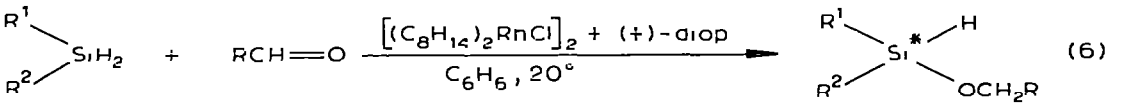
TABLE 2

$R^1R^2SiH_2$	RCH=O	Catalyst[a]	$R^1R^2R^3SiH$[b]	$[\alpha]_D$ (°)	Configuration	Optical purity (%)
1-NpPhSiH$_2$	EtCHO	(+)-Cat.	1-NpPhMeSiH	+5.6	*R*	14
1-NpPhSiH$_2$	n-PrCHO	(+)-Cat.	1-NpPhMeSiH	+4.9	*R*	16
1-NpPhSiH$_2$	i-BuCHO	(+)-Cat.	1-NpPhMeSiH	+1.5	*R*	4
1-NpPhSiH$_2$	n-C_6H_{13}CHO	(+)-Cat.	1-NpPhMeSiH	+4.7	*R*	13
1-NpPhSiH$_2$	PhCHO	(+)-Cat.	1-NpPhMeSiH	+2.5	*R*	7

[a] (+)-Cat. = $[(C_8H_{14})_2RhCl]_2$ + (+)-diop. [b] *R*(+)-1-NpPhMeSiH, $[\alpha]_D$ + 36.0° (pentane) [20].

As we observed earlier [11], 1-NpPhSiH$_2$ leads to optical yields which are higher than are given by the other organosilanes. From organosilanes of such optical purity, optically pure compounds can be obtained by crystallisation [22]. The optical yields obtained are slightly better than those given by the corresponding alcohols [11]. Diop gave better optical yields than an asymmetric phosphine R_3P^* [23].

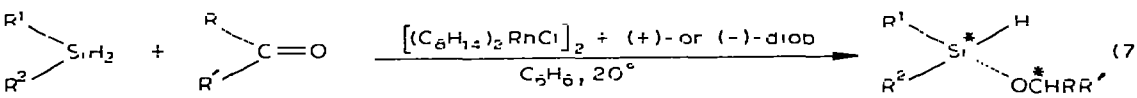
As before, we studied hydrosilylation of aldehydes (eqn. 6).



(6)

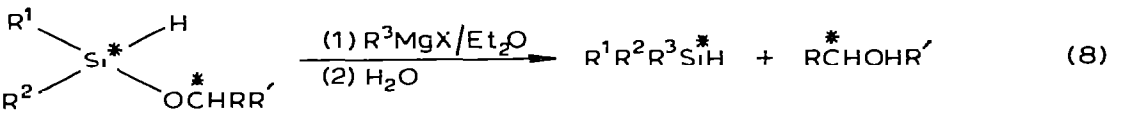
The optical purity is determined as in the previous example, with the results given in Table 2. The optical yields observed in this case are very much lower than those given by ketones.

In the case of a non-symmetric ketone, hydrosilylation by a prochiral silane leads to an asymmetric reaction at both the silicon and carbon centres (eqn. 7).



(7)

Treatment of the reaction mixture with a Grignard reagent allows recovery of an organosilane and an alcohol of different optical purities (eqn. 8).



(8)

The results obtained are shown in Table 3.

The organosilanes obtained are of similar optical purity to those observed for symmetric ketones. The alcohols are obtained with better optical yields than those generally reported for asymmetric reduction of ketones by hydrosilylation [12]. 1-NpPhSiH$_2$ seems to be a better reagent for such asymmetric reductions than the trisubstituted silanes; analogous observations were made by Kagan and coworkers [12].

TABLE 3

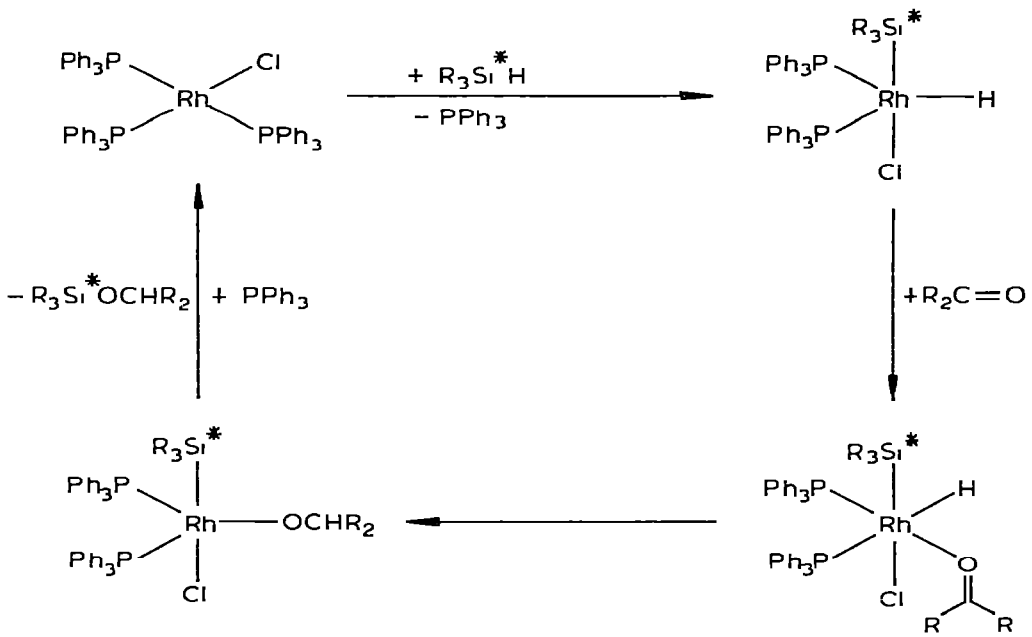
$R^1R^2SiH_2$	RCOR'	Catalyst [a]	$R^1R^2R^3SiH$ [b]	$[\alpha]_D$ (°)	Configuration	Optical purity %	RCHOHR' [c]	$[\alpha]_D$ (°)	Configuration	Optical purity %
1-NpPhSiH$_2$	PhCOMe	(−)-Cat.	1-NpPhEtSiH	− 8.0	*S*	32	PhCHOHMe	+28.0	*R*	55
1-NpPhSiH$_2$	PhCOEt	(+)-Cat.	1-NpPhMeSiH	+10.8	*R*	30	PhCHOHEt	−16.4	*S*	56
1-NpPhSiH$_2$	EtCOMe	(−)-Cat.	1-NpPhMeSiH	−14.2	*S*	40	EtCHOHMe	− 5.8	*R*	42
1-NpPhSiH$_2$	EtCOMe	(+)-Cat.	1-NpPhMeSiH	+14.0	*R*	39				
1-NpPhSiH$_2$	t-BuCOMe	(+)-Cat.	1-NpPhMeSiH	+12.6	*R*	35				

[a] (+)-Cat. = $[(C_8H_{14})_2RhCl]_2$ + (+)-diop; (−)-Cat. = $[(C_8H_{14})_2RhCl]_2$ + (−)-diop. [b] *R*(+)-1-NpPhMeSiH, $[\alpha]_D$ + 36.0° (pentane) [20]; *R*(+)-1-NpPhEtSiH, $[\alpha]_D$ + 24.6° (CCl_4) [3]. [c] *S*(−)-PhCHOHMe, $[\alpha]_D$ −52.5° (CH_2Cl_2) [24]; *S*(−)-PhCHOHEt, $[\alpha]_D$ −29.1° (neat) [25]. *R*(−)-EtCHOMe, $[\alpha]_D$ −13.8° (neat) [26].

Discussion

To explain our results, we envisage a mechanism analogous to that proposed for hydrosilylation [27] or hydrogermylation [28] of olefins and acetylenes (Scheme 5).

SCHEME 5



In the first step, oxidative addition of the silane leads to a pentacoordinate complex [10]. This step probably proceeds with retention of configuration at the silicon atom, as with the platinum complexes [29]. Hydrosilylation with the observed retention of configuration of the organosilane suggests that the next step is coordination of the ketone to the rhodium. Migration of a hydride ion then leads to a new complex which can eliminate the alkoxysilane with retention of configuration of silicon. It is also possible to envisage initial migration of the silicon radical, which would lead to the same result.

Let us now consider the case of a prochiral silane with an asymmetric catalyst. We have in the first place the "in situ" formation of an asymmetric rhodium complex [15] (eqn. 9).

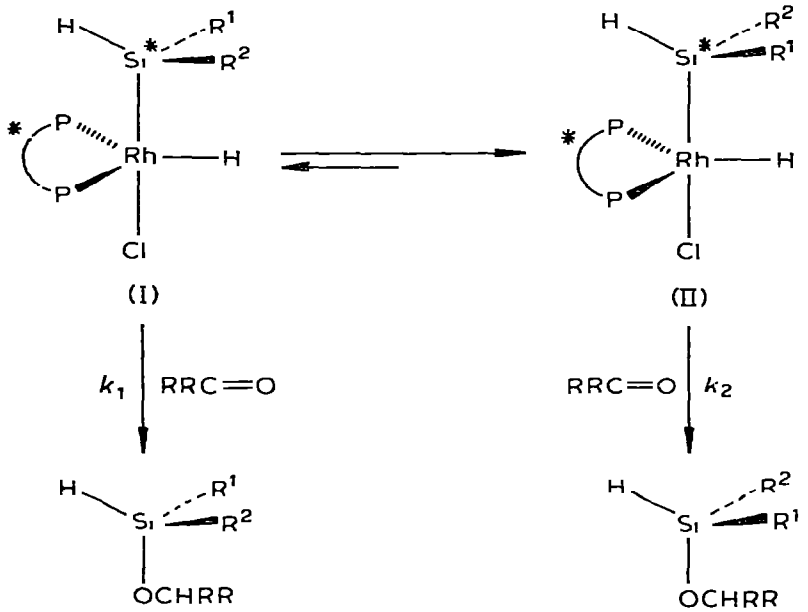
$$[(C_8H_{14})_2RhCl]_2 + 2\ \text{diop} \xrightarrow{S} 2(\text{diop})Rh(Cl)(S) \qquad (9)$$

The oxidative addition of the silane $R^1R^2SiH_2$ to this complex will lead to the formation of two diastereoisomeric complexes (I and II). These two complexes in equilibrium will not occur in the same abundance in the reaction medium (Scheme 6).

They will react with the ketone with different rate constants, k_1 and k_2. If we suppose that complexes I and II are in a rapid equilibrium, greater than the

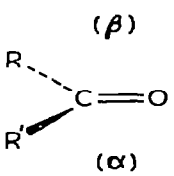
rate of reaction of the ketone, the alkoxysilane enantiomers will be formed in a ratio equal to $k_1[\mathrm{I}]/k_2[\mathrm{II}]$.

SCHEME 6



If we use the phosphine enantiomer, we will have an equilibrium between two complexes $\bar{\mathrm{I}}$ and $\bar{\mathrm{II}}$, respectively enantiomers of the earlier complexes I and II, which will lead to alkoxysilanes of opposite configuration to the previous case.

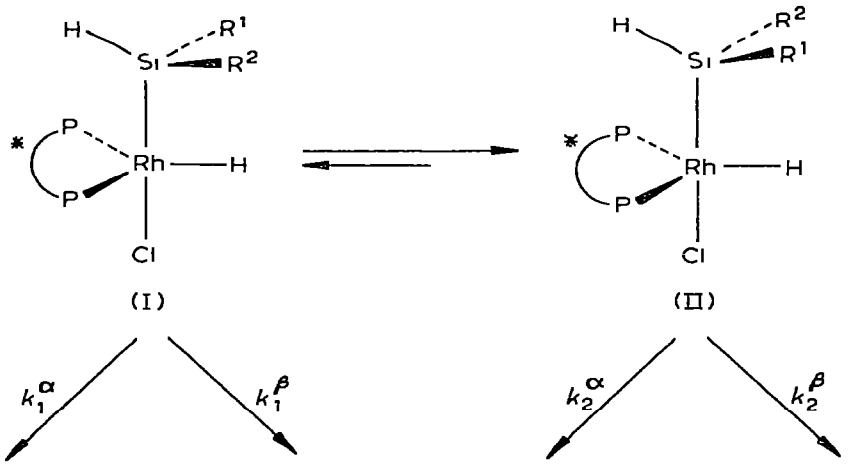
For hydrosilylation of a prochiral ketone, we can write a kinetic scheme of the same type (Scheme 7). It is necessary, however, to distinguish the two faces (α and β) of the ketone.



The diastereoisomeric complexes I and II react at the two faces of the ketone with rate constants k_1^{α}, k_1^{β} for the complex I and k_2^{α}, k_2^{β} for II. The optical purity at the silicon centre (P_{Si}) depends on the relative rates of reaction of the complexes I and II: $P_{\mathrm{Si}} = (k_1^{\alpha} + k_1^{\beta})[\mathrm{I}]/k_2^{\alpha} + k_2^{\beta})[\mathrm{II}]$. The optical purity at the carbon atom centre (P_{C}) will be different. It depends on the attack on the faces (α) and (β): $P_{\mathrm{C}} = k_1^{\alpha}[\mathrm{I}] + k_2^{\alpha}[\mathrm{II}]/k_1^{\beta}[\mathrm{I}] + k_2^{\beta}[\mathrm{II}]$. This explains well why there is no relation between the optical purity of the asymmetric silane and alcohol.

On the other hand it is very interesting to note that addition, in the presence of [(+)-diop]RhCl, of 1-NpPhSiH$_2$ leads to silanes R(+)-1-NpPhMeSiH and that addition of 1-NpMeSiH$_2$ or 1-NpEtSiH$_2$ leads to S(−)-1-NpPhMeSiH and S(−)-1-NpPhEtSiH, respectively. One can explain this by the relative stability of the

SCHEME 7



two diastereoisomeric complexes I and II. The two asymmetric carbon atoms of the (+)-diop impose a conformation in which one of the phenyl groups is quasi-axial and the other quasi-equatorial. In the previous equilibrium between the two diastereoisomers I and II, the more abundant is that for which the steric interactions are minimum. The preferred configuration of the silicon atom is that in which the smallest group S is on the side of the axial phenyl (Fig. 1):

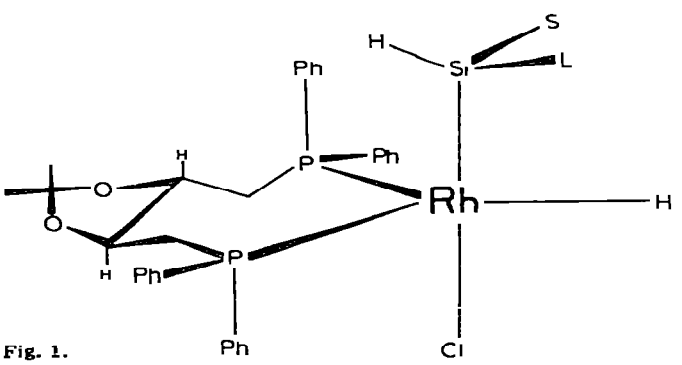
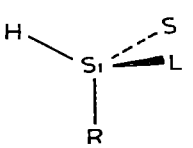


Fig. 1.

The reaction of this preferred diastereoisomer with the ketone, followed by reaction of the Grignard reagent (RMgX) with the alkoxysilane obtained, retains the configuration of the silicon atom. The reactions of 1-NpPhSiH$_2$, 1-NpMeSiH$_2$ and 1-NpEtSiH$_2$ (where L = 1-Np; S = Ph, Me, Et) will therefore lead preferentially to an organosilane of configuration shown below in agreement with the observed results.



[L = 1-Np ; S = Ph ; R = Me ; Silane *R* (+)
L = 1-Np ; S = Me,Et ; R = Ph ; Silane *S* (−)]

Conclusion

Asymmetric hydrosilylation of carbonyl compounds, of interest for the preparation of asymmetric alcohols [12], proves to be a good method for the preparation of bifunctional asymmetric alkoxysilanes. The latter are obtained with sufficient optical purity for stereochemical studies [30]. Mechanistic studies of the reaction explain the observed results.

Experimental

All the manipulations were carried out under nitrogen, using a Schlenk tube and a pressure gradient. The Grignard reagents were prepared in the usual manner and titrated iodometrically. The NMR spectra were recorded on Varian A-60 and T-60 spectrometers. The specific rotations were measured on a Perkin-Elmer 141 polarimeter.

Preparation of the organosilane starting materials and of the catalysts

Optically active 1-naphthylphenylmethylsilane was prepared according to a modification of the original method used by Sommer [22]. Disubstituted organosilanes were obtained by methods analogous to those described [4]. Chlorotris-(triphenylphosphine)rhodium was prepared according to the method of Wilkinson et al. [31]. Dichlorotetrakis(cyclooctene)dirhodium was isolated according to the method described [32]. The two phosphines (+)- or (—)-diop were obtained from *L* or *D* tartaric acids [15].

Determination of stereochemistry

(a). Hydrosilylation of acetone

Benzene solvent. 0.496 g (2×10^{-3} mol) of 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 34.6°) and 0.074 g (8×10^{-5}mol) of chlorotris(triphenylphosphine)-rhodium were dissolved in 2 ml of degassed anhydrous benzene. 0.116 g (2×10^{-3} mol) of acetone diluted with 2 ml of benzene was added using a syringe. The reaction mixture was refluxed for 24 hours. On evaporation of the solvent the product was isolated by preparative thin-layer chromatography (silica gel, eluant pentane/benzene 4/1). 0.545 g (yield 89%) of 1-naphthylphenylmethylisopropyloxysilane ($[\alpha]_D$ — 5.1°, *c* 17.4 (pentane)) was recovered, having physical properties identical to those of an authentic specimen [20].

Without solvent. The same experiment carried out without benzene and with 5 ml of acetone allows isolation of 0.560 g (yield 92%) of 1-naphthylphenylmethylisopropoxysilane ($[\alpha]_D$ —4.4°, *c* = 19.9 (pentane)).

(b). Reduction by lithium aluminium hydride

A solution of 0.306 g (10^{-3} mol) of 1-naphthylphenylmethylisopropyloxysilane ($[\alpha]_D$ — 5.1°) in 5 ml anhydrous ether was added dropwise to a suspension of 0.08 g of lithium aluminium hydride in 5 ml of ether. After 4 hours stirring the mixture was hydrolysed in an acidic medium (HCl 10%). The organic phase was extracted with ether and dried over anhydrous magnesium sulphate. After evaporation of the solvent the residue was purified by preparative thin-layer

chromatography (silica gel, eluant pentane/benzene 9/1). 0.225 g (yield 91%) of 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 30.0°, *c* 10 (pentane)) was obtained.

Reduction of 1-naphthylphenylmethylisopropyloxysilane ($[\alpha]_D$ −4.4°) carried out as above leads to 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 25.3°, *c* 15 (pentane)) in 88% yield.

Asymmetric hydrosilylation of symmetric ketones and aldehydes

General technique

All the hydrosilylation reactions were carried out in the same way at 20° under nitrogen. The asymmetric catalyst was prepared "in situ" by dissolving 5×10^{-6} mol of $[(C_8H_{14})_2RhCl]_2$ and 10^{-5} mol of (+)- or (−)-diop in 5 ml of anhydrous degassed benzene. The mixture was stirred for 10 min and 5×10^{-3} mol of the ketone (or aldehyde) was introduced by a syringe with 5 ml of benzene. Lastly the silane (5×10^{-3} mol) dissolved in 5 ml of benzene was added. The progress of the reaction was controlled by TLC. When all the starting silane had disappeared the solvent was removed under pressure. Quantitative formation of the addition product was controlled by comparison of the NMR and IR spectra of the crude reaction product with those of authentic samples [13]. The residue was dissolved in 5 ml of anhydrous ether and added to a solution of the appropriate Grignard reagent. After reaction the mixture was hydrolysed (HCl 10%). The organic phase was extracted with ether, washed with water, and dried over anhydrous magnesium sulphate. After removal of the solvent the residue was purified by preparative thin-layer chromatography (silica gel, eluant pentane/benzene 9/1).

The trisubstituted silane was obtained with a yield often greater than 90% and has similar properties to those already described [2, 3].

(a) Additions of 1-naphthylphenylsilane

Hydrosilylation of acetone. The earlier method applied to acetone using (+)-diop leads, after treatment with ethylmagnesium bromide to 1-naphthylphenylethylsilane ($[\alpha]_D$ + 7.5°, *c* 13.1 (CCl_4)) in 95% yield.

3-Pentanone. The use of (+)-diop and methylmagnesium bromide gave 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 16.5°, *c* 9.6 (pentane)), yield 92%. Using (−)-diop in the same conditions gave a silane ($[\alpha]_D$ − 15.8°, *c*. 11.3 (pentane)), yield 90%.

4-Heptanone. (+)-diop gave 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 13.9°, *c* 10.4 (pentane)), yield 91%.

2,6-Dimethyl-4-heptanone. (+)-diop gave 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 12.8°, *c* 10.1 (pentane)), yield 91%.

Benzophenone. 1-Naphthylphenylmethylsilane ($[\alpha]_D$ + 11.0°, *c* 12.2 (pentane)) was isolated (yield 93%) using (+)-diop.

Cyclohexanone. 1-Naphthylphenylethylsilane ($[\alpha]_D$ + 7.9°, *c* 13.4 (CCl_4)) was isolated (yield 90%) using (+)-diop.

Cyclopentanone. 1-Naphthylphenylmethylsilane ($[\alpha]_D$ + 12.6°, *c* 9.9 (pentane)) was isolated (yield 95%) using (+)-diop.

Hydrosilylation of aldehydes. Using (+)-diop and treatment with methylmagnesium bromide led to (+)-1-naphthylphenylmethylsilane: with propanal

($[\alpha]_D$ + 4.9°, *c* 16.4 (pentane)) yield 90%; butanal ($[\alpha]_D$ + 5.6°, *c* 7 (pentane)) yield 90%; 3-methylbutanal ($[\alpha]_D$ + 1.5°, *c* 19.3 (pentane)) yield 88%; heptanal ($[\alpha]_D$ + 4.7°, *c* 13.2 (pentane)) yield 86%; benzaldehyde ($[\alpha]_D$ + 2.5°, *c* 14.1 (pentane)) yield 84%.

(b) Additions of 1-naphthylmethylsilane

Using (+)-diop followed by treatment with phenylmagnesium bromide led to (—)-1-naphthylphenylmethylsilane: 3-pentanone ($[\alpha]_D$ —4.3°, *c* 8.9 (pentane)) yield 89%; benzophenone ($[\alpha]_D$ —2.4°, *c* 7.6 (pentane)) yield 88%.

(c) Additions of 1-naphthylethylsilane

Hydrosilylation in the presence of (+)-diop followed by treatment with phenylmagnesium bromide led to 1-naphthylphenylethylsilane: 3-pentanone ($[\alpha]_D$ —5.3°, *c* 17.3 (CCl_4)) yield 91%; benzophenone ($[\alpha]_D$ —8.1°, *c* 17.2 (CCl_4)) yield 90%.

Hydrosilylation of prochiral ketones

The addition reactions of 1-naphthylphenylsilane were carried out as in the previous section. After reaction of the Grignard reagent the organosilicon compound was isolated by TLC and the alcohol by distillation.

Acetophenone. Hydrosilylation in the presence of (—)-diop and treatment with ethylmagnesium bromide gave 1-naphthylphenylethylsilane ($[\alpha]_D$ —8.0°, *c* 15.2 (CCl_4)) yield 92%; and 1-phenylethanol ($[\alpha]_D$ + 28.9°, *c* 5.1 (CH_2Cl_2)) b.p. 100/18 mmHg, yield 86%.

Propiophenone. Hydrosilylation in the presence of (+)-diop followed by action of methylmagnesium bromide gave 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 10.8°, *c* 7.9 (pentane)) yield 90% and 1-phenylpropanol ($[\alpha]_D$ —16.4°, pure) b.p. 110/18 mmHg, yield 75%.

Butanone. Hydrosilylation in the presence of (—)-diop and treatment with methylmagnesium bromide gave 1-naphthylphenylmethylsilane ($[\alpha]_D$ —14.2°, *c* 11.8 (pentane)) yield 94%, and butanol-2 ($[\alpha]_D$ — 5.8°, pure) b.p. 100—110/750 mmHg, yield 25%. The same experiment with (+)-diop gave a silane ($[\alpha]_D$ + 14.0°, *c* 15.3 (pentane)).

1-Phenyl-2,2-dimethylpropanone. Hydrosilylation in the presence of (+)-diop gave 1-naphthylphenylmethylsilane ($[\alpha]_D$ + 12.6°, *c* 9.3 (pentane)) yield 85%.

Acknowledgement

We thank the "Délégation Générale à la Recherche Scientifique et Technique" for financial support.

References

1 R.J.P. Corriu and J.J.E. Moreau, J. Organometal. Chem., 64 (1974) C51.
2 L.H. Sommer and C.L. Frye, J. Amer. Chem. Soc., 81 (1959) 1013.
3 R. Corriu and G. Royo, J. Organometal. Chem., 14 (1968) 291; R. Corriu and J. Massé, Bull. Soc. Chim. Fr., (1969) 3491; D.N. Roark and L.H. Sommer, J. Amer. Chem. Soc., 95 (1973) 969.

4 R.J.P. Corriu, G.F. Lanneau and G.L. Royo, J. Organometal. Chem., 35 (1972) 35; R.J.P. Corriu and G.F. Lanneau, ibid., 64 (1974) 63.
5 R.J.P. Corriu, G.F. Lanneau and M. Leard, J. Organometal. Chem., 64 (1974) 79.
6 J.D. Morrisson and H.S. Mosher, Asymmetric Organic Reactions, Prentice Hall, 1971; J. Mathieu and J. Weill-Raynal, Bull. Soc. Chim. Fr., (1968) 1211.
7 J.F. Klebe and H. Finkbeiner, J. Amer. Chem. Soc., 90 (1968) 7255.
8 A. Holt, A.W.P. Jarvie and G.J. Jervis, J. Chem. Soc., Perkin II, (1973) 114.
9 R.J.P. Corriu and B.J.L. Henner, J. Chem. Soc., Chem. Commun., (1973) 116; R.J.P. Corriu and G.F. Lanneau, J. Organometal. Chem., 67 (1974) 243; R.J.P. Corriu and B.J.L. Henner, J. Organometal. Chem., 71 (1974) 393; R.J.P. Corriu, C. Guerin and J.P. Massé, J. Chem. Soc., Chem. Commun, in press.
10 R.N. Haszeldine, R.V. Parish and D.J. Parry, J. Chem. Soc. A, (1969) 683.
11 R.J.P. Corriu and J.J.E. Moreau, Tetrahedron Lett., (1973) 4469.
12 K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 46 (1972) C65, 54 (1973) C45; W. Dumont, J.C. Poulin, T.P. Dang and H.B. Kagan, J. Amer. Chem. Soc., 95 (1973) 8295; I. Ojima, T. Kogure and Y. Nagai, Chem. Lett., (1973) 541.
13 R.J.P. Corriu and J.J.E. Moreau, J. Chem. Soc., Chem. Commun., (1973) 38.
14 I. Ojima, M. Nihonyanagi and Y. Nagai, Chem. Commun., (1972) 938.
15 H.B. Kagan and T.P. Dang, J. Amer. Chem. Soc., 94 (1972) 6429.
16 W.S. Knowles and M.J. Sabacky, Chem. Commun., (1968) 1445; W.S. Knowles, M.J. Sabacky and B.D. Vineyard, J. Chem. Soc., Chem. Commun., (1972) 10; L. Horner and H. Siegel, Phosphorus, 1 (1972) 199, 1 (1972) 209; J.D. Morrisson, R.E. Burnett, A.M. Aguiar, C.J. Morrow and C. Phillip, J. Amer. Chem. Soc., 93 (1971) 1301; P. Abley and F.J. McQuillin, J. Chem. Soc. C, (1971) 844; P. Bonvicini, A. Levi, G. Modena and G. Scorrano, J. Chem. Soc., Chem. Commun., (1972) 1188; M. Tanaka, Y. Watanabe, T. Misudo, H. Iwane and Y. Takegami, Chem. Lett., (1973) 239.
17 K. Yamamoto, Y. Uramoto and M. Kumada, J. Organometal. Chem., 31 (1971) C9; K. Yamamoto, T. Hayashi and M. Kumada, J. Amer. Chem. Soc., 93 (1971) 5301; N. Langlois, T.D. Dang and H.B. Kagan, Tetrahedron Lett., (1973) 4865.
18 I.Ogata and Y. Ikeda, Chem. Lett., (1972) 487; M. Tanaka, Y. Watanabe, T. Mitsudo, K. Yamamoto and Y. Takegami, Chem. Lett., (1972) 483.
19 B. Bogdanovic, B. Henc, B. Meister, H. Pauling and G. Wilke, Angew. Chem., Int. Ed. Engl., 11 (1972) 1023; G. Consiglio and C. Botteghi, Helv. Chim. Acta, 56 (1973) 460; Y. Kiso, K. Tamao, N. Miyake, K. Yamamoto and M. Kumada, Tetrahedron Lett., (1974) 3.
20 L.H. Sommer and H. Fujimoto, J. Amer. Chem. Soc., 90 (1968) 982.
21 L.H. Sommer, C.L. Frye and G.A. Parker, J. Amer. Chem. Soc., 86 (1964) 3276.
22 R.J.P. Corriu and J.J.E. Moreau, to be published.
23 T. Hayashi, K. Yamamoto and M. Kumada, Tetrahedron Lett., (1974) 331.
24 U. Nagai, T. Shishido, R. Chiba and H. Mitsuhashi, Tetrahedron, 21 (1965) 1701.
25 R. McLeod, F.J. Welch and H.S. Mosher, J.Amer. Chem Soc , 82 (1960) 876.
26 K.B. Wiberg, J. Amer. Chem. Soc., 74 (1952) 3891.
27 A.J. Chalk and J.F. Harrod, J. Amer. Chem. Soc., 87 (1965) 16; L.H. Sommer, J.E. Lyons and H. Fujimoto, J.Amer. Chem. Soc., 91 (1969) 7051.
28 R.J.P. Corriu and J.J.E. Moreau, J. Organometal. Chem., 40 (1972) 55; 40 (1972) 73.
29 C. Eaborn, D.J. Tune and D.R.M. Walton, J. Chem. Soc., Chem. Commun., (1972) 1223; C. Eaborn, P.B. Hitchcock, D.J. Tune and D.R.M. Walton, J. Organometal. Chem., 54 (1973) C1.
30 R.J.P. Corriu and B.J.L. Henner, to be published.
31 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc A, (1966) 1711.
32 L. Porri, A. Lionetti, G. Allegra and A. Immirzi, Chem. Commun., (1965) 336.