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TETRAHEDRON REPORT

ACTIVATION OF GRIGNARD REAGENTS BY TRANSITION METAL COMPOUNDS

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Two well-known reactions, both discovered by Kharasch in the early 1940s, involve the activation of Grignard reagents by transition metal salts. They are the Cu(I)-catalysed 1,4-addition of Grignard reagents to α,β-unsaturated carbonyl compounds, and the Co(II)-catalysed formation of biaryls from arylmagnesium halides and alkyl halides (the Kharasch reaction). Both reactions involving copper,[1] and biaryl formation and related reactions,[2] have recently been reviewed. They will therefore not be discussed in this account, the purpose of which is to survey a number of new, transition metal-catalysed,† reactions of Grignard reagents which have been reported in the course of the last ten years.

These new reactions involve a variety of substrates, the majority of which do not react with Grignard reagents in the absence of catalyst. The catalysts which have been used are either transition metal halides (Ti, Ni, Fe), or complexes of nickel (generally L_2NiX_2, where L = phosphine and X = halogen) and titanium (Cp_2TiCl_2, where Cp = η^5-cyclopentadienyl).

I. REACTIONS CATALYSED BY TRANSITION METAL HALIDES

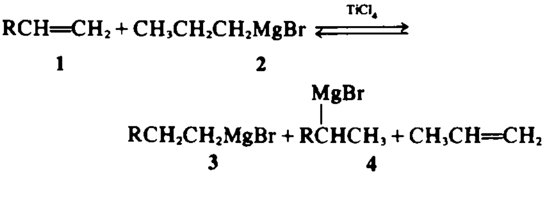
(a) *Reactions with olefins*

Grignard reagents do not generally react with non-activated olefinic carbon–carbon bonds[3a] under the usual conditions.‡

As early as 1924, however, Job and Reich[15] noticed that an ethereal solution of phenylmagnesium bromide absorbs ethylene in the presence of a catalytic amount of nickel chloride, with formation, after hydrolysis, of ethane, ethylbenzene and styrene, among other products:

$$CH_2{=}CH_2 + PhMgBr \xrightarrow[2.\ H_2O]{1.\ NiCl_2} CH_3{-}CH_3 + PhCH_2{-}CH_3 + PhCH{=}CH_2.$$

It was not until many years later that Finkbeiner and Cooper[16] studied this reaction in some detail, using $TiCl_4$ as catalyst. They discovered that when a reducing Grignard reagent,§ such as n-propylmagnesium bromide **2**, and a 1-alkene **1** are refluxed in ether with catalytic amounts (0·03 mol) of $TiCl_4$, a reversible exchange reaction takes place leading to a mixture of olefins and Grignard reagents.∥ When the propylene formed from the starting n-propylmagnesium bromide is allowed to distil from the reaction mixture, the equilibrium is shifted to the right, and a new Grignard reagent (**3** and/or **4**) is obtained.



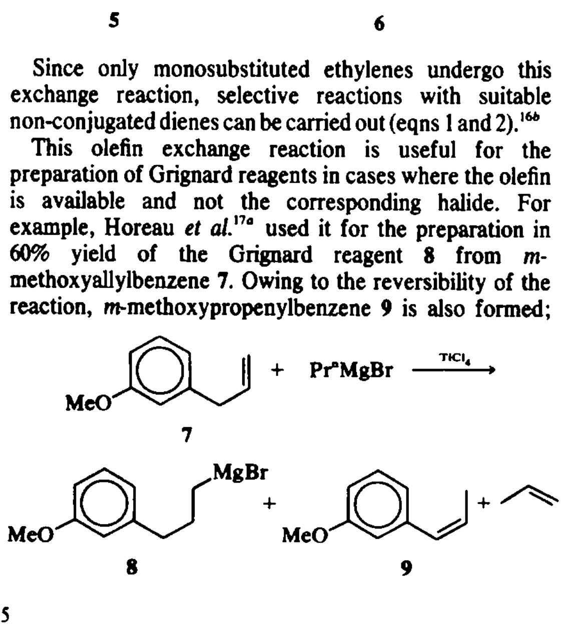
$$\underset{\mathbf{1}}{RCH{=}CH_2} + \underset{\mathbf{2}}{CH_3CH_2CH_2MgBr} \overset{TiCl_4}{\rightleftharpoons} \underset{\mathbf{3}}{RCH_2CH_2MgBr} + \underset{\mathbf{4}}{R\overset{MgBr}{\overset{|}{C}}HCH_3} + CH_3CH{=}CH_2$$

This exchange reaction leads mainly to the primary Grignard reagent **3** when R is an alkyl group, whereas with styrene the secondary Grignard reagent **4** (R = Ph) is obtained. Minor amounts of the compounds **5** and **6**, arising from the addition of the starting Grignard reagent **2** across the double bond, have also been detected. The new Grignard reagents formed were allowed to react with typical substrates (CO_2, aldehydes, ketones, etc.) and the expected products were obtained in 20–60% yields (Table 1).[16b]

$$\underset{\mathbf{5}}{R\overset{Pr^n}{\overset{|}{C}}HCH_2MgBr} \qquad \underset{\mathbf{6}}{R\overset{MgBr}{\overset{|}{C}}HCH_2Pr^n}$$

Since only monosubstituted ethylenes undergo this exchange reaction, selective reactions with suitable non-conjugated dienes can be carried out (eqns 1 and 2).[16b]

This olefin exchange reaction is useful for the preparation of Grignard reagents in cases where the olefin is available and not the corresponding halide. For example, Horeau *et al.*[17a] used it for the preparation in 60% yield of the Grignard reagent **8** from *m*-methoxyallylbenzene **7**. Owing to the reversibility of the reaction, *m*-methoxypropenylbenzene **9** is also formed;



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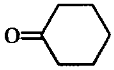
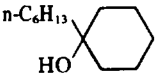
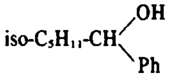
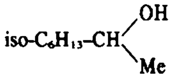
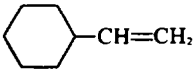
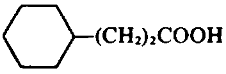
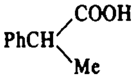
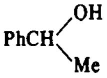
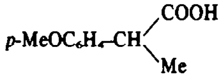
†Two reactions requiring stoichiometric amounts of the transition metal compound are also included.

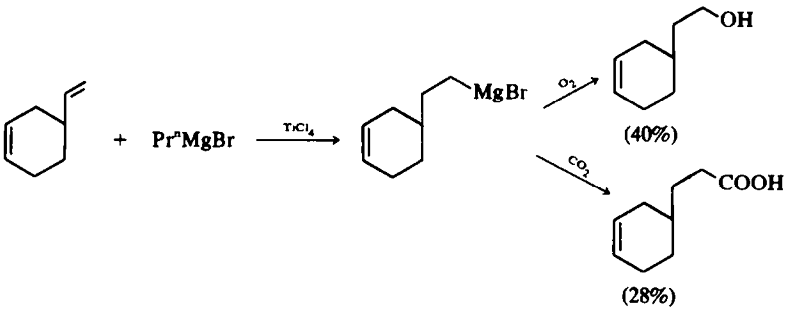
‡Additions of allylic Grignard reagents to the double bond of homoallylic,[4] allylic,[5] and allenic[6] alcohols, and of allylic amines,[7] to the triple bond of propargylic amines[7] and alcohols,[8] and, under pressure, to olefinic hydrocarbons[9] have, however, been described, as have the cyclisations of olefinic,[10] acetylenic[11] and allenic[12] organomagnesium compounds. The reactions between sec- and tert-alkylmagnesium halides and 1-octene, in refluxing 1-octene,[13] and between alkylmagnesium halides and acetylenic amines[14] have also recently been reported.

§Grignard reagents, such as ethyl- and propylmagnesium halides, which have a relatively labile hydrogen atom on the β carbon, will be called "reducing" Grignard reagents, in contrast with Grignard reagents such as methyl-, phenyl-, benzyl-, allyl and vinylmagnesium halides, which will be called "non-reducing".

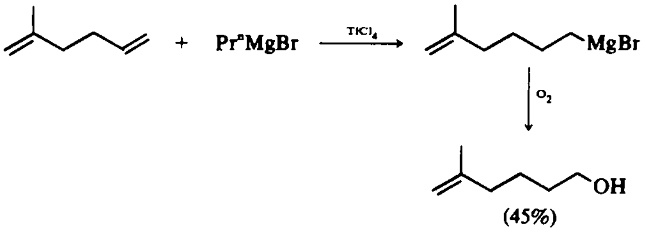
∥Finkbeiner and Cooper[16a] also found that $TiCl_4$ catalyses the isomerisation of isopropylmagnesium bromide into n-propylmagnesium bromide.

Table 1. Reactions of Grignard reagents prepared by the $TiCl_4$-catalysed exchange reaction between olefins and Pr^nMgBr[16b]

Olefin	Substrate	Product (yield)	
Pr^n-$CH{=}CH_2$	HCHO	n-$C_6H_{13}OH$	(45%)
Bu^n-$CH{=}CH_2$			(24%)
n-C_6H_{13}-$CH{=}CH_2$	CO_2, MeOH(H^+)	n-C_8H_{17}-COOMe	(40%)
n-C_6H_{13}-$CH{=}CH_2$	$HC(OEt)_3$	n-C_8H_{17}-$CH(OEt)_2$	(19%)
Pr^i-$CH{=}CH_2$	PhCHO	 iso-C_5H_{11}-$CH(OH)Ph$	(35%)
Bu^i-$CH{=}CH_2$	MeCHO	 iso-C_6H_{13}-$CH(OH)Me$	(37%)
Ph-CH_2-$CH{=}CH_2$	CO_2	$Ph(CH_2)_3COOH$	(62%)
	CO_2		(51%)
$PhCH{=}CH_2$	CO_2	 $PhCH(COOH)Me$	(51%)
$PhCH{=}CH_2$	O_2	 $PhCH(OH)Me$	(40%)
p-$MeOC_6H_4$-$CH{=}CH_2$	CO_2	 p-$MeOC_6H_4$-$CH(COOH)Me$	(22%)



(1)



(2)

this, being a disubstituted olefin, does not react further.

Markó *et al.*[18] have obtained analogous results using nickel chloride as catalyst.† Aliphatic olefins and reducing Grignard reagents, in the presence of $NiCl_2$, lead preferentially to the primary isomer 3, whereas styrene gives the secondary Grignard reagent 4 (R = Ph).

Nickel chloride catalyses the addition of PhMgBr to ethylene (eqn 3), but this is followed by an exchange reaction with the excess of ethylene (eqn 4).[18b] Thus, after hydrolysis, a mixture of ethylbenzene, styrene and ethane is obtained, confirming the observation of Job and Reich.[15]

$$CH_2{=}CH_2 + PhMgBr \xrightarrow{NiCl_2} PhCH_2CH_2MgBr \qquad (3)$$

$$\begin{aligned} CH_2{=}CH_2 + PhCH_2CH_2MgBr &\overset{NiCl_2}{\rightleftharpoons} PhCH{=}CH_2 \\ + CH_3CH_2MgBr &\overset{NiCl_2}{\rightleftharpoons} \underset{\substack{|\\ MgBr}}{PhCH}{-}CH_3 + CH_2{=}CH_2 \end{aligned} \qquad (4)$$

It has been suggested that this alkyl-olefin exchange reaction involves a β-hydrogen transfer within a bis-π-olefin-complex hydride (eqn 5),[16c] but other mechanisms are possible (see Section I.b).

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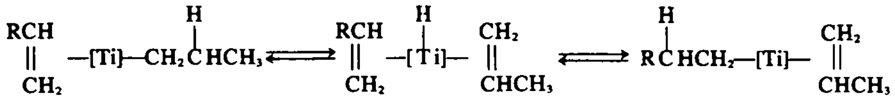
†Iron[17b] and cobalt[18] halides are also effective.



$$\begin{matrix}RCH\\ \|\\ CH_2\end{matrix} -[Ti]-CH_2\overset{H}{\overset{|}{C}}HCH_3 \rightleftharpoons \begin{matrix}RCH\\ \|\\ CH_2\end{matrix} -[\overset{H}{\overset{|}{T}}i]- \begin{matrix}CH_2\\ \|\\ CHCH_3\end{matrix} \rightleftharpoons R\overset{H}{\overset{|}{C}}HCH_2-[Ti]- \begin{matrix}CH_2\\ \|\\ CHCH_3\end{matrix} \qquad (5)$$

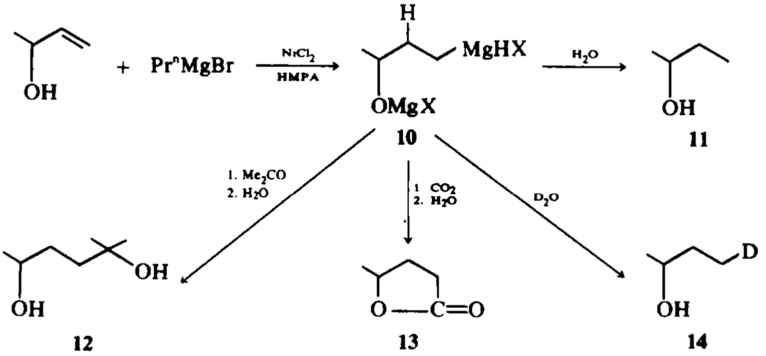
(b) *Reactions with allylic alcohols*

The same exchange reaction occurs between allylic alcohols having a terminal double bond and excess n-propylmagnesium bromide in the presence of nickel chloride (0·1 mol) and HMPA (0·1 mol)[19] (Scheme 1). The formation of the functionalised Grignard reagent **10** was inferred from its reactions with water, acetone and carbon dioxide which lead to the saturated alcohol **11**, the diol **12** and the γ-lactone **13**, respectively. The alcohol **11** is obtained in good yield (80%), but the yields of **12** and **13** are low (~30%). Furthermore, deuteriolysis leads not only to the expected deuteriated alcohol **14** but also to the non-deuteriated alcohol **11** (**14**:**11** = 3:1). A reaction leading directly from the allylic alcohol to the saturated alcohol therefore takes place concurrently.

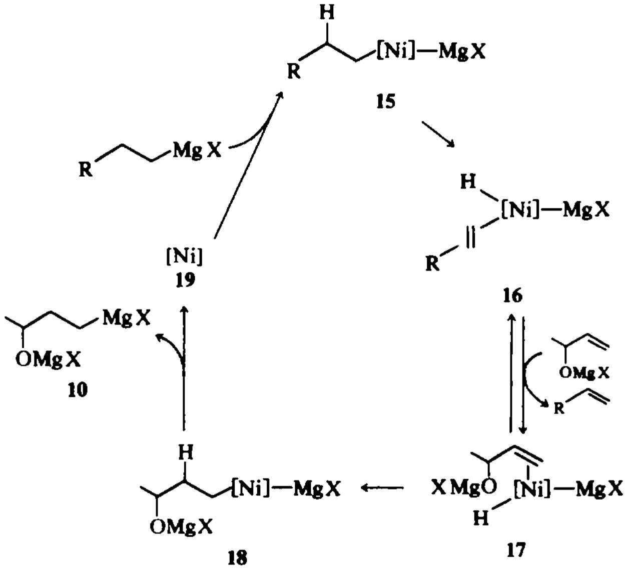
The following catalytic cycle has been proposed for the exchange reaction (Scheme 2).[19] It involves an alkylnickel-magnesium complex **15** which undergoes a β-elimination reaction to yield the π-complex **16**. An exchange reaction with the allylic alkoxide leads to the hydrido-π-complex **17**. Insertion of the C=C double bond into the Ni–H bond then yields a new alkylnickel-magnesium complex **18**. Reductive elimination of the Grignard reagent **10**, and oxidative addition of the starting organomagnesium compound onto **19**, closes the catalytic cycle. A similar catalytic cycle may also apply to the reactions described by Finkbeiner and Cooper[16] and by Markó *et al.*[18] (see Section I.a). Evidence which supports the hypothesis of intermediates having nickel–magnesium bonds is given below (Section II.a.1).

(c) *Reactions with Schiff's bases*

Ethylmagnesium bromide, in the presence of $NiBr_2$ (0·1 mol), has been found[20] to reduce certain Schiff's bases at room temperature (Table 2). It has been suggested that this reduction involves intermediates with a Ni–Mg bond and a catalytic cycle similar to that shown in Scheme 2.



Scheme 1.



Scheme 2.

Table 2. Reduction of Schiff's bases by EtMgBr, in the presence of NiBr$_2$[20]

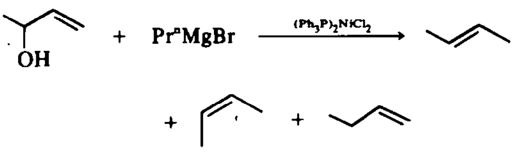
Schiff's bases	Products (yield)
PhCH=NPh	PhCH$_2$–NHPh (78%)
PhCH=NC$_6$H$_4$OMe(*m*)	PhCH$_2$–NHC$_6$H$_4$OMe(*m*) (88%)
m-ClC$_6$H$_4$CH=NPh	*m*-ClC$_6$H$_4$CH$_2$–NHPh (82%)
PhCH=NC$_6$H$_4$OMe(*p*)	no reaction
p-MeOC$_6$H$_4$CH=NBu^n	no reaction
PhCH=NBu^n	no reaction

II. REACTIONS CATALYSED BY TRANSITION METAL COMPLEXES

(a) *Reactions with allylic alcohols*

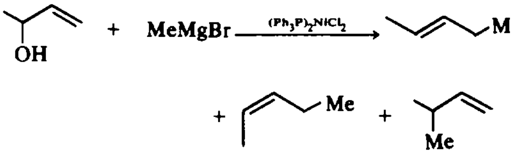
The use of a phosphine–nickel complex such as (Ph$_3$P)$_2$NiCl$_2$, instead of nickel chloride (see Section I.b), as a catalyst in the reaction between allylic alcohols and Grignard reagents completely changes the course of the reaction.

With a reducing Grignard reagent, such as Pr^{n}MgBr, and α-methylallyl alcohol, hydrogenolysis of the alcohol takes place, a mixture of n-butenes being formed[21] (eqn 6).



(6)

With a non-reducing Grignard reagent, such as MeMgBr, a new C–C bond is formed, and a mixture of pentenes is obtained[22] (eqn 7). These reactions are not limited to

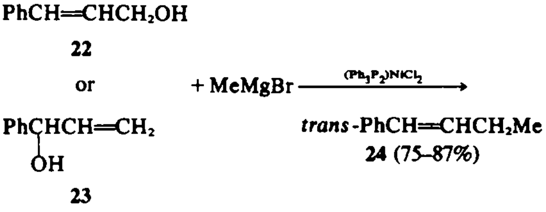


(7)

allylic alcohols with terminal double bonds, but also take place, although less readily, with those possessing di- or trisubstituted double bonds.

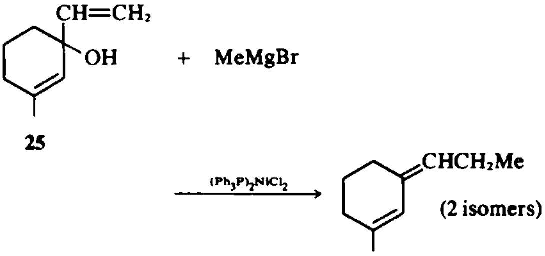
1. *Non-reducing Grignard reagents*. In the presence of catalytic amounts (0·1 mol) of bis(triphenylphosphine)nickel dichloride, allylic alcohols react in ether with an excess of non-reducing Grignard reagents to form mixtures of isomeric olefins **20** and **21**, generally in high yield.[22]

The olefins formed are not isomerised under the reaction conditions. Thus, 1-butene (91%), allylbenzene (68%) (uncontaminated with propenylbenzene), and 4-phenyl-1-butene (90%) are obtained from the reactions between allyl alcohol and the appropriate Grignard reagents. The methylallyl alcohols lead to mixtures in which the least stable terminal olefins predominate in most cases (Table 3). In contrast, *cis*- and *trans*-cinnamyl alcohols **22**, and α-phenylallyl alcohol **23**, yield only the conjugated olefin **24**. The same behaviour is observed



$$\mathrm{PhCH{=}CHCH_2OH}\ (\mathbf{22})\ \text{or}\ \mathrm{Ph\underset{OH}{C}HCH{=}CH_2}\ (\mathbf{23}) + \mathrm{MeMgBr} \xrightarrow{(\mathrm{Ph_3P})_2\mathrm{NiCl_2}} \textit{trans}\text{-}\mathrm{PhCH{=}CHCH_2Me}\ \mathbf{24}\ (75\text{–}87\%)$$

with the alcohol **25** which leads only to the conjugated dienes **26**.



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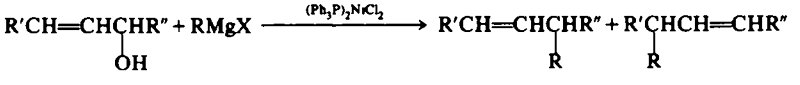
26 (64%)

This reaction may have synthetic applications. With tertiary allylic alcohols, compounds with a quaternary



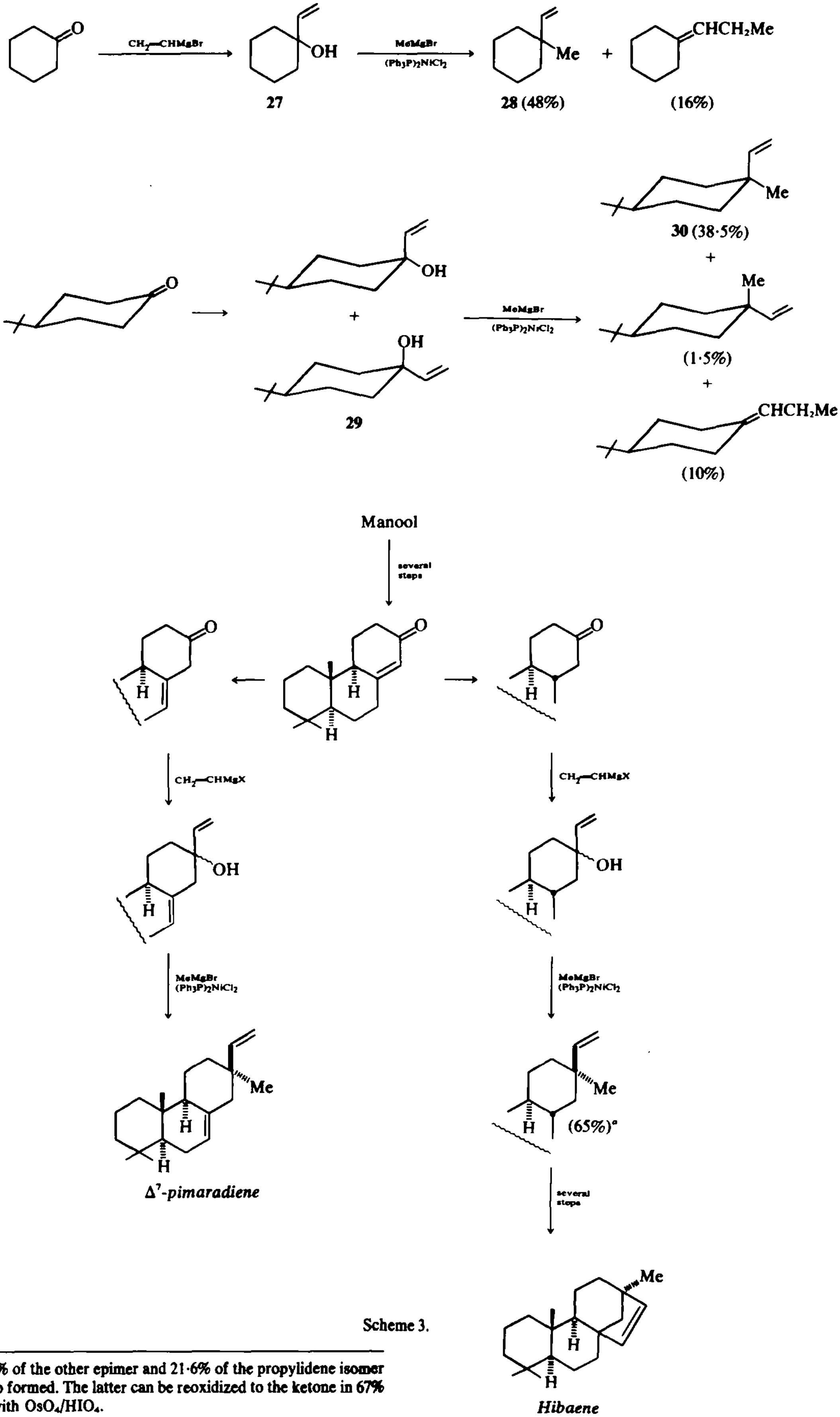
$$\mathrm{R'CH{=}CH\underset{OH}{C}HR''} + \mathrm{RMgX} \xrightarrow{(\mathrm{Ph_3P})_2\mathrm{NiCl_2}} \mathrm{R'CH{=}CH\underset{R}{C}HR''} + \mathrm{R'\underset{R}{C}HCH{=}CHR''}$$

20 **21**

Table 3. Yields (%) of olefins formed in the reaction between the methylallyl alcohols and RMgX, in the presence of (Ph$_3$P)$_2$NiCl$_2$[22b]

	R	*trans*-CH$_3$CH=CHCH$_2$R	*cis*-CH$_3$CH=CHCH$_2$R	$\mathrm{CH_3\underset{R}{C}HCH{=}CH_2}$
trans-CH$_3$CH=CHCH$_2$OH	Me	47·0	0	40·0
	Ph	47·8	0·4	24·8
cis-CH$_3$CH=CHCH$_2$OH	Me	5·9	1·9	72·2
	Ph	4·2	22·3	37·5
$\mathrm{CH_3\underset{OH}{C}HCH{=}CH_2}$	Me	24·1	1·5	56·4
	Ph^a	12·3	5·0	13·7

[a] $\mathrm{PhCH{=}CH\underset{OH}{C}HCH_3}$ (39%) is also obtained in this reaction. This allylic alcohol reacts further with PhMgBr to give the conjugated olefin $\mathrm{PhCH{=}CH\underset{Ph}{C}HCH_3}$ but this reaction is much slower than the reaction with α-methylallyl alcohol.



Scheme 3.

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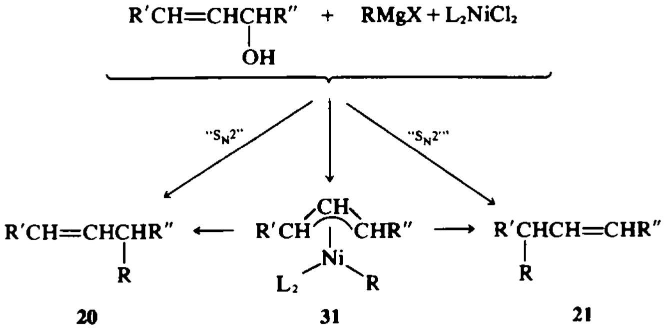
[a] 3·6% of the other epimer and 21·6% of the propylidene isomer are also formed. The latter can be reoxidized to the ketone in 67% yield with OsO_4/HIO_4.

carbon centre are obtained: for example, vinylcyclohexanol **27** and methylmagnesium bromide preferentially afford 1-methyl-1-vinylcyclohexane **28**.[22] Thus, by this method, starting from cyclohexanone, the compound **28** can be synthesised in only two steps.

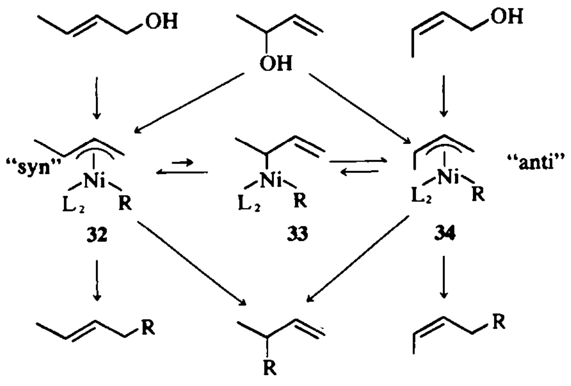
When the stereochemistry of the vinylcyclohexanol is fixed, as in 4-t-butyl-1-vinylcyclohexanol **29**, both the axial and the equatorial epimer lead to a mixture of hydrocarbons containing geminally disposed methyl and vinyl groups, in which the compound **30** with the axial vinyl group predominates.[23] Such an arrangement is present in a number of diterpenes, and this reaction has been used[24] for the synthesis of Δ^7-pimaradiene and of hibaene from manool (Scheme 3).

The question arises as to whether these reactions occur via π-allylnickel intermediates **31**, or by a combination of "S_N2" and "S_N2'" processes catalysed in some way by nickel (Scheme 4).



Scheme 4.

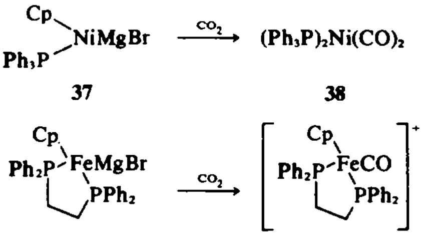
From the proportions of the olefins formed in the reactions of the methylallyl alcohols (Table 3), a stereochemical criterion was found which indicates that these reactions proceed exclusively through the π-allylnickel intermediates **32** and **34** (Scheme 5); it was also found that the interconversion of these intermediates (via **33**) is slower than their conversion to the olefins.[25]



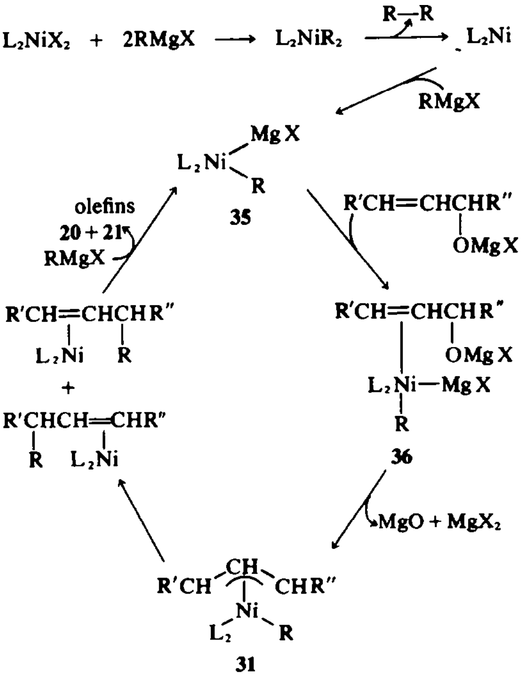
Scheme 5.

A catalytic cycle has been proposed for this nickel-catalysed reaction, the two key intermediates in this cycle being the π-allylnickel complex **31** (cf. **32** and **34**) and a complex **35** with a Ni–Mg bond (Scheme 6).

A number of compounds with transition metal-magnesium bonds have recently been prepared and have been found to reduce carbon dioxide. Thus, compounds **37** and **39** (Cp = η^5-C$_5$H$_5$) afford the carbonyl complexes



38 and **40**, respectively,[26a,27] and similar results have been obtained with compounds containing Mo–Mg and W–Mg bonds.[28,29] It is interesting to note that the catalytic solutions obtained from (Ph$_3$P)$_2$NiCl$_2$ and Grignard reagents also reduce carbon dioxide, the dicarbonyl complex **38** being formed in good yield.[26b] This observation provides some support for the hypothesis that the nickel-catalysed reactions of Grignard reagents involve intermediates such as **35** (Scheme 6) containing Ni–Mg bonds.



Scheme 6.

$$\mathrm{(Ph_3P)_2NiCl_2} \xrightarrow[2.\ \mathrm{CO_2}]{1\ \mathrm{RMgX}} \mathrm{(Ph_3P)_2Ni(CO)_2}$$

38

2. *Reducing Grignard reagents.* As mentioned above, reducing Grignard reagents in the presence of $\mathrm{(Ph_3P)_2NiCl_2}$ lead to the hydrogenolysis of allylic alcohols (eqn 6); some examples are given in Table 4.

Table 4. Yields (%) of olefins formed in the reactions between R-substituted allyl alcohols and $\mathrm{Pr^nMgBr}$, in the presence of $\mathrm{(Ph_3P)_2NiCl_2}$[21b]

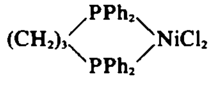
	R	*trans*-RCH=CHCH$_3$	*cis*-RCH=CHCH$_3$	RCH$_2$CH=CH$_2$
trans-RCH=CHCH$_2$OH	Me	76	3	12
	Ph	68	—	8
cis-RCH=CHCH$_2$OH	Me	25	31	25
$\mathrm{R\underset{OH}{C}HCH{=}CH_2}$	Me[a]	32	17	12
	Ph[b]	53	—	4

[a] 32% of $\mathrm{Me\underset{OH}{C}HCH_2CH_3}$ also formed.

[b] 19% of $\mathrm{Ph\underset{OH}{C}HCH_2CH_3}$ also formed (see Section I.b).

The difference in behaviour between reducing (replacement of the OH group by an H atom) and non-reducing (replacement of the OH group by the R group of RMgX) Grignard reagents has been attributed to a β-elimination reaction occurring at some stage (**35**, **36** or **31**) of the catalytic cycle (Scheme 6).

Interesting results have been obtained with reducing Grignard reagents and the nickel complex **41** comprising a



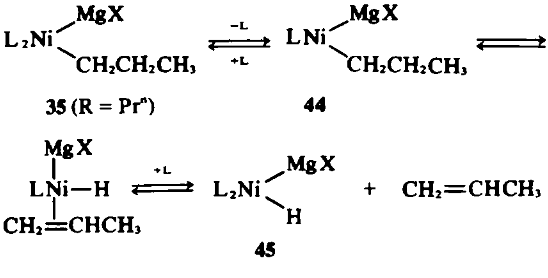
41

bidentate phosphine. With this complex both alkylation and hydrogenolysis occur concurrently (eqn 8).[19] Table 5 shows the results of the reactions between two series of isomeric allylic alcohols and n-propylmagnesium bromide. It can be seen that the alkylated olefins **42** predominate (~90%) in the case of the three phenylallyl alcohols, and are not negligible (23–47%) with the three methylallyl alcohols. With the bismonodentate phosphine complex $\mathrm{(MePh_2P)_2NiCl_2}$, which was chosen as the open-chain analogue of the chelating diphosphine complex **41**, the reaction leads only to the hydrogenolysis products **43**, but, in the presence of an excess of $\mathrm{MePh_2P}$, *trans*-cinnamyl alcohol gives about 45% of the alkylated olefin **42a** (R′ = Ph, R″ = H).

Table 5. Ratios of the yields of the olefins **42**:**43** obtained from the reactions between substituted allyl alcohols and $\mathrm{Pr^nMgBr}$, in the presence of **41**[19]

Allylic alcohol	Ratio **42**:**43**
trans-PhCH=CHCH$_2$OH	8·5
cis-PhCH=CHCH$_2$OH	7·5
$\mathrm{Ph\underset{OH}{C}HCH{=}CH_2}$	6·5
trans-MeCH=CHCH$_2$OH	0·4
cis-MeCH=CHCH$_2$OH	0·3
$\mathrm{Me\underset{OH}{C}HCH{=}CH_2}$	0·9

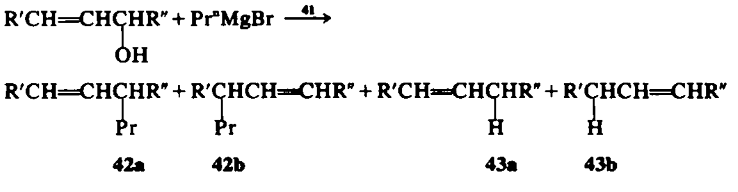
These results show that a β-elimination reaction can only occur if it is preceeded by the dissociation of a monodentate phosphine or one end of a bidentate phosphine from the intermediate involved. It has been deduced that this intermediate is the complex **35** (R = Pr^n) (Scheme 6); dissociation of a phosphine from this would lead to the 14-electron complex **44**, which could then undergo a β-elimination yielding the hydrido complex **45** [≡ **35** (R = H)] (Scheme 7). It has previously been shown



Scheme 7.

by Whitesides[30] that the thermal decomposition of di-n-butylbis(triphenylphosphine)platinum **46** to give n-butane and 1-butene takes place via a β-elimination reaction involving the initial dissociation of one phosphine to yield a 14-electron three-coordinate intermediate **47**.

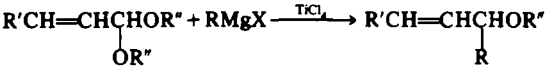
$$\underset{\mathbf{46}}{\mathrm{(Ph_3P)_2Pt(Bu^n)_2}} \underset{+\mathrm{Ph_3P}}{\overset{-\mathrm{Ph_3P}}{\rightleftharpoons}} \underset{\mathbf{47}}{\mathrm{Ph_3PPt(Bu^n)_2}} \longrightarrow \mathrm{C_4H_{10} + C_4H_8}$$



$$\mathrm{R'CH{=}CH\underset{OH}{C}HR'' + Pr^nMgBr} \xrightarrow{\mathbf{41}} \underset{\mathbf{42a}}{\mathrm{R'CH{=}CH\underset{Pr}{C}HR''}} + \underset{\mathbf{42b}}{\mathrm{R'\underset{Pr}{C}HCH{=}CHR''}} + \underset{\mathbf{43a}}{\mathrm{R'CH{=}CH\underset{H}{C}HR''}} + \underset{\mathbf{43b}}{\mathrm{R'\underset{H}{C}HCH{=}CHR''}} \qquad (8)$$

(b) *Reactions with α,β-unsaturated acetals*

In the presence of a stoichiometric amount of $TiCl_4$, allylic acetals **48** react, in THF at −78°, with certain Grignard reagents to give allylic ethers **49** in good yields (Table 6).[31] When, however, the reaction is carried out with phenylmagnesium bromide, it affords the enol ether **50**, instead of the expected allyl ether.

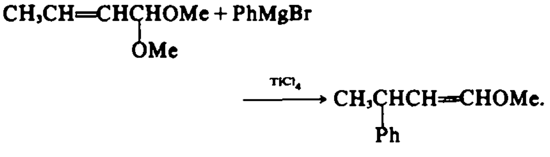


$$R'CH{=}CH\underset{OR''}{C}HOR'' + RMgX \xrightarrow{TiCl_4} R'CH{=}CH\underset{R}{C}HOR''$$

48 **49**

Table 6. Reactions of α,β-unsaturated acetals **48** with Grignard reagents RMgX and $TiCl_4$[31]

Acetal 48 R′	R″	R	Yield of 49
Ph	Me	$PhCH_2CH_2$	81%
Ph	Me	Et	83%
Ph	Me	$CH_2{=}CHCH_2$	71%
Me	Me	$PhCH_2CH_2$	79%
H	Et	$PhCH_2CH_2$	70%



$$CH_3CH{=}CH\underset{OMe}{C}HOMe + PhMgBr \xrightarrow{TiCl_4} CH_3\underset{Ph}{C}HCH{=}CHOMe.$$

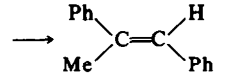
50

It should be pointed out that Grignard reagents and acetals are known to lead to ethers in the absence of catalyst, but the reaction requires a high temperature (75–100°), and with allylic acetals mixtures of **49** and **50** (R instead of Ph) are obtained in most cases.[32]

(c) *Reactions with acetylenic compounds*

Michman[33] found that equimolecular amounts of $(Ph_3P)_3RhBr$ and diphenylacetylene react with excess MeMgBr to yield *trans*-α-methylstilbene **51**, along with other products. The same result is observed with preformed $(Ph_3P)_3RhMe$ [from $(Ph_3P)_3RhBr$ and MeMgBr], whereas with the system $RhBr_3$ + MeMgBr, *cis*-α-methylstilbene is the principal product of the reaction.

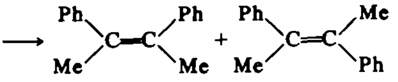
$PhC{\equiv}CPh + MeMgBr + (Ph_3P)_3RhBr$



51

With palladium complexes L_2PdCl_2 [L_2 = (benzonitrile)$_2$ or norbornadiene], the dialkylated compounds *cis*-**52** and *trans*-**53** α,α′-dimethylstilbenes (*cis*/*trans* = 3·7) are formed.[34] No reaction takes place when L is a phosphine or arsine.

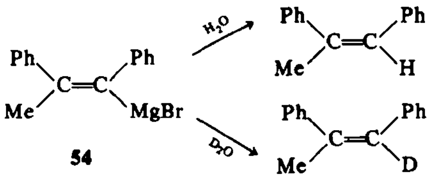
$PhC{\equiv}CPh + MeMgBr + L_2PdCl_2$



52 **53**

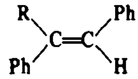
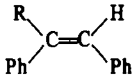
Duboudin and Jousseaume[35] discovered that bis(triphenylphosphine)nickel dichloride catalyses these alkylation reactions. They showed that diphenylacetylene and excess methylmagnesium bromide in the presence of $(Ph_3P)_2NiCl_2$ (0·1 mol) lead stereospecifically to *cis*-α-methylstilbene. The intermediate formation of the Grignard reagent **54** has been confirmed by deuteriolysis.

$PhC{\equiv}CPh + MeMgBr \xrightarrow{(Ph_3P)_2NiCl_2}$



cis-Addition has also been observed[36] for reactions between phenylmagnesium bromide and 1-alkyl-2-phenylacetylenes. These reactions are regiospecific and highly stereoselective (Table 7).

Table 7. Proportions[a] of the olefins obtained by reaction between $RC{\equiv}CPh$ and PhMgBr, in the presence of $(Ph_3P)_2NiCl_2$[36]

R		
Me^b	100	0
Et^b	100	0
$Pr^{i\,c}$	82	18
$Bu^{t\,c}$	95	5

[a] Isolated yields, after hydrolysis, ~50%.

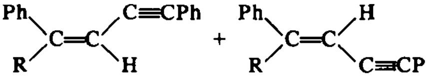
[b] In refluxing ether.

[c] In refluxing benzene; these compounds fail to react in ether.

Reducing Grignard reagents, e.g. Pr^iMgCl, also add to the triple bond of diphenylacetylene, but the yields are low (~30%) owing to the formation of the reduced products, *cis*- and *trans*-stilbene.[35]

The same complex has been reported to catalyse the addition of Grignard reagents to one of the triple bonds of diphenylbutadiyne (eqn 9).[37]

$PhC{\equiv}C{-}C{\equiv}CPh + RMgX \xrightarrow[2.\ H_2O]{1.\ (Ph_3P)_2NiCl_2}$



(9)

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(d) *Coupling reactions with vinyl and aryl halides*

The cross-coupling of the organic moieties of Grignard reagents and organic halides is induced by many transition metal halides;[2,3b] it also occurs in some cases without any catalyst.[3c] This reaction, however, has seldom been employed for synthetic purposes owing to the formation of homocoupling (Kharasch reaction) and disproportionation products in substantial amounts.

Almost simultaneously, Corriu and Massé[38] and Kumada *et al.*[39] recently found that selective cross-coupling reactions are obtained in the presence of catalytic amounts of certain nickel complexes.

Corriu and Massé[38] studied the cross-coupling reaction between aromatic or vinylic halides and aromatic Grignard reagents. They showed that in the presence of Ni(acac)$_2$ this reaction leads to a simple and efficient synthesis of *trans*-stilbenes **55** and **56**, and of terphenyls **57**.

$$\textit{trans}\text{-PhCH}{=}\text{CHBr} + \text{ArMgX} \xrightarrow[\text{Et}_2\text{O, }25^\circ]{\text{Ni(acac)}_2(0{\cdot}2\%)} \textit{trans}\text{-PhCH}{=}\text{CHAr} \quad \mathbf{55}\ (50\text{–}75\%)$$

$$\textit{trans}\text{-ClCH}{=}\text{CHCl} + 2\text{ArMgX} \xrightarrow[\text{Et}_2\text{O, }25^\circ]{\text{Ni(acac)}_2(0{\cdot}2\%)} \textit{trans}\text{-ArCH}{=}\text{CHAr} \quad \mathbf{56}\ (40\text{–}50\%)$$

$$p\text{-BrC}_6\text{H}_4\text{Br} + 2\text{ArMgX} \xrightarrow[\text{Et}_2\text{O, reflux}]{\text{Ni(acac)}_2(1\%)} p\text{-ArC}_6\text{H}_4\text{Ar} \quad \mathbf{57}\ ({>}\,80\%)$$

Kumada *et al.*[39] used phosphine–nickel complexes as catalysts; their results are shown in Table 8. The reactions between phenylmagnesium bromide and *cis*- and *trans*-dichloroethylene are not stereospecific with catalysts containing bidentate phosphines,[40] and this has been ascribed to the intermediate formation of acetylene (see Section II.c). It will be noted that, with bidentate phosphines, the cross-coupling reaction also takes place with alkylmagnesium halides and that n-alkyl Grignard reagents afford n-alkyl derivatives without any rearrangement of the alkyl group (see Table 8), whereas the coupling reaction of isopropylmagnesium chloride with chlorobenzene is accompanied by the isomerisation of the isopropyl group to n-propyl. The extent of this isomerisation seems to be strongly dependent on the electronic nature both of the phosphine bound to the nickel (Table 9)[41] and of the aryl moiety of the halide (Table 10).[42] In addition, it will be noted (Table 9) that benzene is formed in large amounts when non-chelating monophosphines are used as ligands, whereas very little hydrogenolysis occurs with chelating phosphines. A similar effect was found in the reactions between reducing Grignard reagents and allylic alcohols (see Section II.a.2).

Table 8. Cross-coupling reactions of Grignard reagents with organic halides catalysed by (dpe)NiCl$_2$[a], in ether[39]

Grignard reagent	Organic halide	Product (yield)	
EtMgBr	PhCl	Ph–Et	(98%)
Bu^{n}MgBr	PhCl	Ph–Bu^n	(76%)
Bu^{n}MgBr	Dichlorobenzene	Di-Bu^{n}benzene	
	o-	*o*-	(89%)
	m-	*m*-	(94%)
	p-	*p*-	(95%)
n-C$_8$H$_{17}$MgCl	CH$_2$=CHCl	n-C$_8$H$_{17}$CH=CH$_2$	(95%)
PhMgBr	CH$_2$=CHCl	PhCH=CH$_2$	(89%)
PhMgBr	ClCH=CHCl	PhCH=CHPh	
	cis-	*cis* : *trans* = 80 : 20	(90%)
	trans-	*cis* : *trans* = 43 : 57	(81%)
PhMgBr	Cl$_2$C=CH$_2$	Ph$_2$C=CH$_2$	(82%)
α-NpMgBr[b]	CH$_2$=CHCl	α-NpCH=CH$_2$	(80%)

[a] dpe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; [b] α-Np = α-Naphthyl.

Table 9. Products from the reaction of Pr^{i}MgCl with PhCl in the presence of L$_2$NiCl$_2$[41]

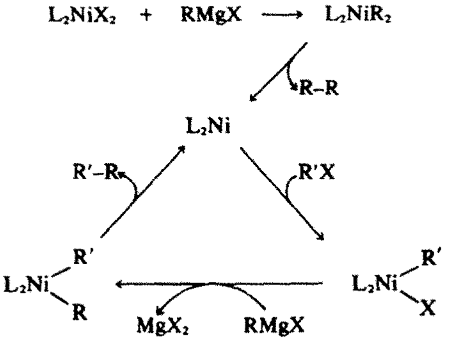
L$_2$ in catalyst	Total yield	Product distribution PhPr^i	PhPr^n	PhH
Ph$_2$PCH$_2$CH$_2$PPh$_2$	74%	96	4	0
Me$_2$PCH$_2$CH$_2$PMe$_2$	84%	9	84	7
Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$	89%	96	4	0
dmpf[a]	48%	8	74	18
(Et$_3$P)$_2$	9%	1	11	88
(Ph$_3$P)$_2$	44%	16	30	54

[a] 1,1′-Bis(dimethylphosphino)ferrocene.

Table 10. Products from the reaction of Pr^{i}MgCl with ArCl in the presence of (dmpe)NiCl$_2$[a] [42]

Ar	Total yield	Product distribution ArPr^i	ArPr^n	ArH
p-MeOC$_6$H$_4$	24%	6	65	29
p-MeC$_6$H$_4$	45%	5	84	11
C$_6$H$_5$	88%	12	78	6
m-CF$_3$C$_6$H$_4$	81%	13	74	13
p-CF$_3$C$_6$H$_4$	100%	46	44	10

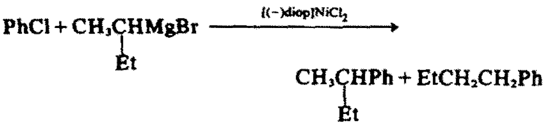
[a] dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$.



Scheme 8.

Kumada *et al.*[39] have proposed the catalytic cycle shown in Scheme 8. They have suggested[41,42] that the sec-alkyl → n-alkyl isomerisation occurs via a hydrido-olefin-nickel intermediate **58** which can also lead to the formation of the reduction products **59** (Scheme 9). It is not clear, however, from this scheme why the structural features in the catalyst and substrate which favour isomerisation do not at the same time favour reduction (see Tables 9 and 10).

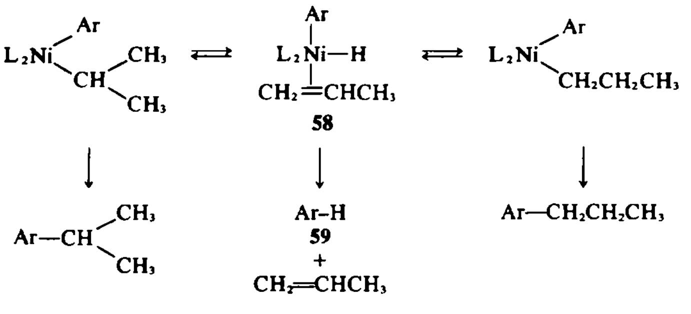
Optically active hydrocarbons can be obtained[43,44] from the reaction of secondary Grignard reagents with vinyl chloride or chlorobenzene, in the presence of [(−)diop]-NiCl$_2$ [diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane].[45] The best optical yield (17%) was obtained in the reaction leading to **60**.[43]



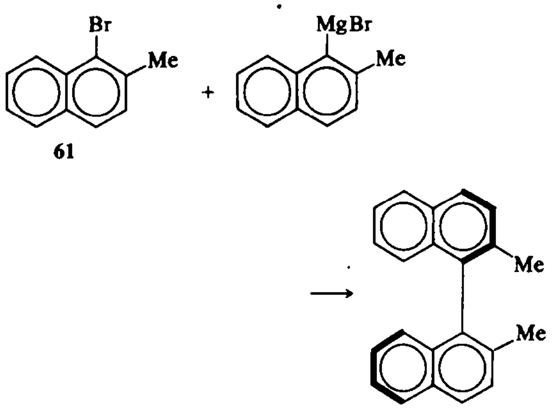
$$\text{PhCl} + \underset{\substack{|\\ \text{Et}}}{\text{CH}_3\text{CHMgBr}} \xrightarrow{[(-)\text{diop}]\text{NiCl}_2} \underset{\substack{|\\ \text{Et}}}{\text{CH}_3\text{CHPh}} + \text{EtCH}_2\text{CH}_2\text{Ph}$$

60

With the same catalyst, an asymmetric synthesis of biaryl atropisomers has been attempted: reaction of 1-bromo-2-methylnaphthalene **61** with its Grignard reagent afforded the binaphthyl **62** in 32% yield and 1·9% optical



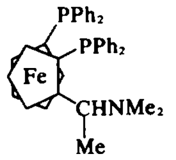
Scheme 9.



61

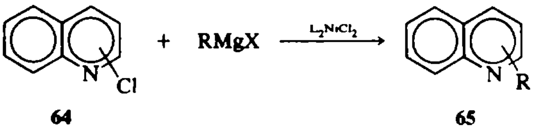
62(*S*)-(+)

purity.[46] The same compound was obtained with an optical purity of 4·6% using a nickel complex of the chiral bidentate phosphine 63.[46]

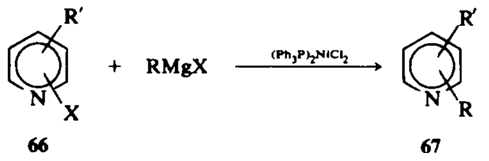


63

The cross-coupling reaction has also been used for the alkylation of haloquinolines 64 (Table 11)[47] and halopyridines 66 (Table 12).[48]



64 65



66 67

Table 11. Cross-coupling reactions between 2-chloroquinoline 64 and Grignard reagents, RMgX, catalysed by L_2NiCl_2[47]

R	L_2	Yield of 65
$PhCH_2$	dpe[a]	23%[b]
$PhCH_2$	$(Ph_3P)_2$	57%
$CH_2{=}CHCH_2$	dpe	17%
$CH_2{=}CHCH_2$	$(Ph_3P)_2$	54%
cyclo-C_5H_9	dpe	72%
cyclo-C_6H_{11}	dpe	90%
Bu^n	$(Ph_3P)_2$	0%[c]

[a] dpe = $Ph_2PCH_2CH_2PPh_2$.
[b] Bibenzyl observed as major product.
[c] Quinoline is isolated as only product.

Table 12. Cross-coupling reactions between halopyridines 66 and Grignard reagents RMgX, catalysed by $(Ph_3P)_2NiCl_2$[48]

Halopyridine 66	R	R-substituted pyridine 67 (yield)	
2-Br	Ph	2-Ph	(80%)
2-Br	$PhCH_2$	2-$PhCH_2$	(80%)
2-Br	Bu^t	2-Bu^t	(0%)
2-Br-3-Me	$PhCH_2$	2-$PhCH_2$-3-Me	(19%)
2-Br-4-Me	$PhCH_2$	2-$PhCH_2$-4-Me	(71%)
2-Br-6-Me	$PhCH_2$	2-$PhCH_2$-6-Me	(81%)
3-Br-4-Me	Ph	3-Ph-4-Me	(36%)
4-Cl-3-Me	Ph	4-Ph-3-Me	(54%)

Neumann and Kochi[49] have found that a number of iron complexes, the most effective of which was Fe(PhCOCHCOPh)$_3$, are good catalysts for the cross-coupling reaction between alkenyl halides and primary, secondary and even tertiary alkylmagnesium halides in THF at room temperature (Table 13). No rearrangement takes place in these iron-catalysed reactions, which seem to be stereospecific since *trans*-1-bromopropene and methylmagnesium bromide, in the presence of Fe(Bu^{t}COCHCOBu^t)$_3$, afford only *trans*-2-butene. Several mechanistic schemes were considered.

Stereospecific cross-coupling reactions have also been carried out with tetrakis(triphenylphosphine)palladium as catalyst (Table 14);[50] a catalytic cycle similar to the one suggested for the nickel-catalysed reactions (Scheme 8) has been proposed.

(e) *Telomerisation of butadiene*

A vast amount of work has been done on the oligomerisation and telomerisation of butadiene catalysed by nickel[51] or palladium[52] complexes. In particular, the nickel complex-catalysed telomerisation of butadiene with alcohols,[53] amines,[54] and active methylene compounds[55] leads to 1-substituted 2,7-octadienes 68, 69, 70, as the main products.

Table 13. Cross-coupling reactions of Grignard reagents with excess alkenyl halides catalysed by $Fe(PhCOCHCOPh)_3$ (0·003 mol)[49]

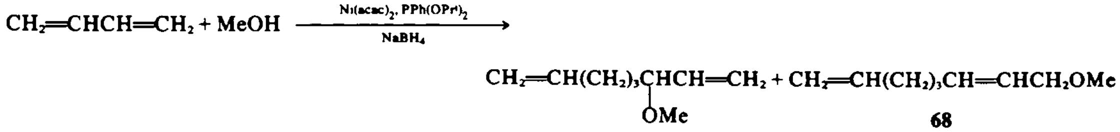
Grignard reagent	Alkenyl halide[a]	Product (yield)[a,b]	
EtMgBr	MeCH=CHBr	MeCH=CHEt	(58%)
EtMgBr	PhCH=CHBr	PhCH=CHEt	(59%)
Pr^iMgBr	MeCH=CHBr	$MeCH{=}CHPr^i$	(60%)
cyclo-$C_6H_{11}MgBr$	MeCH=CHBr	MeCH=CH-*cyclo*-C_6H_{11}	(54%)
Bu^tMgBr	MeCH=CHBr	$MeCH{=}CHBu^t$	(27%)
PhMgBr	PhCH=CHBr	PhCH=CHPh	(32%)

[a] Mixtures of *cis* and *trans* isomers.

[b] Based on RMgBr. Disproportionation and homocoupling products (from the Grignard reagent) are also formed.

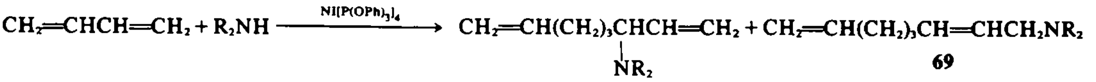
Table 14. Cross-coupling reactions of Grignard reagents with alkenyl halides in benzene catalysed by $Pd(Ph_3P)_4$ (0·03 mol)[50]

Grignard reagent	Alkenyl halide	Product (yield)	
MeMgI	*cis*-PhCH=CHBr	*cis*-PhCH=CHMe	(98%)
MeMgI	*trans*-PhCH=CHBr	*trans*-PhCH=CHMe	(99%)
$CH_2{=}CHMgBr$	*trans*-PhCH=CHBr	*trans*-$PhCH{=}CH{-}CH{=}CH_2$	(81%)
p-MeC_6H_5MgBr	*trans*-PhCH=CHBr	*trans*-$PhCH{=}CH{-}C_6H_4Me(p)$	(86%)



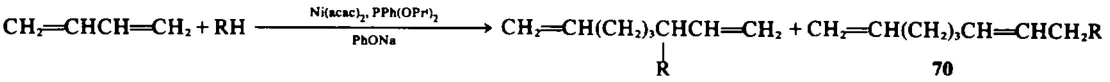
$$\mathrm{CH_2{=}CHCH{=}CH_2 + MeOH \xrightarrow[NaBH_4]{Ni(acac)_2,\ PPh(OPr^i)_2} CH_2{=}CH(CH_2)_3\underset{\displaystyle OMe}{C}HCH{=}CH_2 + CH_2{=}CH(CH_2)_3CH{=}CHCH_2OMe}$$

68



$$\mathrm{CH_2{=}CHCH{=}CH_2 + R_2NH \xrightarrow{Ni[P(OPh)_3]_4} CH_2{=}CH(CH_2)_3\underset{\displaystyle NR_2}{C}HCH{=}CH_2 + CH_2{=}CH(CH_2)_3CH{=}CHCH_2NR_2}$$

69



$$\mathrm{CH_2{=}CHCH{=}CH_2 + RH \xrightarrow[PhONa]{Ni(acac)_2,\ PPh(OPr^i)_2} CH_2{=}CH(CH_2)_3\underset{\displaystyle R}{C}HCH{=}CH_2 + CH_2{=}CH(CH_2)_3CH{=}CHCH_2R}$$

70

[R = PhCHCOMe, PhCHCN, $CH(CO_2Et)_2$, $MeCOCHCO_2Et$]

The formation of 2,7-octadienylmagnesium bromide **71** from butadiene and Pr^nMgBr, catalysed by $(Ph_3P)_2NiCl_2$ (0·02 mol) (Scheme 10), has recently been reported.[56] The open-chain Grignard reagent **71** is unstable and smoothly cyclises[57] with high stereoselectivity to *cis*-(2-vinylcyclopentyl)methylmagnesium bromide **72** (**72**:**73** *ca.* 50). Heating the latter (110°; 24 hr) affords the *trans* epimer **73** (**73**:**72** *ca.* 11). Cyclisation of **71** to **72**, and epimerisation of **72** to **73**, also occur in the absence of nickel catalyst.

The actual catalyst involved in this telomerisation reaction may be the hydrido–nickel–magnesium halide **45** formed as shown in Scheme 7.

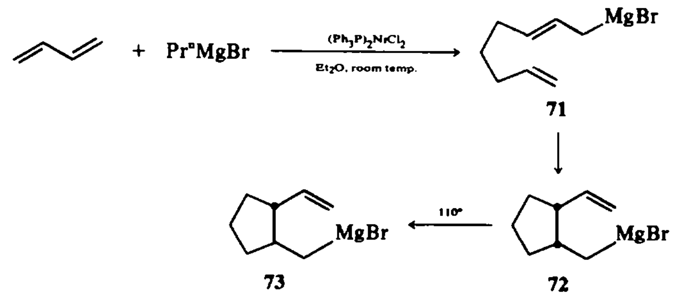
(f) *Reduction of bromides*

In the presence of catalytic amounts of Cp_2TiCl_2 (Cp = η^5-cyclopentadienyl), isopropylmagnesium bromide rapidly and selectively reduces vinyl, aryl, and alkyl bromides in ether at room temperature (Table 15).[58] Since chlorides are not reduced by this system, selective reactions can be carried out: for example, *p*-bromochlorobenzene leads to chlorobenzene.

A mechanism (Scheme 11) involving the titanium hydride **74** has been proposed for these reductions.[58]

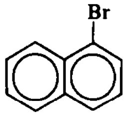
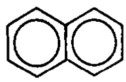
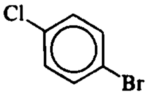
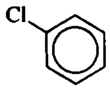
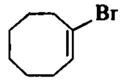
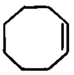
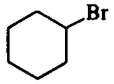
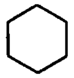
(g) *Substitution and reduction of organosilanes*

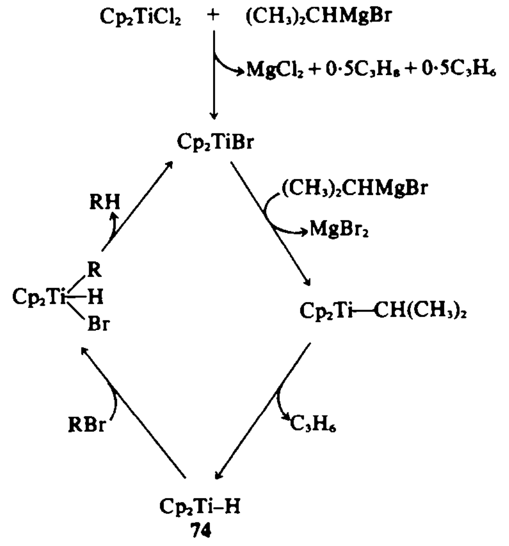
New methods of Si–C bond formation and Si–X bond



Scheme 10.

Table 15. Reduction of bromides by Pr^iMgBr, catalysed by Cp_2TiCl_2[58]

Bromide	Product (yield)	
		(~100%)
		(~100%)
		(~100%)
trans-PhCH=CHBr	$PhCH{=}CH_2$	(88%)
$PhCH_2CH_2Br$	$PhCH_2CH_3$	(92%)
n-$C_{12}H_{25}Br$	n-$C_{12}H_{26}$	(74%)
		(~100%)



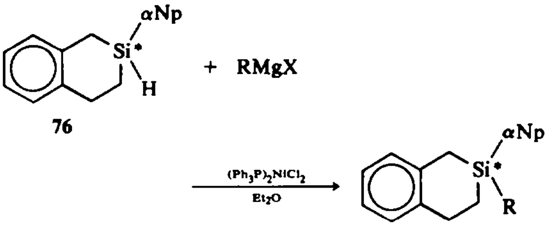
Scheme 11.

reduction, involving catalytic activation of Grignard reagents by transition metal complexes, have been designed by Corriu *et al.*[60–65]

1. ***Substitution reactions.*** Grignard reagents do not normally react with trisubstituted silicon hydrides.[59] In the presence of catalytic amounts of $(Ph_3P)_2NiCl_2$, however, non-reducing Grignard reagents (methyl-, phenyl-, benzyl-, vinyl-, allyl-, crotyl-) react readily, at room temperature in ether, with trisubstituted silanes **75** leading, with good yields, to the substitution of the H atom by the R group of the Grignard reagent involved.[60]

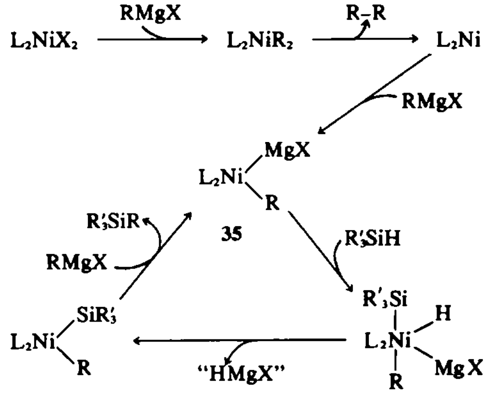
$$\underset{\mathbf{75}}{PhMe_2SiH} + RMgX \xrightarrow[Et_2O]{(Ph_3P)_2NiCl_2} PhMe_2SiR$$

These reactions are highly stereoselective. From the optically active silane **76** (Np = naphthyl), a variety of optically active tetrasubstituted silanes **77** were obtained with more than 95% retention of configuration. This method is a great improvement on previous procedures for the preparation of tetrasubstituted optically active organosilanes.



Organogermanes undergo the same type of reaction.[61]

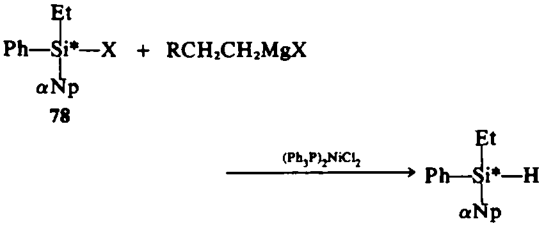
The catalytic cycle shown in Scheme 12, also involving a nickel–magnesium complex **35** (cf. Scheme 6), has been proposed for these substitution reactions.[62]



Scheme 12.

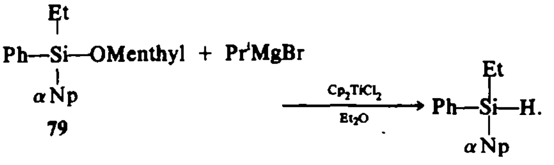
2. ***Reduction reactions.*** When the above reaction is carried out with reducing Grignard reagents, the starting silane is recovered unchanged. With a deuteriosilane, however, deuterium–hydrogen exchange is observed, showing that a reaction does in fact take place.[63]

This feature allowed Corriu and Meunier[63] to develop a new and stereospecific method for the reduction of alkoxy-, chloro- and fluorosilanes **78**. These reactions occur with retention of configuration with the deuterio-, the methoxy- and the fluorosilane, and with inversion of configuration with the chlorosilane. They probably take place via a catalytic cycle similar to that shown in Scheme 12 (**45** instead of **35**, see Scheme 7).[62] They have been used very recently by Corriu and Meunier[64] in a new synthetic route to chiral trisubstituted silanes.



$$\underset{\mathbf{78}}{Ph{-}\overset{Et}{\underset{\alpha Np}{Si^*}}{-}X} + RCH_2CH_2MgX \xrightarrow{(Ph_3P)_2NiCl_2} Ph{-}\overset{Et}{\underset{\alpha Np}{Si^*}}{-}H$$

The system $RMgX{-}Cp_2TiCl_2$ ($Cp = \eta^5{-}C_5H_5$) is an even more powerful reducing agent than the above nickel system, since it readily reduces highly hindered alkoxysilanes such as **79**.[65] Here again, Cp_2TiH is probably the active catalytic intermediate (see Scheme 11).



$$\text{Ph—Si(Et)(}\alpha\text{Np)—OMenthyl} + \text{Pr}^i\text{MgBr} \xrightarrow[\text{Et}_2\text{O}]{\text{Cp}_2\text{TiCl}_2} \text{Ph—Si(Et)(}\alpha\text{Np)—H}$$

CONCLUDING REMARKS

The various transition metal compounds discussed in this review are readily obtainable and easy to handle. Their use as catalysts considerably increases the versatility of Grignard reagents in organic synthesis.

While the detailed mechanism of many of these new reactions remains obscure, they have enough elements in common to suggest that they share basic mechanistic features. In particular, intermediates with transition metal–magnesium bonds are probably involved in many cases.

The catalytic role of transition metal compounds in a variety of reactions involving Grignard reagents was uncovered by chance, and it seems very likely that further unexpected reactions are awaiting discovery by chemists who do not regard "soup chemistry" as an unbecoming occupation.

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