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Olefin complexes of organylmetals as models for organometallic catalysts

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Abstract - Alkyl- and hydrido-metal complexes are believed to be key intermediates in such metal catalyzed transformations of alkenes as isomerization, di-, oligo- or polymerization and hydrogenation.
A variety of routes have been used for the in situ synthesis of coordinatively and electronically unsaturated organylmetals of Ti, Fe, Ru and Ni. These react further either by M-ßH elimination to give η^2-alkene-hydridometal complexes A or by complexation of an alkene molecule to give η^2-alkene organylmetal compounds B. By a sequence of readdition and ßH-eliminat-ion reactions, the alkene in A is transformed into more stable isomers.
In some cases with complexes B, it has proved possible for the first time to observe the sequence which is involved in the catalytical alkene-oligo- or -polymerization: alkene complexat-ion, alkene insertion into the metalorganyl bond and alkene complexation to the insertion product.

INTRODUCTION

In 1928 Ziegler and Bähr (ref. 1) observed the addition of phenylisopropyl potassium to the C=C bond of stilbene as the first example of a carbometallat-ion reaction. This type of reaction also proceeds with butyllithium and buta-diene (ref. 2) and with ethyllithium or triethylaluminium and ethylene (ref. 3,4) to give higher molecular organylmetal compounds as the result of the stepwise insertion of the alkene or alkadiene into the metal-carbon bond.

$$PhCH{=}CHPh + PhMe_2CK \longrightarrow \begin{matrix} PhCH\text{-}CHPh \\ PhMe_2C \quad K \end{matrix} \qquad (1)$$

$$n\ CH_2{=}CHCH{=}CH_2 + BuLi \longrightarrow Bu(C_4H_6)_n\text{-}Li \qquad (2)$$

$$n\ CH_2{=}CH_2 + EtLi \longrightarrow Et(CH_2CH_2)_n\text{-}Li \qquad (3)$$

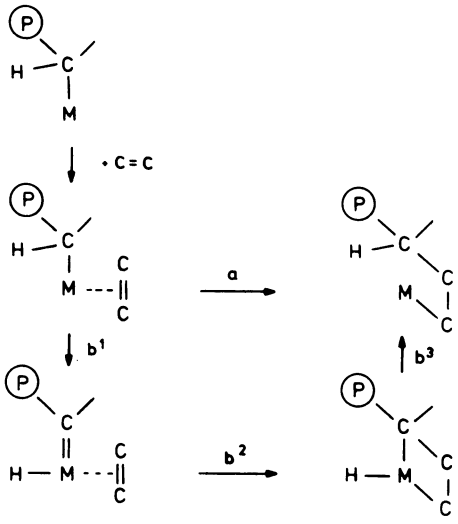
$$n\ CH_2{=}CH_2 + Etal \longrightarrow Et(CH_2CH_2)_n\text{-}al \qquad (4)$$

al = 1/3 Al

In the course of these investigations Ziegler et al. (ref. 5) discovered that, in the presence of certain transition metal compounds, the course of the react-ion of ethylene with triethylaluminium can be directed either to give ethylene dimers or polyethylene in a catalytic manner.

It has been assumed, that both the carbometallation reactions and the organo-metal catalyzed alkene polymerization involve insertion of a complexed olefin into the metal carbon bond of an intermediate η^2-alkene-alkylmetal complex, see Scheme 1a (ref. 6).

In general for alkyl compounds of main group metals, complexation of the metal to a C=C bond is not observed. Only in the case of a few alkenylmetals could weak intramolecular interaction be detected by ^1H- or ^{13}C-NMR (ref. 7). According to gas-phase electron diffraction data for bis-3-butenyl and -4-pentenyl-zinc about 80 % of the alkenyl chains are found to be in a coiled-back conformation which brings the C=C bond into the vicinity of the zinc atom: the interaction energy is estimated to be 4.5 and 6 KJ mole^{-1} respect-ively, see Fig. 1 (ref. 8).



Scheme 1

a) Insertion-migration (Cossee-mechanism).-
b) Carbene-metallacyclobutane (Green-mechanism)

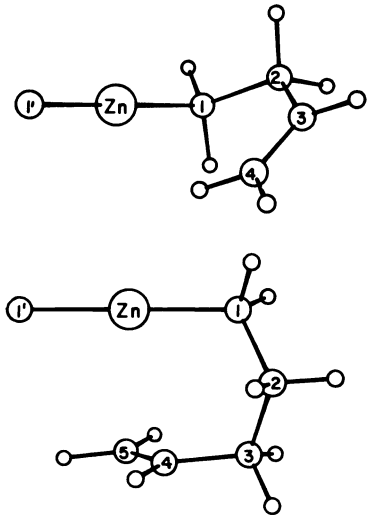
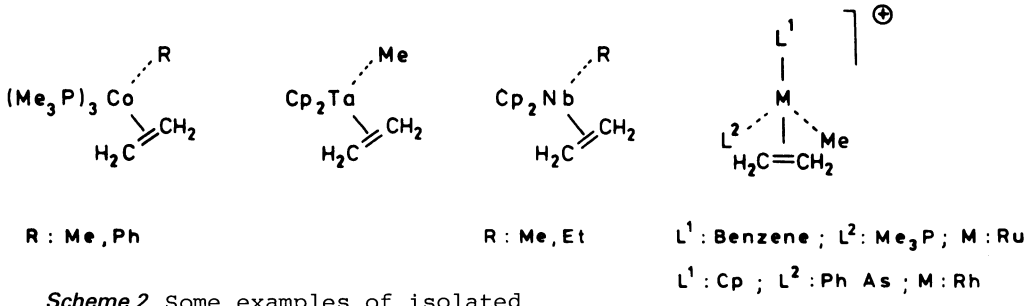


Fig. 1. Molecular fragment of a) bis-3-butenyl-zinc showing coiled-back conformation of the alkenyl chain and b) bis-4-pentenylzinc (ref. 8)

In the transition metal series few well defined η^2-alkene-alkylmetal complexes have been isolated and these either do not react with the complexed olefin by insertion (ref. 9-13) or the products of insertion have not been well characterized (ref. 14,15).



Scheme 2 Some examples of isolated η^2-ethylene-alkylmetal complexes

Other alkylmetal compounds react with olefins, but the formation of an η^2-alkene complex as a precursor was not observed, see eq. 5.

$$Cp^*_2Lu\text{-}CH_3 + CH_2{=}CHCH_3 \longrightarrow Cp^*_2Lu\text{-}CH_2CH(CH_3)_2 \quad (5)$$

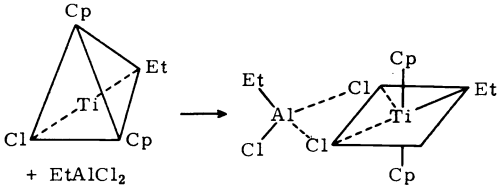
(ref. 16)

tert-Butyllithium (ref. 17), isopropyl- and tert-butylaluminium react in a similar 1:1 manner with alkenes as do the sec-, tert-alkyl- and allylmagnesium halides, the corresponding diorganozinc compounds (ref. 18) and (PCy_3)-Ni(acac)methyl (ref. 19).

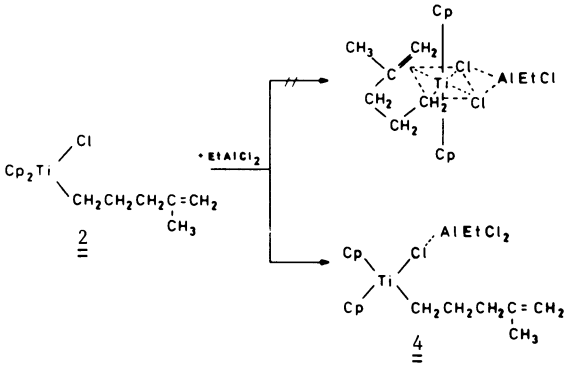
This lack of well defined examples supporting Cossee's insertion mechanism has resulted in the postulation recently of two alternative pathways for C-C coupling in organometal catalyzed reactions: 1. αH elimination from an alkylmetal species to give a hydrido-carbene complex which reacts further to give a hydrido-metallacyclobutane followed by hydride transfer to the γC atom, see Scheme 1b (ref. 20) and 2. oxidative coupling of two alkenes in an (alkyl)-M(alkene)$_2$ species to give a metallacyclopentane derivative followed by H transfer from the alkyl group to the δC atom of the metallacycle (ref. 21).

ALKENYL METAL COMPLEXES

Following the Cossee model for heterogeneous Ziegler catalysts (ref. 6), it has been assumed (ref. 22), that complexation with an organoaluminium compound changes the coordination around the titanium in homogeneous alkyltitanium(IV) complexes from tetrahedral to octahedral, see Scheme 3.

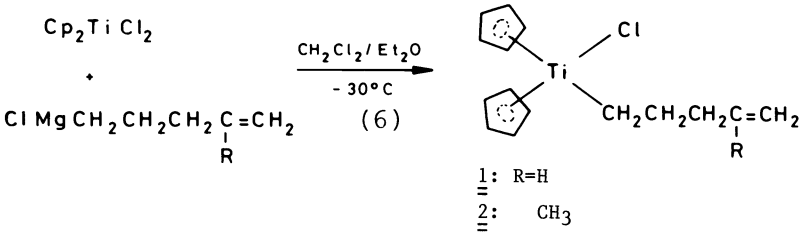


Scheme 3 Model for the change in coordination at the Ti atom on complexation (ref. 22a)



Scheme 4 Complexation of 2 with $EtAlCl_2$ to give 4

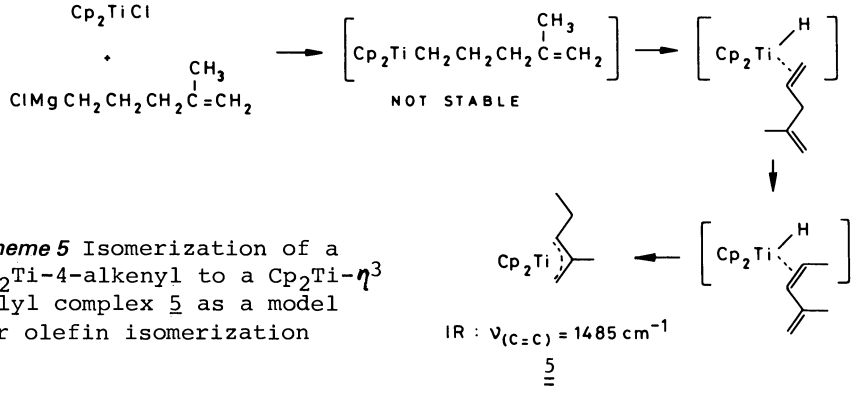
This model was investigated by studying the reactions of the complexes 1 and 2. A 4-alkenyl ligand bonded to the titanium atom was chosen in the hope of both promoting an interaction between the C=C bond and the Ti as the result of the chelating effect of this ligand and at the same time of preventing polymerization of the olefinic component following complexation, see eq. 6 (ref. 23).



(6)

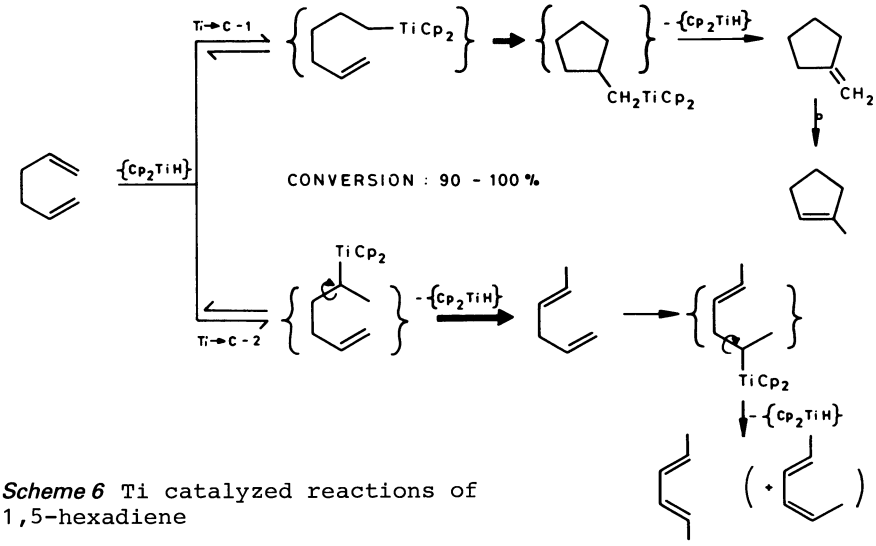
In 1 and 2 and their complexes with $EtAlCl_2$ 3 and 4 no complexation of the C=C bond to the titanium atom can be observed: The ^{13}C-NMR chemical shifts of the olefinic carbon atoms remain unchanged between -97° and 20°C. The Ti atoms in 3 and 4 appear to remain in a coordinatively saturated environment, see Scheme 4 (ref. 23).

The corresponding Ti(III) compounds of the type Cp_2Ti-alkenyl are expected to be coordinatively unsaturated so that the C=C bond of the alkenyl ligand could interact with the titanium atom. However, this complexation appears to be so weak, that an isomerization of the 3- or 4-alkenyl ligand occurs very rapidly via ßH-elimination according to Scheme 5 (ref. 23).



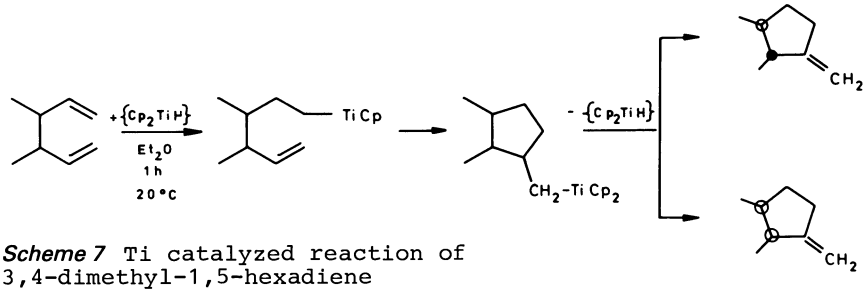
Scheme 5 Isomerization of a Cp_2Ti-4-alkenyl to a Cp_2Ti-η^3 allyl complex 5 as a model for olefin isomerization

In the presence of an excess of diene, the α,ω-alkadienes can be isomerized into the thermodynamically more stable conjugated alkadienes (ref. 25). In the case of 1,5-hexadienes, in addition to the isomerized hexadienes, methylenecyclopentane is formed at 20°C in THF with 93 % conversion and 76 % yield in a catalytic reaction (ref. 26). Cp_2TiCl combined with isopropylmagnesium bromide (1:1) results in the in situ formation of Cp_2Ti-hydride, which acts as the catalyst in these systems. Cp_2Ti-5-hexenyl, formed by Ti-H addition to 1,5-hexadiene, is believed to be an intermediate and reacts by intramolecular Ti-C addition to the C=C bond of the alkenyl ligand followed by ßH-elimination according to Scheme 6.



Scheme 6 Ti catalyzed reactions of 1,5-hexadiene

With 1,5-hexadienes having substituents in both the 3- and 4-position cyclic products are formed exclusively, see Scheme 7.



Scheme 7 Ti catalyzed reaction of 3,4-dimethyl-1,5-hexadiene

In contrast to the corresponding Ti compounds, which isomerize very rapidly into the η^3-allyl complexes, CpNi-4-alkenyl compounds are stable up to 70°C and can be distilled in vacuo as red oils (ref. 27). The coordination of the C=C bond to the Ni atom is accompanied by high-field-coordination shifts of the olefinic atoms of -2.3 to -0.7 ppm ($\Delta\delta$ (^{1}H)) and -70 to -60 ppm ($\Delta\delta$(^{13}C)) and has been confirmed by X-ray analysis for the crystalline derivative 6, see Fig. 2 (ref. 28).

The coordination geometry of the nickel atom in these compounds is trigonal planar, with the middle points of the Cp group, and of the π-bonded C=C bond as well as the σ-bonded α-C atom of the alkenyl ligand occupying coordination sites around the central nickel atom. The conformation of the chelating 4-alkenyl group is rigid which may be one reason for the stability of these compounds. The conformation of the 4-pentenyl group in 7 has been determined from the ^3J(H,H) coupling constants. The ßH-atoms at C-2 are directed away from the nickel atom (see Fig. 3) and the necessary ßH transfer which would lead to alkene elimination (as the reverse reaction of cis addition of a metal hydride to an alkene) cannot occur. The coplanarity of the Ni and ßH-atoms can only be attained after decomplexation of the C=C bond and therefore

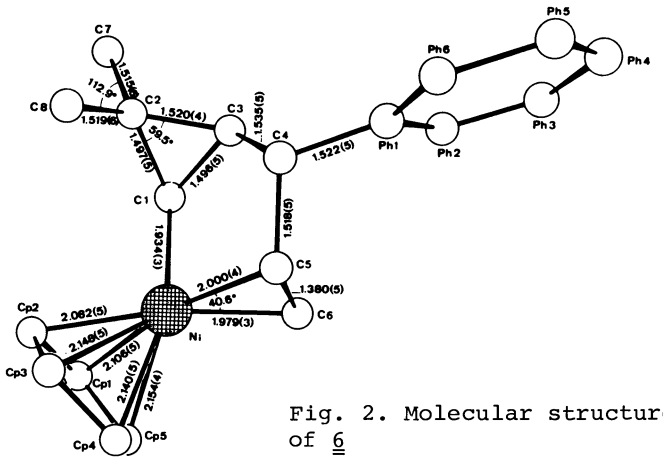


Fig. 2. Molecular structure of 6

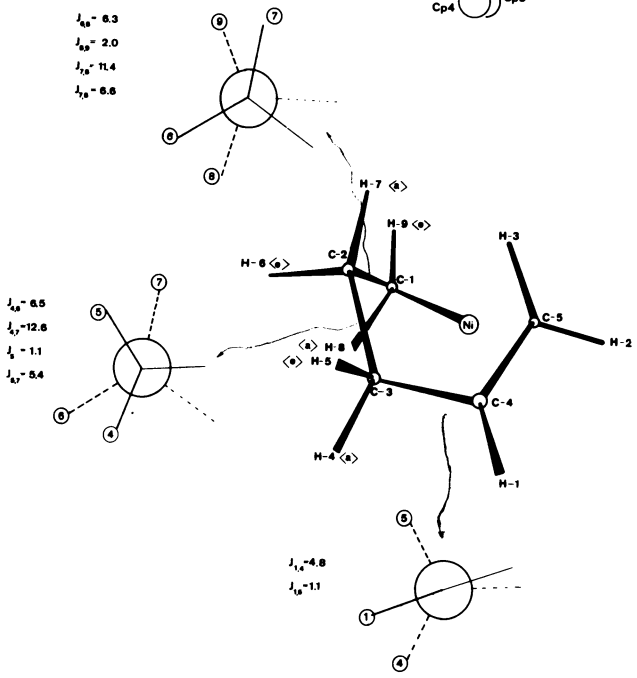
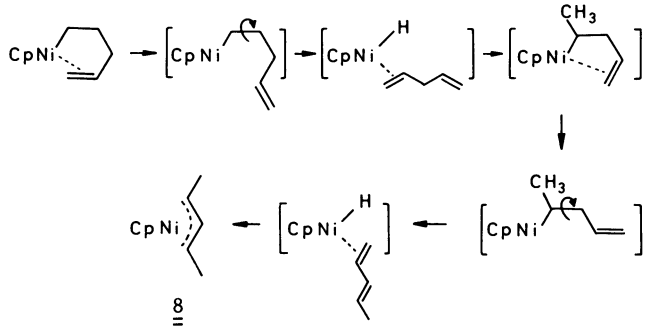


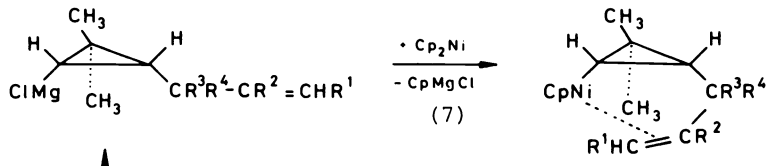
Fig. 3. Conformational situation at the 4-pentenyl ligand in 7 (ref. 27)

isomerization to the thermodynamically more stable η^3-allyl complexes, e.g. 8, occurs at higher temperatures, at which decomplexation will be favoured, see Scheme 8.



Scheme 8 Mechanism of the isomerization of 4-pentenyl- into 1,3-dimethyl-η^3-allylnickel 8 (ref. 28)

Incorporation of the atoms C-1 and C-2 of the 4-alkenyl ligand into a cyclopropyl system and fixation of the sole ßH-atom in a trans configuration in complexes 6, 9 - 13 increases the stability with respect to ßH-elimination, see eq. 7 (ref. 28).



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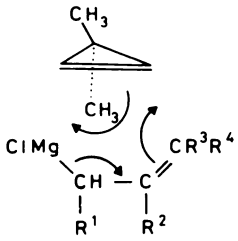
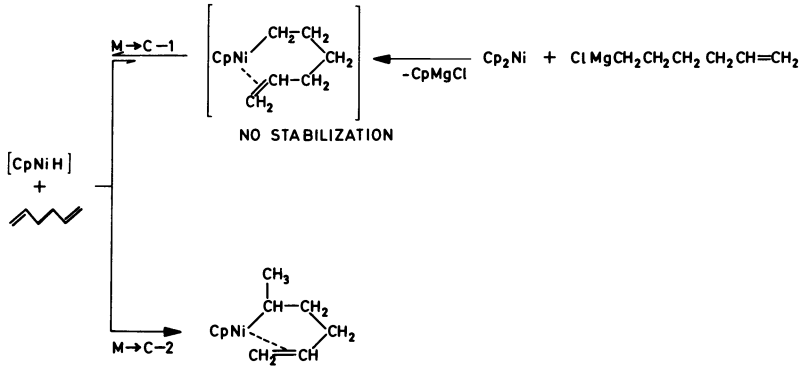


	R^1	R^2	R^3	R^4	YIELD [%]
9	H	H	H	H	69
10	H	CH_3	H	H	88
11	H	H	CH_3	H	90
12	H	H	CH_3	CH_3	96
13	CH_3	H	CH_3	H	89
6	H	H	Ph	H	12

With the 5-pentenyl ligands, the chelating ring seems to be more fluxional. The complexes are not stable at 20°C and isomerize into 4-alkenylnickel complexes, e.g. 14, see eq. 8 (ref. 27).

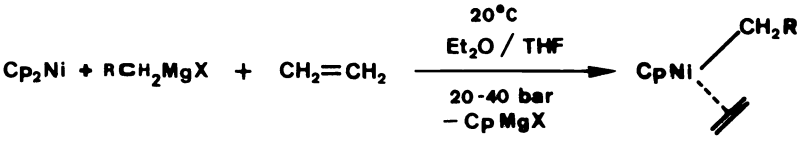


(8)

14

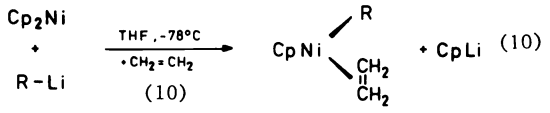
η^2-ALKENEORGANYL METAL COMPLEXES

Separation of the alkenyl ligand in these complexes into an alkyl and an alkene part causes a loss of the chelating effect of the ligands and a decrease in the stability is to be expected. In spite of this, a variety of CpNi-organyl complexes with different alkenes (including ethylene) and alkadienes as well as various organyl groups have been prepared, isolated and identified (ref. 29). These complexes are normally stable up to 20°C; above this temperature they decompose after decomplexation of the alkene leaving a coordinatively and electronically unsaturated CpNi-organyl species, which decomposes (ref. 29,30). The (η^2-alkene)(η^5-cyclopentadienyl)organyl nickel complexes have been prepared by reaction of nickelocene with organyl lithium or -magnesium halides in the presence of alkene between, depending on the stability, 20° and -70°C according to eq. 9-11 (ref. 29).



(9)

14 : R=H (72 %); R=$SiMe_3$ (62 %)



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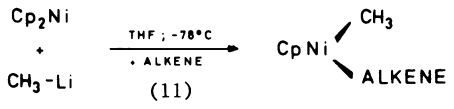
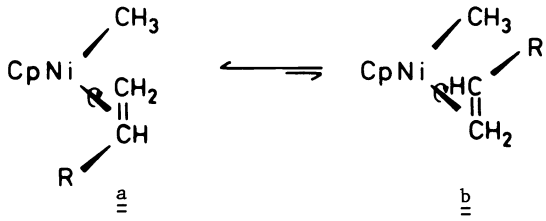


(11)

	R	YIELD [%]
15	$-CH_2CH_3$	78
16	$-CH_2CH_2CH_3$	46
	$-CH(CH_3)_2$	58
17	$-CH_2CH_2CH_2CH_3$	81
18	$-CH_2CH(CH_3)_2$	38
	-Ph	34
19		75

ALKENE TYPE I	YIELD [%]	ALKENE TYPE II	YIELD [%]
$CH_2=CHCH_3$	54	$CH_2=C(CH_3)_2$	40
$CH_2=CHPh$	40	$CH_2=$	80
$CH_2=CHSiMe_3$	63	$CH_2=$	62
	60		40
	73		

In these complexes the Ni atom also has a trigonal planar coordination geometry with the alkene orthogonal to the trigonal plane. Temperature dependent NMR spectra are observed as a result of rotation of the alkene around the coordination axis. In the case of the CH_2=CHR and CH_2=CR(1)R(2) complexes two rotamers a and b are observed below -60°C, see Scheme 9 (ref. 29). In the complexes with 1,3-alkadienes only one, normally the least substituted C=C bond is coordinated to the metal.

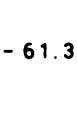


a/b = 90 : 10 to 80 : 20

Scheme 9 The formation of two rotamers a and b as the result of alkene rotation around the coordination axis

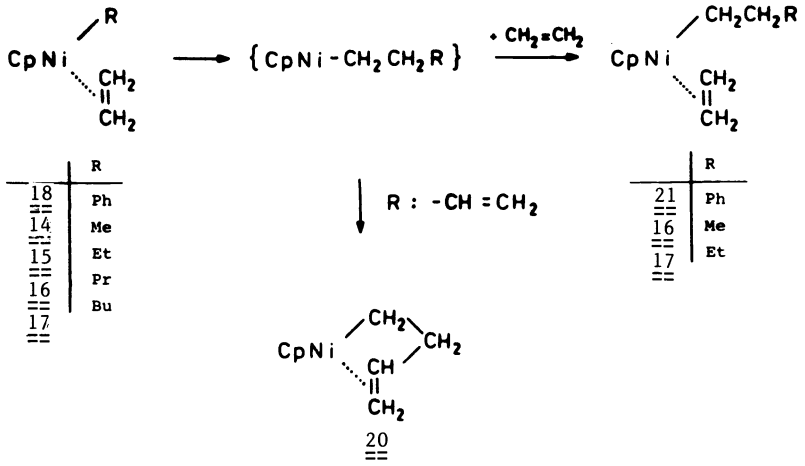
The decreasing average values $\overline{\Delta\delta}$ of the coordination shifts (^{13}C-NMR) of the olefinic C atoms in the η^2-alkene complexes suggest that the ability of the alkenes to coordinate decreases in the order shown in Table 1 (ref. 29).

Table 1. The arithmetic mean $\overline{\Delta\delta}$ of the ^{13}C-NMR coordination shifts at C-1 and C-2 of the alkene in the a-rotamers of (η^2-alkene) complexes of CpNi-methyl

ALKENE	$\overline{\Delta\delta}$	ALKENE	$\overline{\Delta\delta}$
$CH_2=CHSiMe_3$	-74.9	$CH_2=$	-63.4
$CH_2=CH_2$	-71.4		
$CH_2=CH-Vin$	-64.6		
$CH_2=CHPh$	-64.5	$CH_2=$ 	-61.3
$CH_2=CHMe$	-60.5		
$CH_2=CHEt$	-60.1		
$CH_2=CHCMe_3$	-59.5	$CH_2=$	-59.4
$CH_2=CMe_2$	-59.1		
$MeCH\overset{(E)}{=}CHMe$	-56.3	$CH_2=$	-55.9
$MeCH\overset{(Z)}{=}CHMe$	-52.1		

ALKENE INSERTION INTO ORGANOMETAL BONDS

Some of the CpNi-organyl complexes mentioned above react further with insertion of the complexed alkene into the Ni-C bond. The η^2-ethylene complex of CpNi-vinyl cannot be isolated since even at -80°C it reacts further with insertion to give the 3-butenyl compound 20 (ref. 31), see Scheme 10. The Ni-Ph bond in 18 reacts with insertion of the complexed ethylene at ca. -30°C and the primary insertion product can be trapped by complexation with ethylene to give 21. No further reaction occurs up to 20°C because of the lower reactivity of the prim. alkyl nickel species. The methyl and ethylnickel complexes 14 and 15, for example, react very slowly with insertion of ethylene at 20°C to give 16 and 17 respectively. After 48 h the conversion is 16 mole % (ref. 29). The corresponding propyl- and butylnickel complexes 16 and 17 do not react with the coordinated ethylene below 40°C.



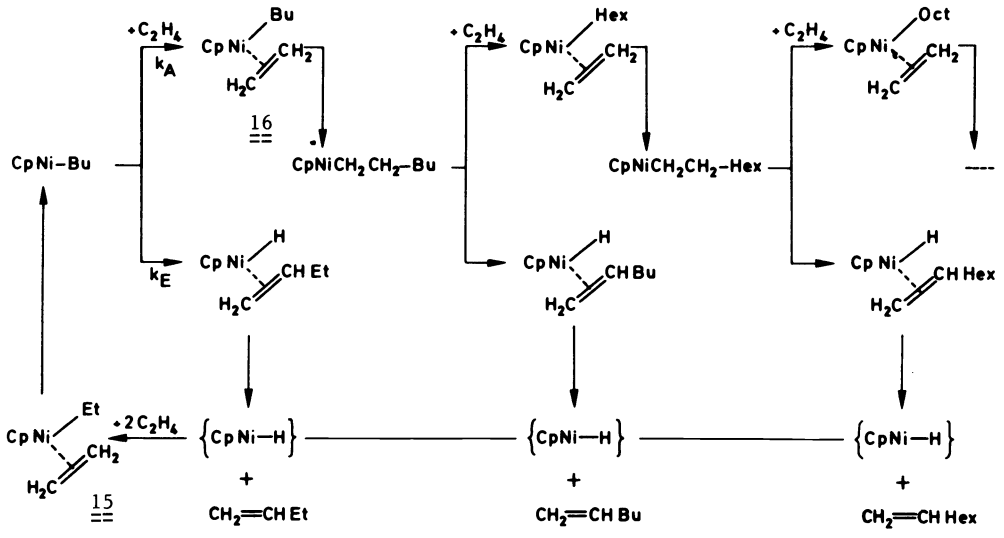
Scheme 10 Insertion of coordinated ethylene into the Ni-C bond of (η^2-ethylene)(η^5-cyclopentadienyl)organylnickel complexes

The ^{13}C-NMR coordination shifts ($\Delta\delta$) of the ethylenic C atoms increase in the same order as the reactivity with respect to the insertion decreases, see Table 2. In other words there is an inverse dependence between the reactivity and strength of the interaction between Ni and ethylene.

Table 2. ^{13}C-NMR coordination shifts $\Delta\delta$ of the ethylenic C atoms in (η^2-C_2H_4)CpNi-R complexes and the temperature of ethylene insertion

R	$\Delta\delta$	INSERTION AT
-CH=CH$_2$	NOT KNOWN	-80 TO -30°C
-Ph	-67.9	≥ -30°C
	-69.7	20°C
-Me	-71.4	≥20°C (SLOW)
-Et	-72.3	≥20°C (SLOW)
-Bu	-72.4	≥40°C (SLOW)
-Pr	-72.5	≥40°C (SLOW)

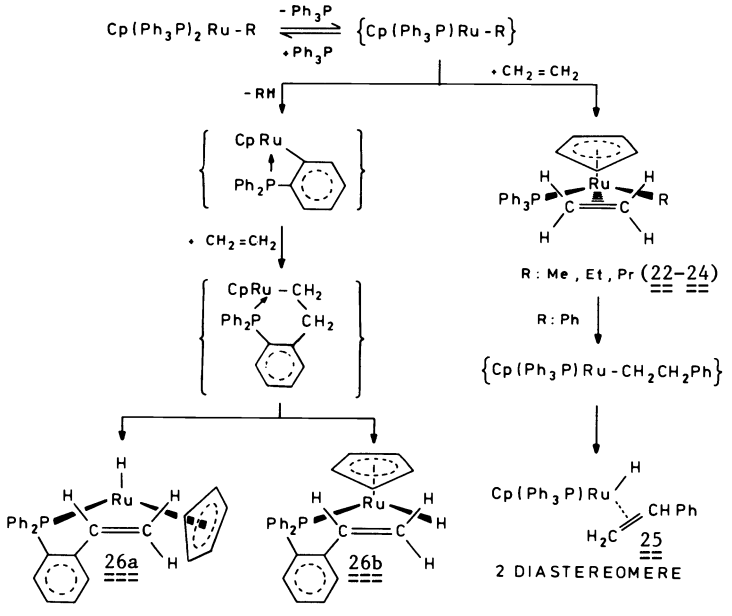
At higher temperatures (toluene, 120°C), 15 catalyzes the oligomerization of ethylene to a mixture of butenes, hexenes and octenes with 1-butene as the main product (80 to 90 %), see Scheme 11 (ref. 29).



Scheme 11 Ethylene oligomerization catalyzed by 15

The particular reactivity of metal-vinyl and -phenyl bonds towards insertion of ethylene has not been observed with the main group metals Mg and Al but has been reported for other transition metals such as Ru (ref. 32,33), Fe (ref. 34) and Ti (ref. 35).

Above ca. 60°C ruthenium complexes of the type $Cp(Ph_3P)_2Ru$-R react with dissociation of one phosphane ligand. If these complexes are heated to above 60°C in the presence of ethylene, then the reaction products depend upon the ethylene concentration being used: under ethylene pressure of 50 to 80 bar and with R = methyl, ethyl or propyl, the corresponding coordinatively unsaturated monophosphane rutheniumalkyls have been trapped as the (η^2-alkene)-Ru complexes 22 - 24, see Scheme 12 (ref. 33). Under the same conditions the phenyl-Ru complex inserts one ethylene molecule to give after immediate M-ßH elimination the (η^2-styrene)hydridoruthenium compound 25. At low ethylene pressure (5-10 bar) dissociation of one phosphane is followed by ortho metallation of one phenyl group of the coordinated PPh_3 ligand to give a new phenyl-Ru bond. This bond inserts one ethylene molecule and the product stabilizes itself by M-ßH elimination forming a pair of diastereomeric π-(o-styryl)diphenylphosphane ruthenium hydrides 26a and b.



Scheme 12 Ethylene reactions of Ru compounds

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