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STRUCTURE AND REACTIVITY OF SOME TRANSITION METAL COMPLEXES

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Abstract

The so-called "nickel effect" is based on olefine complexation to nickel(0) as well as the formation of three-centre-bonds between nickel(0) and α-carbon atoms of organo-aluminum or -lithium compounds. Well defined complexes have been isolated and characterized by X-ray structural analysis as well as by NMR-spectroscopy. Recent results of neutron defraction experiments and ab initio calculations for $(\eta^3\text{-}C_3H_5)_2Ni$ are described together with some remarkable addition reactions.

In 1954, i.e. 30 years ago, K. Ziegler and coworkers (1) published for the first time the so-called "nickel effect" which became the fundamental observation for further developments which finally led to the Ziegler-catalysts. Accidentally, it was found that small amounts of nickel salts co-catalyzed the reaction of triethylaluminum and ethene towards the formation of butene instead of towards higher aluminumtrialkyls.

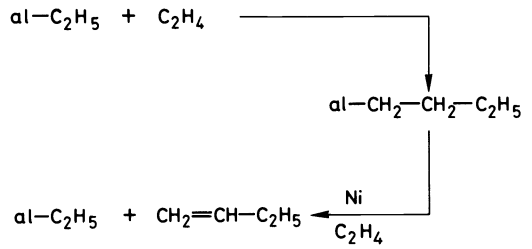


Fig. 1 The "nickel effect"

About 20 years later we (2) explained the "nickel effect" by assuming an electrocyclic process involving a π-complex and three-centre-bonds (Fig. 2).

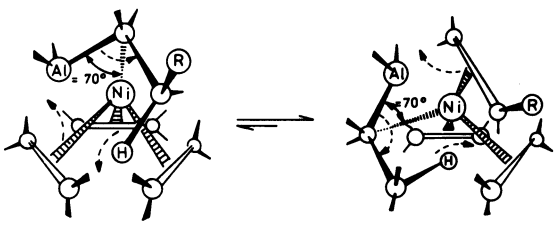


Fig. 2 Assumed complex formed by trisethenenickel(0) and tributylaluminum

A simplified picture is shown in the following figure.

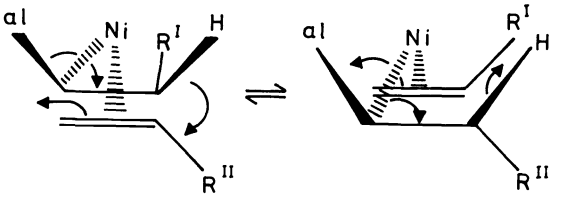


Fig. 3 Simplified Scheme

The process can be described as a 1.5-shift and may be compared to the thermal rearrangement of 1-vinyl-2-methylcyclopropane to give 1.4-hexadiene (3).

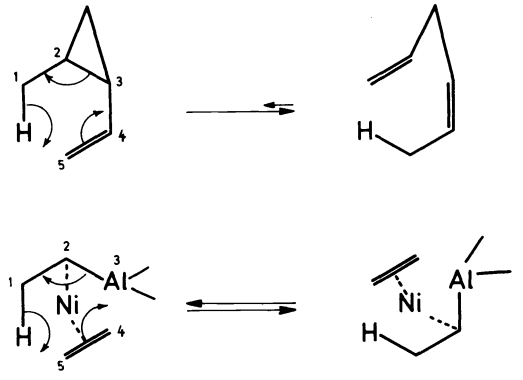


Fig. 4 Analogy between a concerted thermal 1.5-shift and a nickel(0) catalyzed reaction

The fundamental problem which remained was the proof of the existence of three-centre-bonds between nickel(0) and the organoaluminum component. Very recent NMR-spectroscopic investigations failed to provide any evidence for complexes of this kind. The ^{1}H-NMR-spectra of 1:1 mixtures of triethylaluminum and trisethenenickel(0) at -80°C show only the signals of the separate components.

$$[C_2H_4]_3\,Ni + Al(C_2H_5)_3 \rightleftharpoons [C_2H_4]_3Ni{\cdot}Al(C_2H_5)_3$$

Fig. 5 Complex formation in equilibrium

The equilibrium - if it exists - must lie largely to the left. On the other hand it was possible to show that even at temperatures below -50°C the ethene molecules of trisethenenickel(0) do exchange when d_4-ethene is introduced (4).

$$[C_2H_4]_3\,Ni + C_2D_4 \overset{-50°C}{\rightleftharpoons} [C_2H_4]_2[C_2D_4]Ni + C_2H_4$$

Fig. 6 Exchange of ethene molcules

Similar experiments were carried out with 1:1 mixtures of triethylaluminum and trisethenenickel(0) with the addition of d_4-ethene. Below -50°C only an exchange of ethene was observed, whereas, the organoaluminum compound did not react. Raising the temperature, however, caused an immediate scrambling of all the hydrogen- and deuterium-atoms of the ethene molecules as well as of the ethyl groups.

$$[C_2H_4]_3\,Ni + C_2D_4 + Al(C_2H_5)_3 \xrightarrow{-50°C}$$

$$[C_2H_4]_2\,Ni[C_2D_4] + C_2H_4 + Al(C_2H_5)_3 \xrightarrow{0°C}$$

$$[C_2(H/D)_4]_3\,Ni + C_2(H/D)_4 + Al(C_2(H/D)_5)_3$$

Fig. 7 Scrambling caused by the "nickel effect"

The scrambling is the result of the "nickel effect" (4).

Trisethenenickel(0) and tributylaluminum react in an analogous manner liberating butene under formation of triethylaluminum. The driving force for this reaction might well be the somewhat higher energy of association of triethylaluminum compared to that of tributylaluminum while butene is energetically more favoured than ethene.

$$[C_2H_4]_3\,Ni + Al(C_4H_9)_3 \longrightarrow$$

$$Al(C_2H_5)_3 + [Ni + 3\,C_4H_8]$$

Fig. 8 The transalkylation

This example was indeed the first one in which a well defined nickel(0) complex caused the "nickel effect" (4).

On the basis of these observations we developed a catalytic process which is of technical interest. Tri-n-octylaluminum is technically produced by a thermal reaction between tri-iso-butylaluminum and 1-octene at temperatures of 120-140°C (5). Isobutene is liberated. Under these conditions, in addition to the displacement reaction dimerisation of octene occurs. The resulting organoaluminum compound therefore contains both tri-n-octylaluminum and other components which have C_{16}-units. These impurities must be excluded for the production of tetra-octylstannane from $Al(C_8H_{17})_3$ and $SnCl_4$. A very pure tri-n-octylaluminum can be obtained by our process (4) which is based on the reaction of triisobutylaluminum and 1-octene in presence of catalytic amounts of nickel(0) in form of $Ni(C_2H_4)_3$, $Ni(COD)_2$ or Ni(CDT) (Al:Ni ~ 1-2000:1) at 0°C.

$$Al(i\text{-}C_4H_9)_3 + 3\,CH_2{=}CH{-}C_6H_{13} \xrightarrow[0°C]{[COD]_2Ni}$$

$$Al(C_8H_{17})_3 + 3\,i\text{-}C_4H_8$$

Fig. 9 The catalytic process for the synthesis of $Al(C_8H_{17})_3$

The catalytic amount of nickel(0) which is present can, if necessary, be removed in the form of $Ni(CO)_4$ by treating the product with CO.

Now, I would like to discuss the problem of interaction between nickel(0) and main group organometallics. The first example does not exactly fit in but, nevertheless, is quite instructive. Formally, η^3-pentenylnickelmethyl does not contain nickel(0) but the net charge on the metal atom will not be very different from that in nickel(0) complexes. The compound is a dimer with bridging methyl groups and is even dimeric in the vapor (6). Interestingly, a mixed dimer is formed if it is treated with trimethylaluminum. The resulting methyl bridges - three-centre-bonds - are apparently more stable than those of the homo dimers.

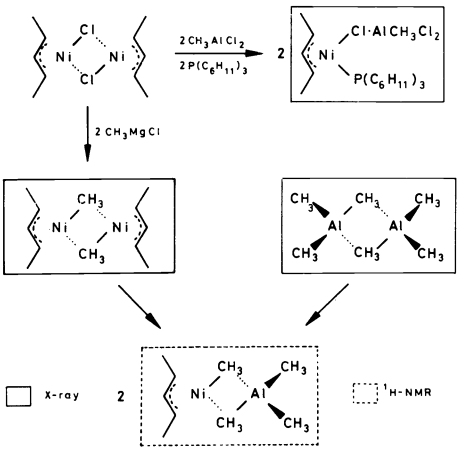


Fig. 10 Formation of a mixed complex containing Ni

At low temperatures (-35°C) four different methyl groups can be observed in the ^{1}H-NMR-spectrum: the bridging methyl groups, two different methyl groups on aluminum and the methyl groups of the pentenyl ligand. At 0°C the system becomes dynamic, i.e. beside the pentenylmethyl groups only one other methyl species appears.

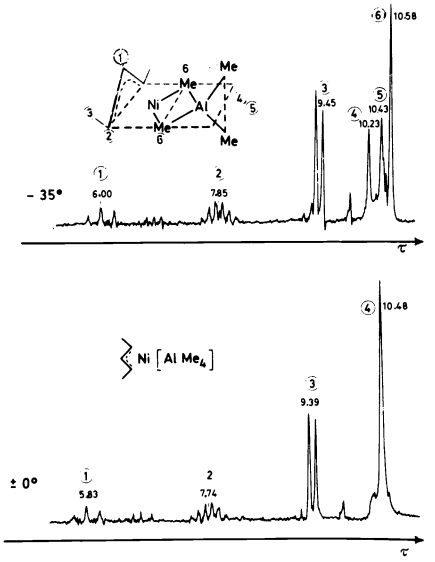


Fig. 11 -35°C and 0°C ^{1}H-NMR-spectrum of the mixed complex

The dynamic effect is based on a rapid exchange of the bridging and outer methyl groups (6a,b).

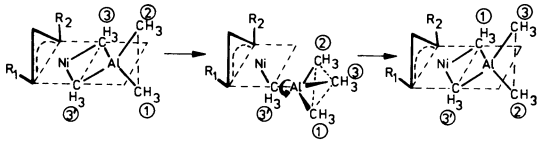


Fig. 12 Dynamic exchange of methyl groups

In this context the X-ray structure of (η^3-pentenylnickelmethyl)$_2$ (I) (6c) is of interest.

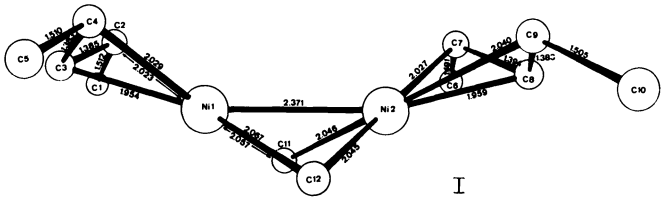


Fig. 13 X-ray structure of $(\eta^3\text{-}C_5H_9NiCH_3)_2$

The following example, however, describes the complex formation of nickel(0) and an organometallic entity. Trisethenenickel(0) reacts with methyllithium to give, depending on the ligands present, two different complexes. In the presence of tetramethylethylenediamine (TMEDA), an ionic species (II) is formed, whereas, pentamethyldiethylenetriamine (PMDTA) leads to the formation of an addition product (III) which is stabilized by a three-centre-bond (4).

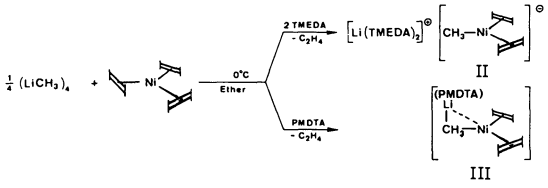


Fig. 14 Complexes of trisethenenickel(0) and methyllithium (II and III)

Both complexes have been characterized by X-ray structural analysis (7,8).

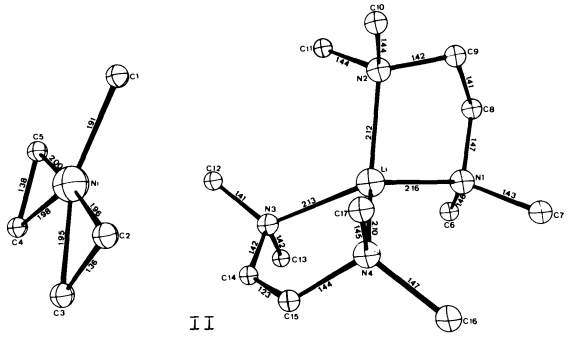


Fig. 15 X-ray structure of $[(TMEDA)_2Li][CH_3Ni(C_2H_4)_2]$ (II)

Complex II is completely dissociated and can be described as a nickolate and exhibits high conductivity.

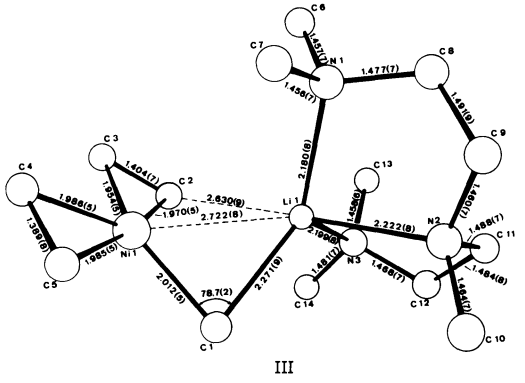


Fig. 16 X-ray structure of $PMDTALiCH_3Ni(C_2H_4)_2$ (III)

Complex III on the other hand is characterized by the three-centre-bond and has a typical angle of 78°. This complex corresponds to the moiety we were looking for in the context of the "nickel effect". In the following figure the nuclei of complexes I and III are compared.

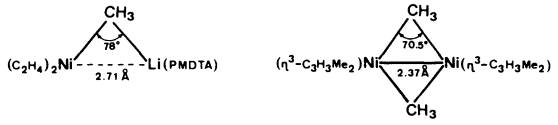


Fig. 17 Three-centre-bonds in complexes I and III

The three-centre-bond angles as well as the Ni-Ni distances differ a little but in principal the complexes of Ni(0) and Ni(II) show considerable similarity.

Complexes of this kind are observed not only with trisethenenickel(0) but also with 1.5.9-cyclododecatrienenickel (CDTNi) (8). The resulting complexes, however, differ in that the nickel atom is coordinated to three instead of only two C=C double-bonds. The fourth coordination site of nickel(0) is occupied by the methyl group of methyllithium and leads to the formation of a nickolate or an electron deficient bonding system.

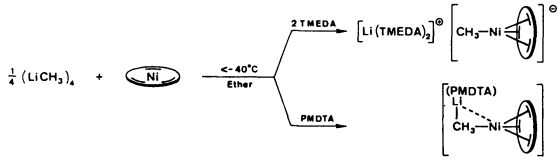


Fig. 18 Complexes of CDT·Ni and methyllithium

It was interesting to study the influence of different ligands which occupy the fourth coordination site of CDT·Ni by ^{1}H-NMR-spectroscopy. The following scheme shows the 400-MHz-NMR-spectra of CDT, CDT·Ni and three complexes of CDT·Ni. The chemical shift of the olefinic protons is highly dependent upon the extent of back donation. Furthermore, the spectra prove clearly that all three double bonds are still coordinated.

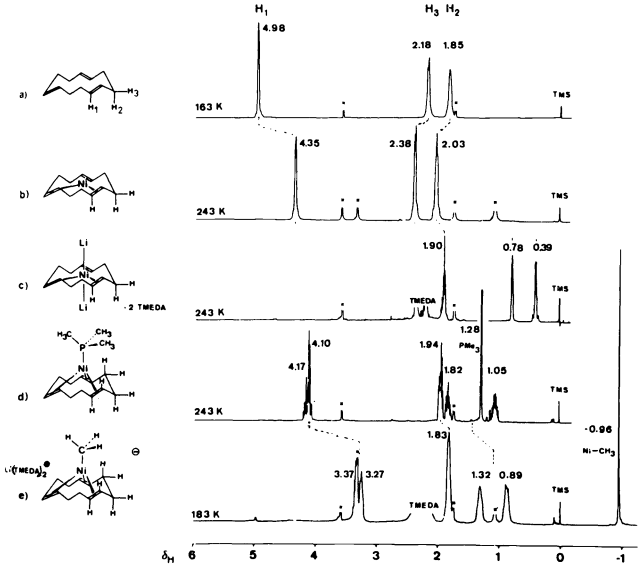


Fig. 19 400-MHz-^{1}H-NMR-spectra of CDT and CDT·Ni complexes

CDT·Ni acts as a Lewis-acid towards methyllithium. By treatment with stronger Lewis-acids, such as trimethylaluminum, CDT·Ni can be released.

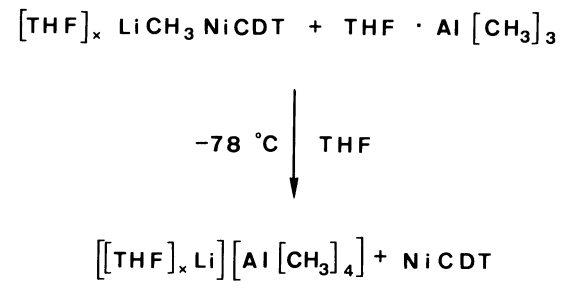


Fig. 20 Regeneration of CDT·Ni and formation of $[(THF)_x Li][Al(CH_3)_4]$

This can also be achieved by reacting methylcopper; a cuprate if formed.

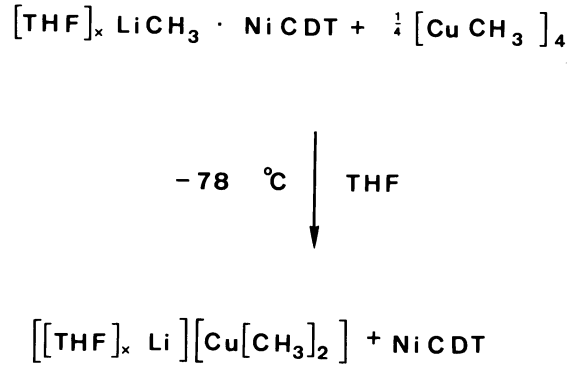


Fig. 21 Regeneration of CDT·Ni and formation of $[(THF)_x Li][Cu(CH_3)_2]$

The complex formation of nickel(0) as described above is not limited to methyllithium; butyllithium also forms 1:1-adducts with tris-ethenenickel(0) (4). In presence of PMDTA at temperatures below -20°C a complex is formed analogous to complex II and this was characterized by NMR-spectroscopy and shows the typical three-centre-bond system.

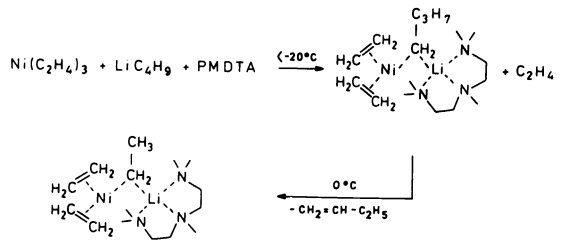


Fig. 22 Complex of trisethenenickel(0) with butyllithium and trans-alkylation

Of considerable interest was the fact that by warming up the mixture in the presence of excess ethene to 0°C, the "nickel effect" could be observed. The butyllithiumnickel(0) complex was transformed into an ethyllithiumnickel(0) complex under displacement of butene. This seems to be an obvious model for the organoaluminum system, too. The different behaviour regarding the ability to form observable complexes with nickel(0) of organolithium or -aluminum compounds is based on the higher basisity of the alkyl groups of the organolithium compounds which give definite complexes, whereas, the corresponding organoaluminum complexes appear, at best, in low equilibrium concentrations. One more example supports this explanation even if the analogy is not a direct one: organoaluminumnickel(0) complexes have been obtained from CDT·Ni as well as from $Ni(C_2H_4)_3$ by treatment with hydridoaluminates (9,10). The coordination takes place through the hydride atoms, the donor property of which now seems to be comparable with that of the alkyl groups of organolithium compounds.

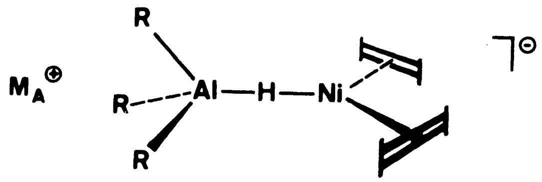


Fig. 23 Formation of a nickel(0) complex with an aluminumhydride

Finally, I would like to discuss some recent results concerning the structure and reactivity of bis-η^3-allylnickel and η^3-bis-methallylnickel, respectively (11). The ratio of the isomers present depends on the conditions during the synthesis (12).

Synthesis	t°C	$[\eta^3\text{-}C_3H_5]_2Ni$ trans	$[\eta^3\text{-}C_3H_5]_2Ni$ cis	$[\eta^3\text{-}C_4H_7]_2Ni$ trans	$[\eta^3\text{-}C_4H_7]_2Ni$ cis
$NiX_2 + 2CH_2{=}C(R){-}CH_2MgX$; X=Cl,Br; R=H, CH_3	-20	75	25	69	31
[2 R-⟨ Ni-CH_3]	-75	90	10	20	80
[2 R-⟨ Ni-H]	-150	95	5	94	6

Fig. 24 Cis-trans ratio of bis-η^3-allylnickel complexes depending on conditions of the synthesis

The cis-trans ratio has been determined both by ^{1}H-NMR-spectroscopy as well as by a remarkable chemical reaction. Diazomethane reacts even at very low temperatures with $(\eta^3\text{-}C_3H_5)_2Ni$ (13) and the reaction products can be correlated with the ratio of cis-trans-isomers. The trans-isomer reacts to give derivatives of diallyl, whereas, the cis-isomer forms dicyclopropylmethane.

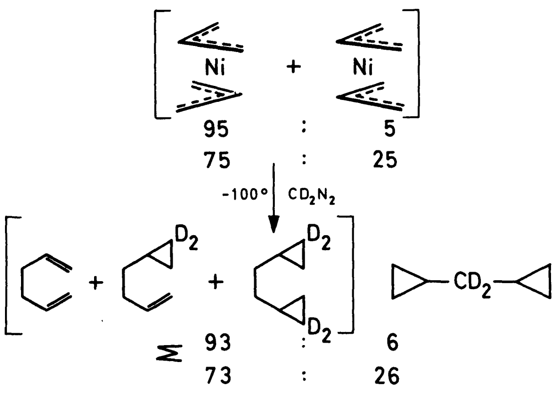


Fig. 25 Reaction of $(\eta^3\text{-}C_3H_5)_2Ni$ with diazomethane

The derivatives of diallyl are formed, after coupling of the allyl groups, by reaction with methylene. Of greater interest is the formation of dicyclopropylmethane which can be explained by the following scheme.

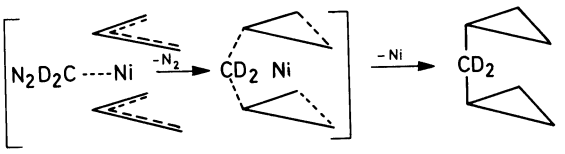


Fig. 26 C-C-coupling by a CD_2-group

These recent experiments using CD_2N_2 show clearly the coupling of CD_2-groups with the meso-carbon atoms.

A neutron defraction analysis of trans-bis- η^3-allylnickel enabled the hydrogen atoms to be localized (14). Furthermore, ab initio calculations at the double-ζ-level have been carried out independently (14) and they both indicate the remarkable fact that the hydrogen atoms do no lie in the plane of the allyl-carbon atoms: The meso- and syn-hydrogen atoms are bent towards the metal atom while the anti-hydrogen atoms are bent away. This structural arrangement causes the total energy of the molecule to be lowered by ~ 45 Kcal.

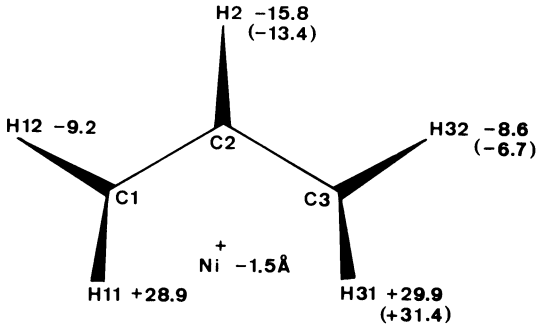


Fig. 27 Angles of hydrogen bonding derived by neutron diffraction and ab initio calculations ( )

All former calculations were based on an assumed planarity.

(η^3-C_3H_5)$_2$Ni contains two latent double bonds within the delocalized allyl groups. These double bonds react with dialkylaluminumhydride even at -78°C. Obviously the complexation causes an enormous activation. If the reaction is carried out with a ratio Ni:Al = 1:2 at -78°C, the primary product seems to be an aluminum substituted nickeldialkyl. The Al-H-stretching band (1764 cm^{-1}) in the IR-spectrum measured at -60°C is no longer observable. Hydrolysis gives ethane and propane (4:2) and no hydrogen.

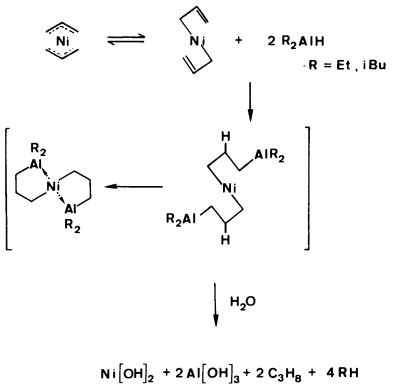
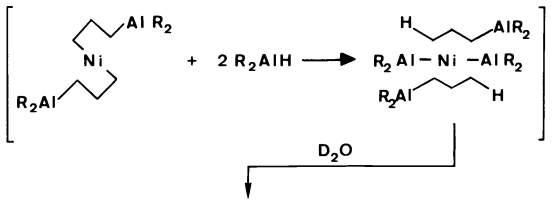


Fig. 28 Addition of R_2AlH to (η^3-C_2H_5)$_2$Ni (2:1) and results of hydrolysis

If the reaction is carried out with a Ni:Al ratio of 1:4 and the product is deuterolized one obtains d_1-ethane, d_1-propane and deuterium = 8:2:1. This can be explained by the following scheme.



$$Ni[OD]_2 + 4\,Al[OD]_3 + 2\,C_3H_7D + 8\,RD + 2\,D_2$$

Fig. 29 Addition of R_2AlH to $(\eta^3\text{-}C_3H_5)_2Ni$ (4:1) and results of deuterolysis

Apparently the Ni-C-bonds formed during the initial addition (Fig. 28) are cleaved in a subsequent reaction with the Al-H-groups to give species having Al-Ni-bonds which have not been identified as such but their existence has been proved indirectly by the deuterolysis which yielded the expected amount of deuterium.

The aim of these investigations was to throw some light on the nature of the interaction between nickel(0) and organoaluminum compounds. These interactions play an important role in catalysis and the experimental results discussed help to understand the "nickel effect".

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