Journal of Organometallic Chemistry, 200 (1980) 349—364
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CONTRIBUTIONS TO HOMOGENEOUS CATALYSIS 1955—1980

G. WILKE

Max-Planck-Institut für Kohlenforschung D-4330 Mülheim a.d. Ruhr (F.R.G.)

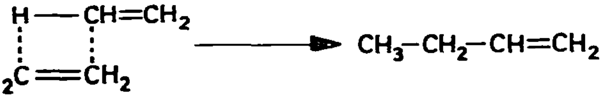
Introduction

Considerable attention has been given in recent years to the topic of research planning. Any meaningful discussion of this theme must be based on an analysis of the question as to the extent to which it is possible or even desirable to plan research. In this context, it would be appropriate to investigate the development of a research area over a longer period and to try to identify those factors and sources of inspiration which have been responsible for the direction it has taken. Bearing this in mind, I intend in this essay to present a survey of our own work during the last twenty-five years and to try, at least for a limited area, to give a partial answer to the question.

In 1953 Ziegler and coworkers discovered the so-called "metallorganische Mischkatalysatoren" [1] which were later termed "Ziegler-catalysts" by Natta [1b]. These were heterogeneous catalysts, formed for example from $TiCl_4$ and Et_2AlCl, suspensions of which were able to convert ethylene into high molecular polyethylene at atmospheric pressure. Soon after this Martin discovered a homogeneous system ($Ti(OC_4H_9)_4 + Al(C_2H_5)_3$) which was able to dimerize ethylene with great facility [2]. Initial experiments indicated, however, that this system did not react with butadiene.

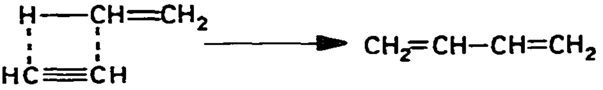
Around this period a global effort was being made to develop rational processes based on ethanol, ethylene, acetylene or butane for the large-scale production of butadiene. The $Ti(OC_4H_9)_4/Al(C_2H_5)_3$ catalyst seemed to me to offer a new possibility. The dimerization of ethylene mentioned above can formally be regarded as proceeding by the addition of a C—H-bond of one ethylene molecule to the C=C-bond of a second.

SCHEME 1



By analogy, ethylene might be expected to codimerize with acetylene to give butadiene.

SCHEME 2

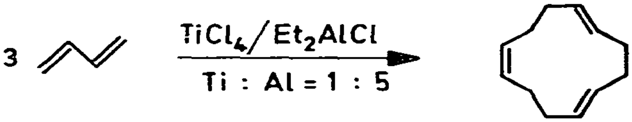


Initial experiments (1955) showed, however, that this homogeneous catalyst causes the conversion of butadiene and isoprene almost exclusively into high molecular weight 1,2-polybutadiene and 3,4-polyisoprene, respectively [3] *.

Cyclooligomerizations

On the basis of these results one could make what at first sight seems to be the rather naive suggestion that perhaps the heterogeneous and homogeneous Ziegler-catalysts react in inverse fashion with ethylene and 1,3-dienes with respect to oligomerization or polymerization and so I next investigated the behaviour of a typical heterogeneous polyethylene catalyst ($TiCl_4$-Et_2AlCl) with butadiene. To my surprise the naive assumption was borne out (1955): butadiene reacted very vigorously to give a liquid product without any rubber-like material. Fortunately at this time my knowledge of the oligomers and polymers of butadiene was very limited; as I discovered later, it had been known for some time by polymer experts that the lower oligomers of butadiene had no commercial value and they had invariably discarded them, whereas I distilled my reaction mixture and obtained a single, previously unknown oligomer whose structure turned out to be that of the twelve-membered ring *trans,trans,cis*-1,5,9-cyclododecatriene. This was the original discovery [5] from which a research area developed which is devoted nowadays mainly to homogeneous catalysis.

SCHEME 3



Around this time I read an article by Hopf [6] in which it was suggested that it would be interesting to synthesize higher polyamides since these might be expected to have properties differing from those of nylon-6, and so be of technical interest. It was obvious that the product of the cyclotrimerization of butadiene is a potentially useful starting material, since it could be converted into lauryl lactam (a precursor of nylon-12) as well as into the 1,12-dicarboxylic acid of dodecane [5b], and, indeed, several large scale processes now operate on this basis: for example, Vestamid ** is a nylon-12 product while Qiana ***

---

* The same observation was made simultaneously and independently by Natta [4].

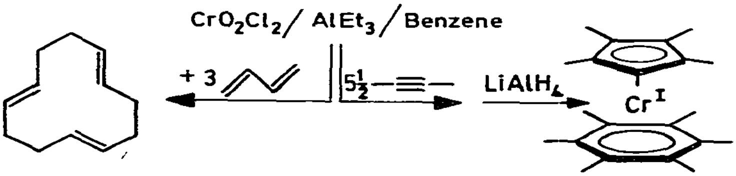
** Chemische Werke Hüls, Marl, F.R.G.

*** E.I. DuPont, U.S.A.

is produced from the C_{12}-dicarboxylic acid and bis(cyclohexylamino)methane.

The mechanism of this highly selective cyclotrimerization reaction was of course of great interest, particularly since we discovered that the reaction was not confined to titanium but that other metals were also active and in some cases led to other isomers. For example, the reaction with $CrO_2Cl_2/AlEt_3$ in benzene produced mainly all-*trans*-1,5,9-cyclodocedatriene [5c,d,7]. The discovery of bis(benzene)chromium by Fischer and Hafner in 1955 [8] encouraged us to look for π-complexes as intermediates in the catalysis, and from experiments involving 2-butyne and the chromium catalyst mentioned above we were able to isolate a complex which we initially identified as bis(hexamethylbenzene)chromium(0) [7]. At a much later date [9], however, we were able to show that this complex should be formulated as (hexamethylbenzene)-(pentamethylcyclopentadienyl)chromium(I), and is the product of a reaction involving the dichotomy of a 2-butyne molecule.

SCHEME 4



The chromium catalyst is thus not only able to cyclotrimerize butadiene and 2-butyne but also to bring about the formal cleavage of a C≡C bond.

Having cyclotrimerized butadiene, we next attempted to develop catalysts capable of cyclodimerizing butadiene to 1,5-cyclooctadiene. We turned our attention to nickel catalysts, since Reppe in 1948 [10] had already shown that acetylene in the presence of nickel acetylacetonate is catalytically converted into cyclooctatetraene, while H.W.B. Reed had shown in 1954 [11] that $Ni(CO)_4$, although a relatively inactive catalyst, is able to convert butadiene into 1,5-cyclooctadiene in 35—40% yield. Our initial attempts were unsuccessful: $NiCl_2/Et_2AlCl$, for example, catalyzes the polymerization of butadiene.

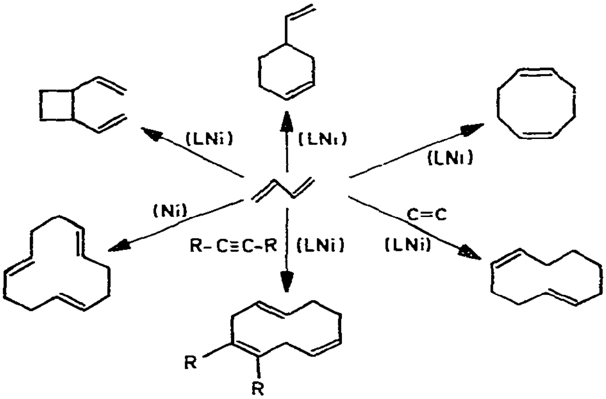
An important breakthrough was made when I turned to an observation which I had made in 1953 [13] during investigations on the so called "nickel effect" [12]. Ziegler and Holzkamp had shown that traces of nickel salts suppress the reaction of ethylene with aluminum triethyl to give higher alkyls of aluminum, and instead the only reaction observed is the dimerization of ethylene to 1-butene [13]. I tried to repeat these experiments using pure ethylene, only to discover that in my hands the catalyst rapidly lost its activity. After some searching, I was able to show that the differences lay in the ethylene which had been used; in the original experiments technical ethylene, which contained 0.3% acetylene, was employed, whereas I had used a highly purified gas. It turned out that acetylene, or alkynes in general, stabilized the nickel catalyst [13]. The successful recipe for generating the cocatalyst was

> "2 g of nickelacetylacetonate are dissolved in 100 ml of benzene and 3.2 g of phenylacetylene added. The mixture is cooled in an ice bath and a solution of 30 g of $AlEt_2OEt$ in 100 ml of benzene is slowly added. A red-orange solution results"

Small amounts of this solution in conjunction with $AlEt_3$ gave a stable catalyst which readily dimerized ethylene.

In 1959 we treated a solution of this co-catalyst at 80°C with butadiene, and the very first experiment led in yields of 90—95% to a mixture of vinylcyclohexene (VCH), 1,5-cyclooctadiene (COD), and all-*trans*-cyclododecatriene (CDT) in the ratio 10 : 25 : 65. Thus for the first time we had in our hands a catalyst capable of converting butadiene into COD (25%), although the high yield of CDT (65%) surprised us [5c,d]. We quickly learned to develop more effective catalysts modified by phosphines and, in particular, phosphites, and were soon able to prepare COD with over 95% selectivity [14,18]; the unmodified catalyst I christened "naked nickel", and this reacted with butadiene to give CDT [15]. Further developments were the isolation of a third dimer *cis*-1,2-divinylcyclobutane in ca. 40% yield [14] and the co-cyclooligomerization of butadiene with olefins or acetylenes to give ten-membered ring systems such as cyclodecadienes [16] and cyclodecatrienes [17], which had up until then been difficult to prepare.

SCHEME 5



These investigations led to the following conclusions:

1) Nickel salts are reduced by organo-main group metal compounds (in particular aluminum alkyls) to "naked nickel", i.e. nickel(0).

2) If the reaction is carried out in the presence of suitable ligands the nickel(0) can be trapped in the form of its complexes.

3) All of the coordination positions on the "naked nickel" are available for the catalytic transformation of substrate molecules (CDT synthesis).

4) Occupation of one coordination position by a ligand molecule e.g. tri-*o*-phenylphenylphosphite, leads to a ligand-nickel catalyst having only three available coordination sites (COD synthesis).

5) The course of the catalytic reaction is dependent on the electronic and, especially, the steric properties of the ligand *.

6) A suitable choice of the reaction conditions enables intermediates in the transformation of 1,3-dienes to be isolated. The characteristic structural feature of these intermediates is the presence of η^3-allyl groups.

---

* This basic principle [18] later found an important application in the ligand controlled hydroformylation [19].

The synthesis of complexes by the method mentioned in 2) has since become a general method for synthesizing transition metal complexes [20]. The first examples of what was, in 1959, a very unusual class of complexes were (all-*trans*-CDT)Ni, $(COD)_2Ni$ and (cyclooctatetraene)nickel(0) [20a–d]. (This last complex has been shown by X-ray crystallography to be more correctly formulated as $(COT)_2Ni_2$ [20d]). Complexes which were isolated later and have special interest include (all-*cis*-CDT)Ni [21], tris(bicycloheptene)Ni [22], tris(*trans*-cyclooctene)Ni [23] and tris(ethylene)Ni [24].

It is appropriate to introduce at this point a historical curiosity: Sabatier describing to the Société Chimique de France how he discovered metal-catalyzed hydrogenation remarked [25], "Le but de nos recherches était d'abord tout différent". He intended, by analogy with the discovery by Mond that nickel reacts with carbon monoxide to give $Ni(CO)_4$, to prepare similar compounds by reacting unsaturated organic molecules such as ethylene with nickel [25]. However, instead of complex formation the reaction that was observed was that of hydrogenation of ethylene to ethane [26]. Another 80 years were to pass before we were able to prepare $Ni(C_2H_4)_3$ [24]. It is also interesting to note that Sabatier and Senderens had to use temperatures above 180°C in order to hydrogenate benzene using a nickel catalyst [26]. A solution of $(COD)_2Ni$ on the other hand readily hydrogenates benzene at 20°C to give cyclohexane (in addition to cyclooctane); in other words "naked nickel" is a highly active hydrogenation catalyst [27].

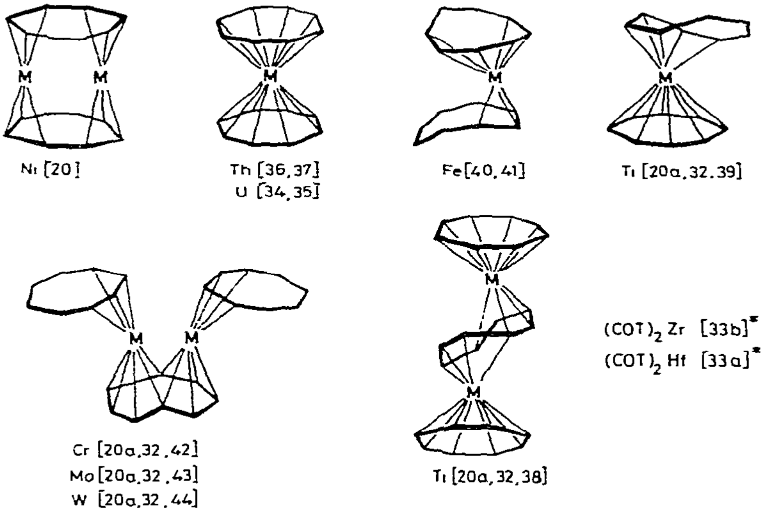
Tetrakis(triphenylphosphine)nickel(0), which can also be prepared by the method outlined above [18 (in situ), 20a,28], later became the subject of a controversy concerning its structure or even its existence [29]. However, recent ^{31}P NMR investigations [30] show without doubt that at low temperatures in solution all four triphenylphosphine molecules are bonded identically through the P-atom to the metal. At room temperature, in solution, dissociation occurs [30,31].

The same synthetic procedure can be used to prepare complexes in which cyclooctatetraene is the only molecule interacting with the metal. In addition to the original complex $(COT)_2Ni_2$, we isolated $(COT)_2Ti$ as well as $(COT)_3Ti_2$, and showed them to have completely different structures [20a,32]. It is probable that related complexes can be prepared from all the transition metals [20a,32,33], particularly if salts of transition metals are treated with Na_2COT [32]. Using this method Streitwieser and Müller-Westerhoff isolated uranocene in 1968 [34]. Its stability is suggested to be a result of the involvement of the *f*-orbitals in the bonding. At least six different types of COT complexes can be distinguished.

The structures of $(COT)_2Ni_2$ and $(COT)_3M_2$ (M = Cr, Mo and W) are particularly interesting, since in these the individual COT molecules interact with two neighbouring metal atoms. One can speculate that a $COTNi_2$-system may play a rôle in Reppe's COT synthesis: the acetylene cyclotetramerizing on the two COT-complexed nickel atoms [45].

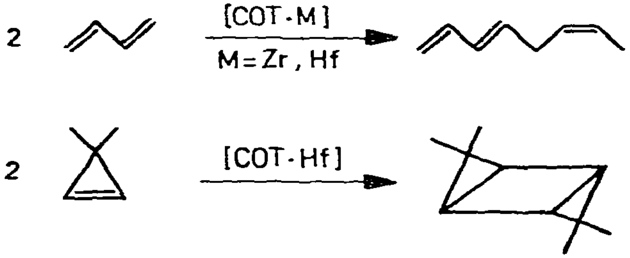
In certain cases COT acts as a ligand, modifying the properties of a catalytic system [33b,45]. For example, (COT)M-systems (where M is Zr or Hf)

SCHEME 6



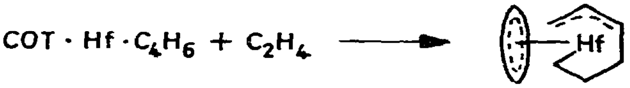
dimerize butadiene and 3,3-dimethylcyclopropene catalytically and stereospecifically to 1,3-*trans*,6-*cis*-octatriene and 3,3,6,6-tetramethyltricyclo(3,1,0,$0^{2,4}$)-hexane, respectively [45].

SCHEME 7



The (COT)M systems (M = Ti, Zr, Hf) are also able to polymerize ethylene in the homogeneous phase. In this case we used as catalysts the (COT)M(C_4H_6) complexes, and of particular interest was the isolation from the reaction involving hafnium of the complex shown in Scheme 8, which can be regarded as being formed in the first step of the polymerization [45].

SCHEME 8



π-Allyl-systems

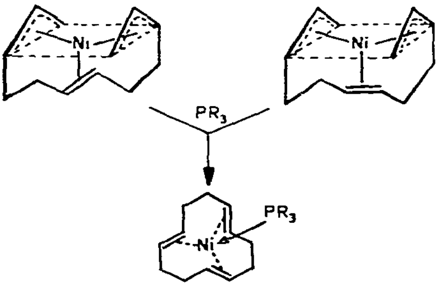
The recognition that allyl systems are formed as intermediates in the catalytic transformation of 1,3-dienes (see Scheme 9) [46] is of fundamental im-

---

* No crystal structure determination has been published.

portance and has had far reaching consequences. We first became aware of the significance of allyl complexes in 1961; the reaction of "naked nickel" with butadiene at −40° C led to formation of a complex having the composition $NiC_{12}H_{18}$, in which a C_{12} chain is bonded to the nickel by π-allyl groups (these are now normally termed η^3-allyl groups). This complex could be recrystallized from liquid butadiene and reacts with PR_3 to give $(CDT)NiPR_3$ [46]. A recent NMR investigation has confirmed that two isomers are present having the following structures [47].

SCHEME 9



These then are the intermediates involved in the "naked nickel" catalyzed cyclotrimerization of butadiene. This successful synthesis of a bis-η^3-allyl-C_{12} nickel complex suggested to us that bis(π-allyl)nickel (i.e. $(\eta^3\text{-}C_3H_5)_2Ni$) might well be isolable. We therefore treated $NiBr_2$ with C_3H_5MgCl in ether and obtained a discouragingly black mixture very suggestive of decomposition; however, the ether which we distilled off was bright yellow, and from it we isolated bis(π-allyl)nickel as a yellow volatile solid having a melting point of +1° C. This complex is the prototype of the "pure" transition metal allyls * [48].

At this time (1961) a few metal-allyl complexes were known, e.g. $(C_3H_5PdCl)_2$ [49], $(C_3H_5NiBr)_2$ [50], $C_3H_5Co(CO)_3$ [51], $C_3H_5Mn(CO)_4$ [52] as well as $C_3H_5MC_5H_5$ (M = Ni, Pd) [52], but these invariably involved cyclopentadienyl groups, carbon monoxide, or halogen atoms in addition to the allyl group. We were able to show that many of the transition metals were able to form "pure" allyl-metal complexes although, many, such as $(\eta^3\text{-}C_3H_5)_3Co$, could only be synthesized and manipulated at −60° C to −80° C. The "pure" transition metal allyl complexes are highly reactive and most of them are catalytically active (see below). A general classification was made many years later on the basis of an IR and ^1H NMR spectroscopic study of the complexes of zirconium and hafnium [54]. Three categories, each involving two possibilities, can be distinguished: 1a) π-dynamic, 1b) π-static; 2a) σ-dynamic, 2b) σ-static; 3a) π- and σ-dynamic, 3b) π- and σ-static [54]. By making allowance for the energies involved, this classification accounts for the various spectra observed.

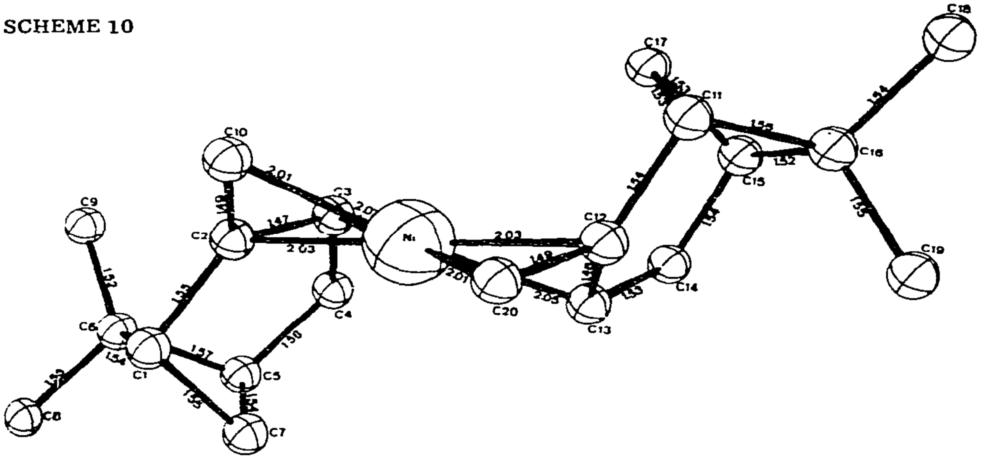
Substitution of the allyl group can lead to a considerable stabilization [47], and in individual cases, e.g. bis(π-methallyl)nickel [55], the structures have

---

* The term isoleptic has also been used, and in this case denotes complexes in which the only groups attached to the metal atom are allyl groups.

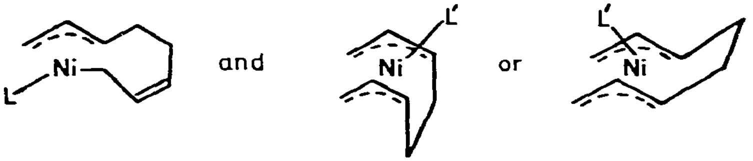
been confirmed crystallographically. Of particular interest is the structure of the optically active bis(π-pinenyl)nickel [56].

SCHEME 10



Recently we have conducted a systematic study of the 1 : 1 adducts formed by the bis(π-allyl)metal complexes of Ni, Pd and Pt with PR_3 ligands [57], since complexes of this type, viz. $C_8H_{12}NiPR_3$, are believed to be involved as intermediates in the cyclodimerization of butadiene [58]. The following intermediates have been isolated and characterized by NMR spectroscopy [58], and their structures shown to be dependent upon the nature of the ligand R_3P.

SCHEME 11



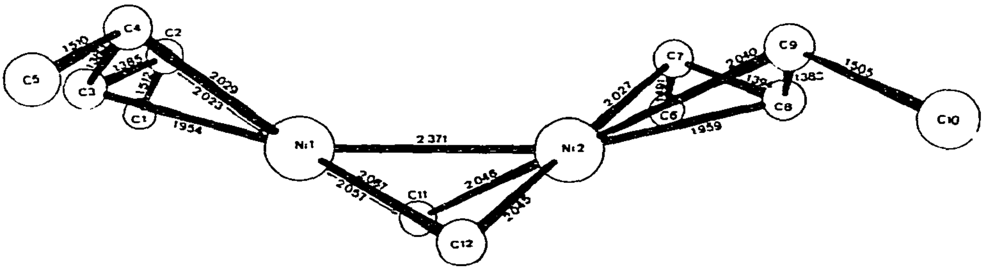
L = $P(C_6H_{11})_3$

L′ = $P(C_6H_5)_3$

The properties of the ligand involved dictate whether a π-allyl, σ-allyl or a bis-π-allyl arrangement is adopted. As in the case of the cyclotrimerization reaction, intermediates are formed having terminal η^3-allyl or η^1-allyl groups.

The (η^3-allylNiCH$_3$)$_2$ complexes can be regarded as models for these systems. The complex $(\eta^3\text{-}C_3H_5NiCH_3)_2$ is thermally unstable and has been prepared only at —100°C [59]. In contrast, $(\eta^3\text{-}1,3\text{-}(CH_3)_2C_3H_3NiCH_3)_2$ is considerably more stable and its structure has been studied by X-ray crystallography [50].

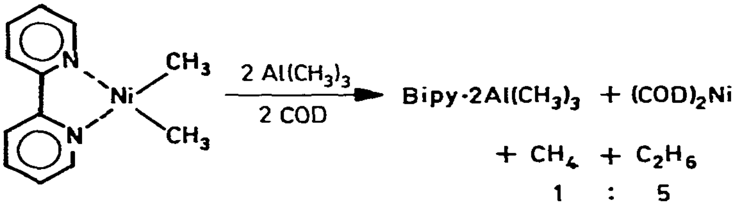
SCHEME 12



The molecule is dimeric. The methyl groups bridge the nickel atoms to give electron deficient bonds of the type familiar from $(\text{Al}(\text{CH}_3)_3)_2$. In this case the methyl groups on the allyl fragment lead to a remarkable increase in stability. A similar effect has been observed for bis(trityl)nickel [61], which is stable even at 100—120°C.

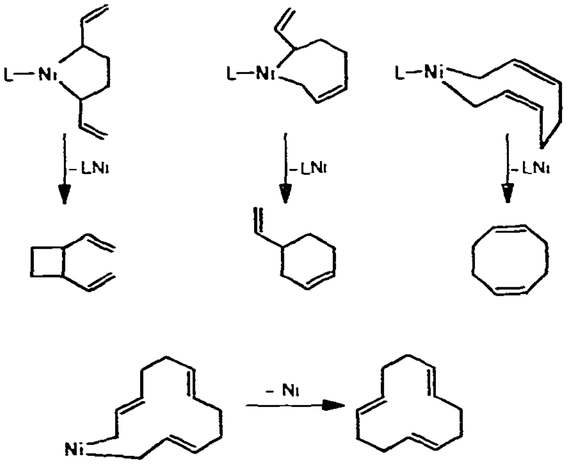
The evidence available indicates that the intermediates discussed above are involved in the catalytic cycles. However, no definite proof exists for this assumption since these isolable species may well be the products of side-reactions. Without discussing this possibility further, we should mention that it is probable that additional intermediates are involved, and by analogy with the reductive elimination of ethane from dipyridyl nickel dimethyl (Scheme 13) [62] I

SCHEME 13



assume that the final step in the catalytic cycles, in which C—C bond formation occurs, proceeds through a bis(η^1-allyl)metal system.

SCHEME 14

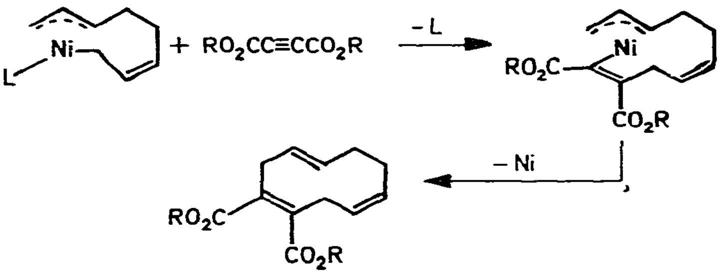


This suggestion is supported, e.g., by the isolation by Binger et al. of metallacyclopentanes from the cyclodimerization of strained olefins such as 3,3-dimethylcyclopropene [63]. Intermediates have also been isolated in the following cases [64] and [65] (Schemes 15 and 16).

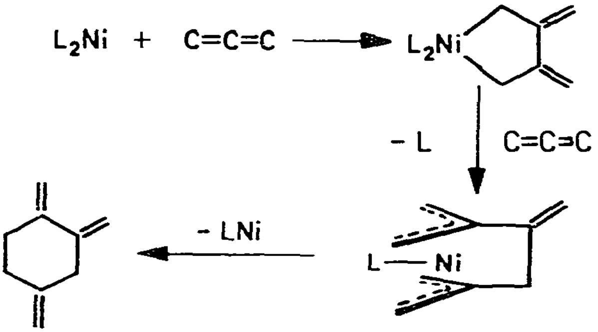
It is appropriate to mention here two features which are characteristic of these systems:

a) the catalytic cycles involve repeated changes in the formal oxidation state of the metal atom e.g. $\text{Ni}^0 \rightleftharpoons \text{Ni}^{II}$, $\text{Cr}^I \rightleftharpoons \text{Cr}^{III}$, perhaps $\text{Ti}^{II} \rightleftharpoons \text{Ti}^{IV}$, $\text{Zr}^{II} \rightleftharpoons \text{Zr}^{IV}$, $\text{Hf}^{II} \rightleftharpoons \text{HF}^{IV}$ [5d,53a,33b,45]. In other words, the catalysis proceeds by

SCHEME 15



SCHEME 16

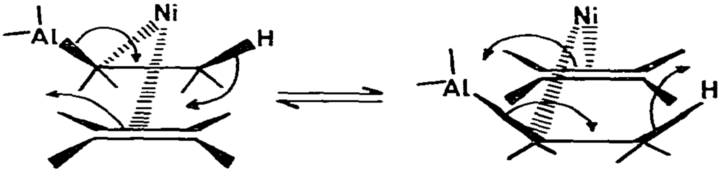


repeated oxidative addition and reductive elimination.

b) The reactions are multi-step processes involving a number of intermediates and do not have a concerted mechanism [58b]. The concept propagated by Mango [66] of a "forbidden to allowed" catalysis, involving the direct application of the Woodward-Hoffmann rules, is not applicable. As far as I am aware no completely convincing example of a concerted process of this nature is known.

The organonickel chemistry which I have developed above has its origin in the "nickel effect". One of the more pleasing results is that the investigations have also led to an explanation of this effect [13b]. We believe that an electrocyclic process is involved in which an olefin is complexed to a nickel(0) atom which also interacts with an aluminum trialkyl from which a β-H-atom transfer occurs.

SCHEME 17



Recent observations include the following: The presence of a complex of the type shown in Scheme 17 cannot be detected at −50°C in the ^{1}H NMR spectrum of a 1 : 1 mixture of $Ni(C_2H_4)_3$ and $Al(C_2H_5)_3$ in toluene-d_8, presumably because the stationary concentration is too small. On addition of C_2D_4 the spectra show that replacement of C_2H_4 by C_2D_4 in the nickel complex occurs without the $Al(C_2H_5)_3$ being involved. At 0°C H- and D-atoms are statistically exchanged both in the complexed ethylene and free ethylene as well as in the ethyl groups of the $Al(C_2H_5)_3$, demonstrating that the "nickel effect" in the sense shown above is operating even at this temperature [67]. It should be mentioned here that organometallic compounds having strongly polar M—C bonds, such as lithium phenyl, react with nickel(0) to give isolable complexes with electron deficient bonds. One of the most interesting examples is $((C_6H_5Li)_6Ni_2N_2(ether)_2)_2$ discovered by Jonas, which contains side-on bonded dinitrogen molecules [68].

Our formulation of the cyclooligomerization of butadiene as proceeding through π-allyl intermediates [46] was carried over to the transition metal catalyzed polymerization of 1,3-dienes [69] and, for example, Natta et al. in 1964 suggested a mechanism involving π-allyl intermediates for the π-allylnickel bromide catalyzed polymerization of butadiene [70].

I have already mentioned that the "pure" transition metal allyl complexes are active catalysts [71]. Bis(π-allyl)nickel reacts with butadiene with displacement of hexadiene (reductive elimination) to give "naked nickel" which reacts further with butadiene to give $(C_{12}H_{18})Ni$ (oxidative addition) or, at higher temperatures, the product of catalytic cyclotrimerization [46]. At least in this case the "pure" allyl-metal complex acts as a source of naked metal atoms. In the hope that other "pure" transition metal allyls might also act as the naked metal, we investigated their catalytic activity with butadiene. The results are shown in Scheme 18 [53,71].

SCHEME 18

Catalyst	Reaction Products from Butadiene
NiA_2	all-trans-1.5.9-Cyclododecatriene
PdA_2	$(C_{12}H_{18}) \xrightarrow{H_2}$ n-Dodecane
PtA_2	no reaction
CoA_3	5-Methyl-1.3.6-heptatriene
FeA_3	Oligomers C_8-C_{36} and >
CrA_3	1.2-Polybutadiene
MoA_4	no reaction
WA_4	no reaction
ZrA_4	Oligomers and Polymers
HfA_4	Oligomers and Polymers
ThA_4	Traces of n-Decatrienes

Selective behaviour is observed only in the case of Ni, Pd, Co, and Cr. The remaining metals showed some catalytic activity but did not lead to uniform products.

In some cases we observed a dramatic change in the catalytic behaviour if one allyl group was replaced by a halide or a complex anion [53,71].

SCHEME 19

Catalyst	Reaction Products from Butadiene
ANiX	1.4-*cis*-Polybutadiene
ANiBr	1.4-*trans*-Polybutadiene (70)
A_2CoJ	1.4-*cis*-Polybutadiene
A_2CrJ	1.5.9-Cyclododecatriene

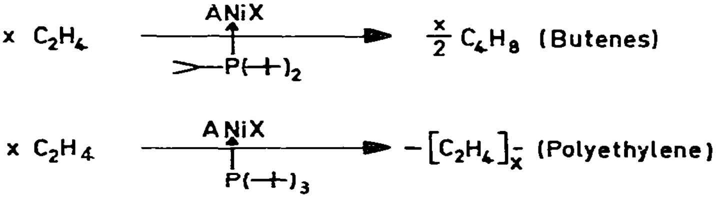
A = C_3H_5

These investigations led us to the discovery that transition metal allyls are able to catalyze reactions involving monoolefins [71]. Particularly interesting was the observation made in 1963 that tris(π-allyl)chromium acts as a homogeneous catalyst (15 atm, 20°C) for the conversion of ethylene into high molecular weight linear polyethylene [71a,b]. This was the first example of a catalyst of a type completely different from the standard Ziegler-catalysts: a) it consists only of an organo-transition metal compound without a second component (aluminum alkyl), b) it contains no halide and c) it is active in the homogeneous state. These advantages seemed to be so great that a Japanese firm intended to produce polyethylene on a large scale using tris(π-allyl)chromium as catalyst. A few years later (from 1968) Ballard was able to show that other "pure" organo-transition metal compounds can also be used as polymerization catalysts [72].

Steering of catalytic reactions

The allylNiX systems, mentioned above, turned out to be effective not only for the polymerization of 1,3-dienes [71a] but also to be highly active catalysts for the dimerization of ethylene and propylene [71a,73]. Here again, as in the case of the cyclooligomerization, the addition of phosphines having different electronic and in particular steric properties allowed the direction of reaction to be altered at will [71a,73,45]. This is illustrated below for ethylene.

SCHEME 20



The reaction takes a completely different course in the presence of a catalyst involving tri-tert-butylphosphine instead of isopropyl-di-tert-butylphosphine, even though these ligands differ only by one methyl group in the substituents [45,74]. This is presumably a steric effect associated with the bulky nature of the ligand: β-H-elimination, which in the ethylene dimerization leads to butene, is suppressed, and instead polymerization occurs.

A similar phosphine effect is observed for the dimerization of propylene [73,45]:

SCHEME 21

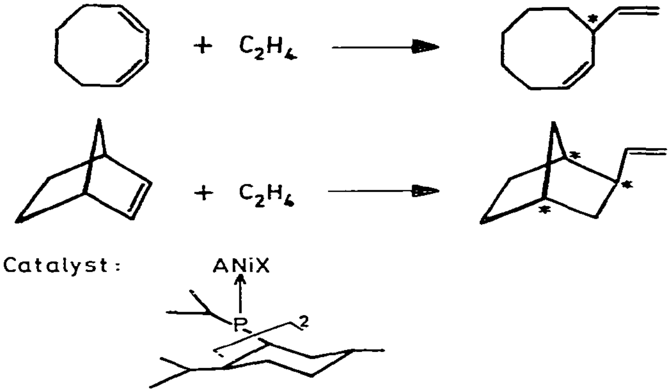
Catalyst ANiX·L	Reaction Temperature	n-Hexenes	Methyl-pentenes	2.3-Dimethyl-pentenes
L =	°C	%	%	%
$P(C_6H_5)_3$	-20	21.6	73.9	4.5
$t\text{-}C_4H_9P(i\text{-}C_3H_7)_2$	+20	3.8	35.6	60.6
	-20	~ 0.1	19.0	80.9
	-60	~ 0.1	3.5	96.4

$A = C_3H_5$

The activity of this catalyst system is quite amazing. One method of carrying out the catalytic propylene dimerization is to bubble the gaseous propylene into the catalyst solution at —20° C with intensive stirring and cooling. Under these conditions the catalyst has a high activity (3—6 kg product/gNi/h). However, recently it has become clear that this value is much too low and is associated with the design of the experiment. The actual activity has been measured using, for example, 5 μmol of catalyst in 100 ml C_6H_5Cl and 300 g of liq. propylene and a reaction temperature of —75 to —55° C. As expected, the amount of propylene converted doubled for every 10° C rise in temperature, and at —55° C 600 kg of product/gNi/h was formed. Extrapolation to —20° C would give a value of ca. 6000 kg/gNi/h; in other words the activity of the catalyst is about 1000 times as high as we had originally supposed. This catalyst system is at the moment the most active organometallic catalyst known, and its activity can be compared to that of the enzymes [45,75].

The extremely high activity of this system even at low temperatures, combined with the ability to direct the course of reaction by adding ligand molecules, led us to investigate the use of this system in asymmetric synthesis. Catalytic asymmetric synthesis is probably the most sophisticated area of homogeneous catalysis. We began to interest ourselves in this field in about 1966. Initially, following experiments by Akabori [76] who used palladium on silk as a catalyst, we had in mind the possibility of using heterogeneous catalysts such as a Ziegler-catalyst deposited on finely ground optically-active quartz. However, the first experiments were actually carried out using homogeneous catalysts modified by phosphines having optically active substituents such as tris(myrtanyl)phosphine. In 1968 two publications appeared independently from Knowles et al. [77] and Horner et al. [78] describing the use of Wilkinson's catalyst modified by Horner-phosphines $P(R^1R^2R^3)$ in asymmetric hydrogenation. The chiral centre is introduced upon formation of a C—H-bond. Twelve years later, it is almost impossible to survey all of the very many publications devoted to the topic of asymmetric hydrogenation. Our work had a somewhat different objective and we were able for the first time to form new chiral centres catalytically as the result of C—C-bond formation. As a new approach we modified the catalysts by using phosphines containing optically active substituents [79] instead of Horner-phosphines which are not easy to prepare. For example, the allylNiX system mentioned above was modified with isopropyldimenthylphosphine and used in the cooligomerisation of olefins. We achieved the best results with the following systems [80]:

SCHEME 22



The optical yield (e.e.) was found to increase on decreasing the reaction temperature and could be as high as 60—80%. From the temperature dependence of the activation energy a $\Delta\Delta E^*$ value of 1—1.5 kcal/mol has been calculated for the formation of the enantiomers [80]. A basic difference between the mechanism of the hydrogenation mentioned above (C—H-formation) and this cooligomerization reaction (C—C-formation) should be mentioned: recent experiments [81] have shown that during the hydrogenation the prochiral substrate coordinates to the chiral catalyst through two positions (C=C and C=O) and is then converted into the optically active product. In our case this is not possible and coordination involves only the C=C-bond. The same applies to the phosphines used to induce optical activity; hydrogenation occurs in the presence of a chelating diphosphine while we use monophosphines. It is therefore somewhat surprising that in spite of the less optimal reaction conditions, we are able to obtain such high optical induction.

Let me finally return to the remark that I made at the beginning of this essay concerning planned research. I believe that it is clear from the development of our own work that although the individual observations which led to the discovery of new areas were made during the course of systematic investigations, they had little direct relevance to the original objective. The major breakthroughs were, however, in all cases made during the course of experiments in the laboratory. Once a new field is opened up, its further development is, to a certain extent, foreseeable, although even in this case flexibility to take advantage of the unexpected is essential. Any attempt to programme fundamental discoveries is of course a contradictio in adjecto.

References

1 a) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, Angew. Chem., 67 (1955) 541, 426; b) G. Natta, Ital. Pat., 535, 712.

2 H. Martin, Angew. Chem., 68 (1956) 306.

3 G. Wilke, Angew. Chem., 68 (1956) 306.

4 G. Natta, Makromol. Chem., 16 (1955) 213, 232.

5 a) Studiengesellschaft Kohle mbH, Erf. G. Wilke, Prior.: 23.2.1956; b) G. Wilke, Angew. Chem., 69 (1957) 397; c) H. Breil, P. Heimbach, M. Kröner, H. Müller and G. Wilke, Makromol. Chem., 69 (1963) 18; d) G. Wilke u.a., Angew. Chem., 75 (1963) 10.

6 H. Hopf u.a., Die Polyamide, Springer-Verlag, Berlin, 1954, p. 31.

7 G. Wilke and M. Kröner, Angew. Chem., 71 (1959) 574.

8 E.O. Fischer and W. Hafner, Z. Naturforsch., 10b (1955) 665.

9 H. Benn, G. Wilke and D. Henneberg, Angew. Chem., 85 (1973) 1052; Angew. Chem. Int. Ed., 12 (1973) 1001.

10 W. Reppe, O. Schlichting, K. Klager and T. Toepel, Liebigs Ann. Chem., 560 (1948) 1.

11 H.W.B. Reed, J. Chem. Soc., London (1954) 1931.

12 K. Ziegler, Brennstoff-Chemie, 35 (1954) 321.

13 a) K. Ziegler, H.-G. Gellert, E. Holzkamp, G. Wilke, E.W. Duck and W.-R. Kroll, Liebigs Ann. Chem., 629 (1960) 172; b) K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem., 85 (1973) 1002; Angew. Chem. Int. Ed., 12 (1973) 943.

14 W. Brenner, P. Heimbach, Hj. Hey, E.W. Müller and G. Wilke, Liebigs Ann. Chem., 727 (1969) 161.

15 B. Bogdanović, P. Heimbach, M. Kröner, G. Wilke, E.G. Hoffmann and J. Brandt, Liebigs Ann. Chem., 727 (1969) 143.

16 P. Heimbach and G. Wilke, Liebigs Ann. Chem., 727 (1969) 183.

17 W. Brenner, P. Heimbach and G. Wilke, Liebigs Ann. Chem., 727 (1969) 194.

18 G. Wilke and E.W. Müller, DB Pat. 1 140 930, Prior.: 22.12.1959.

19 L.H. Slaugh and R.R. Mullineaux, U.S. Pat. 3 239 569, 3 239 570, Prior.: 29.7.1960.

20 a) G. Wilke, E.W. Müller, M. Kröner, P. Heimbach and H. Breil, DB Pat. 1 191 375, Prior.: 28.4.1960. b) G. Wilke, Angew. Chem., 72 (1960) 581; c) B. Bogdanović, M. Kröner and G. Wilke, Liebigs Ann. Chem., 699 (1966) 1; d) D.J. Brauer and C. Krüger, J. Organometal. Chem., 122 (1976) 265.

21 K. Jonas, P. Heimbach and G. Wilke, Angew. Chem., 80 (1968) 1033; Angew. Chem. Int. Ed., 7 (1968) 949.

22 K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem., 85 (1973) 1002; Angew. Chem. Int. Ed., 12 (1973) 943.

23 K. Jonas, Dissertation, Bochum, 1968.

24 K. Fischer, K. Jonas and G. Wilke, Angew. Chem., 85 (1973) 620; Angew. Chem. Int. Ed., 12 (1973) 565.

25 P. Sabatier, Bull. Soc. Chim. France, (1939) 1261.

26 P. Sabatier and J.-B. Senderens, Comp. Rend., 124 (1897) 616, 1358.

27 M. Kröner, Dissertation, Aachen, 1961.

28 G. Wilke, E.W. Müller and M. Kröner, Angew. Chem., 73 (1961) 33.

29 a) C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956; b) C.A. Tolman, W.C. Seidel and D.H. Gerlach, J. Amer. Chem. Soc., 94 (1972) 2669, 2675; c) C.A. Tolman, W.C. Seidel and L.W. Gosser, J. Amer. Chem. Soc., 96 (1974) 53; d) C.A. Tolman, D.W. Reutter and W.C. Seidel, J. Organometal. Chem., 117 (1976) C30; e) Ph.E. Garrou and G.E. Hartwell, Inorg. Chem., 15 (1976) 730.

30 R. Mynott, A. Mollbach and G. Wilke, J. Organometal. Chem. 199 (1980) 107.

31 P. Heimbach, Angew. Chem., 76 (1964) 586; Angew. Chem. Int. Ed., 3 (1964) 648.

32 H. Breil and G. Wilke, Angew. Chem., 78 (1966) 942; Angew. Chem. Int. Ed., 5 (1966) 898.

33 a) H.-J. Kablitz, R. Kallweit and G. Wilke, J. Organometal. Chem., 44 (1972) C49; b) H.-J. Kablitz and G. Wilke, J. Organomet. Chem., 51 (1973) 241.

34 A. Streitwieser, jr., and U. Müller-Westerhoff, J. Amer. Chem. Soc., 90 (1968) 7364.

35 A. Zalkin and K.N. Raymond, J. Amer. Chem. Soc., 91 (1969) 5667.

36 A. Streitwieser, jr., and N. Yoshida, J. Amer. Chem. Soc., 91 (1969) 7528.

37 A. Avdeef, K.N. Raymond, K.O. Hodgson and A. Zalkin, Inorg. Chem., 11 (1972) 1083.

38 H. Dierks and H. Dietrich, Acta Crystallogr. B, 24 (1968) 58.

39 H. Dietrich and M. Soltwisch, Angew. Chem., 81 (1969) 785; Angew. Chem. Int. Ed., 8 (1969) 765.

40 A. Carbonaro, A. Greco and G. Dall'Asta, Tetrahedron Lett., (1967) 2037.

41 G. Allegra, A. Colombo and E.R. Mognaschi, Gazz. Chim. Ital., 102 (1972) 1060.

42 D.J. Brauer and C. Krüger, Inorg. Chem., 15 (1976) 2511.

43 F.A. Cotton, S.A. Koch, A.J. Schultz and J.M. Williams, Inorg. Chem., 17 (1978) 2093.

44 F.A. Cotton and S.A. Koch, J. Amer. Chem. Soc., 99 (1977) 7371.

45 a) G. Wilke in: M. Tsutsui (Ed.), Fundamental Research in Homogeneous Catalysis, Vol. 3, Plenum Press, New York and London, 1979, p.1; b) G. Wilke, Pure and Appl. Chem., 50 (1978) 677.

46 G. Wilke, M. Kröner and B. Bogdanović, Angew. Chem., 73 (1961) 755.

47 B. Henc, P.W. Jolly, R. Salz, G. Wilke, R. Benn, E.G. Hoffmann, R. Mynott, G. Schroth, K. Seevogel, J.C. Sekutowski and C. Krüger, J. Organometal. Chem., 191 (1980) 425.

48 G. Wilke and B. Bogdanović, Angew. Chem., 73 (1961) 756.

49 J. Smidt and W. Hafner, Angew. Chem., 71 (1959) 284.

50 E.O. Fischer and G. Bürger, Z. Naturforsch., 16b (1961) 77.

51 R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 82 (1960) 750.

52 W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, J. Amer. Chem. Soc., 83 (1961) 1601.

53 a) G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, Angew. Chem., 78 (1966) 157; Angew. Chem. Int. Ed., 5 (1966) 151; b) G. Wilke, DB Pat. 1 190 939, Prior.: 18.4.1962, there NiA_2, PdA_2, PtA_2, CoA_3, FeA_3, CrA_3, Mo_2A_4, WA_4, VA_3, ZrA_4 ($A = C_3H_5$).

54 E.G. Hoffmann, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle and G. Wilke, J. Organometal. Chem., 87 (1975) 183.

55 H. Dietrich and R. Uttech, Naturwissenschaften, 50 (1963) 613, Z. Kristallogr., 122 (1965) 60.

56 B. Henc, H. Pauling, G. Wilke, C. Krüger, G. Schroth and E.G. Hoffmann, Liebigs Ann. Chem., (1974) 1820.

57 B. Henc, P.W. Jolly, R. Salz, S. Stobbe, G. Wilke, R. Benn, R. Mynott, K. Seevogel, R. Goddard and C. Krüger, J. Organometal. Chem., 191 (1980) 449.

58 a) P.W. Jolly, I. Tkatchenko and G. Wilke, Angew. Chem., 83 (1971) 329; Angew. Chem. Internat. Ed., 10 (1971) 329; b) B. Barnett, B. Büssemeier, P. Heimbach, P.W. Jolly, C. Krüger, I. Tkatchenko and G. Wilke, Tetrahedron Lett., (1972) 1457; c) B. Büssemeier, Dissertation, Bochum, 1973.

59 B. Bogdanović, H. Bönnemann and G. Wilke, Angew. Chem., 78 (1966) 591; Angew. Chem. Int. Ed., 5 (1966) 582.

60 a) H. Schenkluhn, Dissertation, Bochum, 1971; b) C. Krüger, J.C. Sekutowski, H. Berke and R. Hoffmann, Z. Naturforsch., 33b (1978) 1110.

61 G. Wilke and H. Schott, Angew. Chem., 78 (1966) 592; Angew. Chem. Int. Ed., 5 (1966) 583.

62 G. Wilke and G. Herrmann, Angew. Chem., 78 (1966) 591; Angew. Chem. Int. Ed., 5 (1966) 581.

63 P. Binger, M.J. Doyle, J. McMeeking, C. Krüger and Y.-H. Tsay, J. Organometal. Chem., 135 (1977) 405.

64 B. Büssemeier, P.W. Jolly and G. Wilke, J. Amer. Chem. Soc., 96 (1974) 4726.

65 M. Englert, P.W. Jolly and G. Wilke, Angew. Chem., 84 (1972) 120; Angew. Chem. Int. Ed., 11 (1972) 136.

66 a) F.D. Mango, Adv. Catal. 20 (1969) 291; b) F.D. Mango, Tetrahedron Lett., (1969) 4813.

67 A. Mollbach and G. Wilke, unpublished.

68 a) K. Jonas, Angew. Chem., 85 (1973) 1050; Angew. Chem. Int. Ed., 12 (1973) 997; b) C. Krüger and Y.-H. Tsay, Angew. Chem., 85 (1973) 1051; Angew. Chem. Int. Ed., 12 (1973) 998.

69 G. Henrici-Olivé, S. Olivé and E. Schmidt, J. Organometal. Chem., 39 (1972) 201.

70 L. Porri, G. Natta and M.C. Gallazzi, Chim. Ind. (Milan), 46 (1964) 428.

71 a) Studiengesellschaft Kohle mbH Erf.: G. Wilke, U.S. Pat. 3 379 706, Prior.: 10.8.1963; b) W. Oberkirch, Dissertation, Bochum, 1963.

72 D.G.H. Ballard, W.H. Janes and T. Medinger, J. Chem. Soc. B, 1968, 1168.

73 B. Bogdanović and G. Wilke, Brennstoff-Chemie, 49 (1968) 323.

74 a) B. Bogdanović, H.-G. Karmann and G. Wilke, unpublished; b) H.-G. Karmann, Dissertation, Bochum, 1970.

75 B. Bogdanović, B. Spliethoff and G. Wilke, Angew. Chem., in press.

76 S. Akabori, S. Sakurai, Y. Izumi and Y. Fujii, Nature, 178 (1956) 323.

77 W.S. Knowles and M.J. Sabacky, Chem. Commun., (1968) 1445.

78 a) L. Horner, H. Büthe and H. Siegel, Tetrahedron Lett., (1968) 4023; b) L. Horner, H. Siegel and H. Büthe, Angew. Chem., 80 (1968) 1034; Angew. Chem. Int. Ed., 7 (1968) 942.

79 a) B. Bogdanović, B. Henc, H.-G. Karmann, H.-G. Nüssel, D. Walter and G. Wilke, Ind. Engng. Chem., 62, No. 12 (1970) 35; b) DB Pat. 2 039 125, Studiengesellschaft Kohle mbH, Erf.: B. Bogdanovič, H. Pauling and G. Wilke, Prior.: 6.8.1970.

80 B. Bogdanović, B. Henc, A. Lösler, B. Meister, H. Pauling and G. Wilke, Angew. Chem., 85 (1973) 1013; Angew. Chem. Int. Ed., 12 (1973) 954.

81 J. Halpern, Trans. Amer. Cryst. Assoc., 14 (1978) 59.