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Cationic nickel and palladium complexes with bidentate ligands for the C–C linkage of olefins

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Dedicated to Professor Wilhelm Keim on the occasion of his 65th birthday

Contents

Abstract

Cationic complexes of late transition metals with multidentate ligands have recently been found to catalyze various novel homo- and copolymerization reactions of olefins. In this

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context, preparative routes to cationic nickel and palladium complexes and corresponding in situ preparations of catalysts have been developed. These recent advances are reviewed (229 references). © 2000 Elsevier Science S.A. All rights reserved.

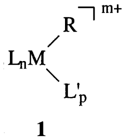
Keywords: Catalysis; Olefin polymerization; Cationic late transition metal complex; Bidentate ligand; Nickel; Palladium

Nomenclature

Ar	aryl
Ar^F	aryl group containing fluoro-atoms
$BAr_4^{F\,-}$	tetrakis{3,5-bis(trifluoromethyl)phenyl}borate anion
bipy	2,2′-bipyridyl
Bz	benzyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
dba	dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one
dippe	1,2-bis(diisopropylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
en	1,2-diaminoethane
L ^ L	bidentate ligand (coordinating via both donors)
MAO	methylalumoxane
Mes	mesityl = 2,4,6-$Me_3C_6H_2$–
OTf^-	triflate = $CF_3SO_3^-$
OTs^-	*p*-toluenesulfonate = *p*-CH_3–C_6H_4–SO_3^-
phen	1,10-phenantroline
py	pyridine
r.t.	room temperature
terpy	2,2′:6′,2″-terpyridine
tht	tetrahydrothiophene
tmeda	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
TO	turnovers = mol substrate converted/mol metal

1. Introduction

In catalysis with transition metal complexes, insertion-type C–C linkage of olefins resulting in formation of oligomers or polymers represents one of the most important reactions. Thus, olefin polymerization with metallocene catalysts [1] has been subject to immense research efforts over the past years. The nickel catalyzed Shell Higher Olefin Process for the oligomerization of ethylene to linear α-olefins is currently applied on a scale of nearly 1 million tons per year [2]. As a recent development, polymerization of olefins to high molecular weight polymers by late transition metal complexes is finding strong attention [3]. The latter reactions, namely the vinyl-type (to distinguish from metathesis reactions) homo- and copolymerization of monoolefins, are most often performed with nickel or palladium catalysts. Other metals have also been applied [4], and very recently highly active ethylene polymerization catalysts based on iron or cobalt complexes have been reported [5]. Mechanistically, these reactions are generally assumed to involve migratory insertion in alkyl–olefin complexes as the C–C linkage reaction step, as illustrated by a simplified representation of ethylene polymerization (Scheme 1).



L = group V or VI donor 'controlling' ligand
L' = weakly coordinating ligand stabilizing catalyst precursor
m ≥ 0 (neutral or cationic complex)

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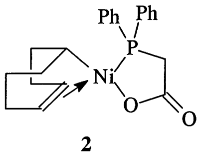

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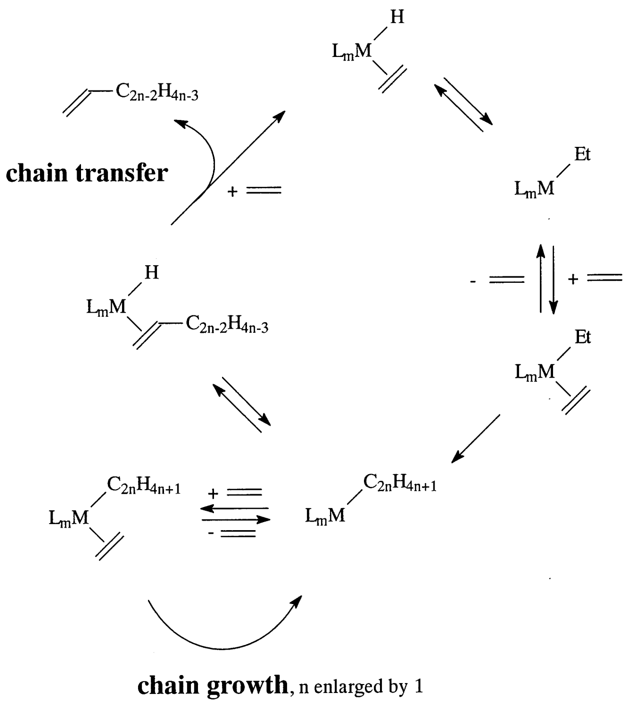
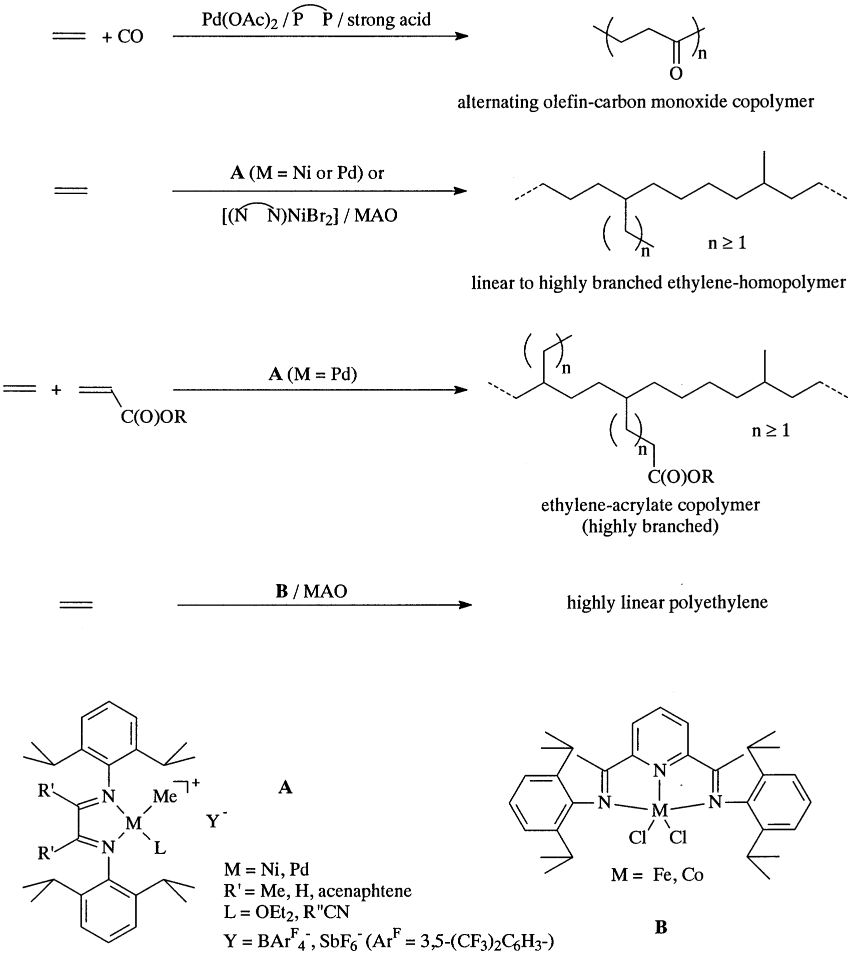


Scheme 1. Mechanism of ethylene polymerization by late transition metal complexes (simplified scheme; isomerization excluded).

Most often the catalysts employed contain ligands with Group V or VI donors, which coordinate not only in the catalyst precursor, but also in the active species, in contrast to ligands merely intended to stabilize the catalyst precursor. For this reason, they have been termed ‘spectator ligands’, though they are of course far from being passive ‘spectators’ but control catalyst selectivity and activity via steric and electronic interactions; therefore the term ‘controlling’ ligand may be more appropriate. This concept is illustrated by the general structure **1** of an organometallic complex suited as a single-component catalyst precursor. In addition to the ‘controlling’ ligands L and the ‘stabilizing’ ligands L′, it features a formally monoanionic ligand R bound to the metal via a carbon atom, which enables facile entry into the catalytic cycle (e.g. R = alkyl). To allow for facile removal from the metal center, e.g. by displacement by coordination of olefin monomer, L′ will most often be neutral, whereas L may also have a formal (anionic) charge. Depending on its electronic configuration, which can be translated to formal charges of the ligands and the oxidation state of the metal center, the entire complex will obviously be neutral or (cationically) charged. An example of a neutral nickel(II) complex is provided by **2**, prepared by Keim and coworkers [6] as a precursor for olefin oligomerization. The ‘controlling’ ligand in **2** is a formally monoanionic P,O-chelate. In terms of the general structure **1**, the stabilizing ligand L′ in **2** is the olefinic function, which is covalently linked to the R group in this case. It should be noted that the above considerations regarding the charge of the precursor complex also apply to the metal species involved in the mechanism in Scheme 1, the R group being replaced by the growing polymer chain or a hydride-ligand.

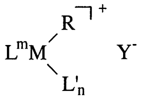
In early work, the ‘controlling’ ligands were most often monodentate neutral, or bidentate monoanionic entities, resulting in cationic or neutral M(II) complexes, respectively, as constituents of the catalytic cycle. Prominent examples of catalysts employing the former class of ligands are the phosphine-modified nickel systems developed by Wilke et al., which are highly active for the dimerization of propene [7]. The latter class of ligands is exemplified by the anionic chelating P,O-ligands already referred to, nickel(II) complexes of such ligands being the basis of the Shell Higher Olefin Process, i.e. the linear *oligomerization* of ethylene to α-olefins. In terms of current developments, it is interesting to note that ethylene *polymerization* to higher molecular weight products by nickel catalysts with monoanionic ligands has also found continued interest (S,O ligands: [8a]; N,N ligands, yielding branched polymer: [8b,c]; P,O derived systems: [8d–g]; N,O ligands, yielding moderately branched, high molecular weight polymer: [9]). In addition to catalysts containing ‘controlling’ ligands, ‘weakly coordinated’ catalysts, exemplified by the precursor structure $[RM(L')_n]^+$ (R = σ- or π-bound formally monoanionic hydrocarbon ligand; L′ = weakly coordinating ‘stabilizing’ ligand), have also been thoroughly investigated. Particularly, they have been used for the polymerization of conjugated dienes [10a], and in a recent development nickel and palladium complexes of the above general structure have been found to be highly active precursors for the polymerization of cyclic olefins [11,57,124].



Scheme 2. Cationic late transition metal complexes with multidentate ligands in catalysis.

Catalytic dimerization and oligomerization of monoolefins and the related organometallic chemistry have been extensively investigated for complexes with monodentate neutral ligands and bidentate anionic ligands, and some of the excellent reviews which have appeared on the subject are given in Ref. [12]. By contrast, late transition metal catalysts based on cationic complexes containing multidentate ligands have only recently found strong attention, e.g. in the work of Drent et al. [13] and Brookhart and coworkers [14]. Such catalysts can be highly active, and allow for novel reactions, such as the alternating copolymerization of olefins with carbon monoxide to high molecular weight polyketones, the copolymerization of ethylene and α-olefins with functionalized olefins such as acrylates, or the homopolymerization of ethylene to high molecular weight, highly branched materials (Scheme 2).

Mechanistic investigations, as well as efficient and reliable catalyst synthesis on a laboratory scale, require well-defined, highly reactive, versatile transition metal reagents. The current surge of interest in catalyst discovery via automated parallel syntheses [15] further underlines this demand, e.g. for screening of new ligands. In terms of the above discussion, a cationic complex containing a multidentate 'controlling' ligand L^m, which is suited as a catalyst precursor, can be represented by structure **3**.



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L^m = multidentate ligand
Y^- = non-coordinating anion
L' = weakly coordinating ligand

In a cationic complex, the counterion Y^- obviously must be very weakly or non-coordinating to prevent unfavorable interaction with the metal center, resulting, e.g. in displacement of labile ligands L' in structure **3** or corresponding blocking of coordination sites during catalysis [16]. While the finding of suitable non-coordinating anions has been critical to the activation of metallocene catalysts with excess [1b] or stoichiometric amounts [33] of cocatalyst, the subject of interaction of the anion with the metal center has been given less systematic consideration with respect to polymerization reactions catalyzed by late transition metals. In general, late metal catalysts are less sensitive to anion coordination due to the lower electrophilicity of the metal center. In cationic palladium(II) compounds anions such as SbF_6^-, PF_6^- and BF_4^- are usually regarded as very weakly or non-coordinating [16]. For cationic nickel catalysts, the picture is less clear. In terms of the general trend throughout the periodic table, they will be more electrophilic than a respective complex of the higher homologues. The effect of different anions on the polymerization of butadiene by cationic nickel complexes has been investigated, revealing PF_6^- to be essentially non-coordinating [10]. However, due to the different mechanisms (allyl vs. alkyl complexes, different ligand environments), these results can not simply be transferred to polymerization reactions of monoolefins.

Concerning the use of cationic complexes of late transition metals with multidentate ligands in vinyl-type olefin polymerization, investigations utilizing well-defined organometallic complexes as catalyst precursors have been limited mostly to nickel and palladium[1]. While the organometallic chemistry of these metals in general has been a subject of continued strong interest for a long time, cationic complexes with multidentate ligands had received comparatively less attention. In view of their applications in catalysis, this paper reviews recent advances in the preparation of cationic complexes of these two metals.

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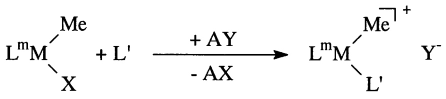
[1] A slow reaction of ethylene yielding low molecular weight polymer, using a rhodium methyl complex with a multidentate nitrogen-donor ligand as a catalyst precursor, has been described [4c].

2. Cationic alkyl complexes

As previously mentioned, in the C–C linkage of monoolefins by late transition metal catalysts chain growth is generally assumed to proceed via migratory insertion of alkyl–olefin complexes (Scheme 1). Thus, alkyl complexes of the general type **3** (vide supra, R = alkyl) as catalyst precursors may be considered as the most 'direct' entry to the catalytic cycle, and they represent good models for mechanistic studies, allowing for ready reaction of unsaturated substrates with the M–alkyl moiety even at low temperatures. Particularly in view of in situ generation of the cationic species, the weakly coordinating stabilizing ligand L′ may also be a solvent molecule or it may represent the olefin monomer, if the cationic complex is generated in the presence of the latter. As alkyl complexes of late transition metals are prone to β-hydride elimination, most work has employed alkyl substituents R without β-hydrogen atoms, i.e. predominantly methyl groups or groups $-CH_2CR_3$ or $-CH_2SiR_3$, or alkyl groups in which steric restrictions disfavor β-hydrogen elimination.

2.1. Preparation from neutral monomethyl complexes

Halide abstraction from neutral halide complexes in the presence of a weakly coordinating ligand (vide infra) represents a general route to cationic complexes (Eq. (1)).



$$L^mM(Me)(X) + L' \xrightarrow[-AX]{+AY} [L^mM(Me)(L')]^+ \; Y^-$$

A = Ag; alkali metal
X = halide
Y⁻ = weakly- or non-coordinating anion
L' = weakly coordinating ligand(s)
L^m = multidentate ligand (1)

For preparation of the neutral starting compounds, the complex [(cod)PdMeCl] is a versatile precursor. A new route to the preparation of [(cod)PdMeCl] was recently introduced by van Leeuwen et al., employing selective monoalkylation of $[(cod)PdCl_2]$ with a slight excess of $SnMe_4$ [17]. The cod ligand can be replaced by a variety of bidentate ligands L–L, to yield complexes [(L ^ L)PdMeCl] (e.g. diphosphines [18], diimines [19], polymer-bound diimines [15b], pyridine–imines [17b], P ^ N-ligands [20], P ^ O-ligands [21], S ^ N-ligands [22]). By comparison, reaction of [(cod)PdMeCl] with one equivalent of a monodentate ligand L (L = phosphine, CN^tBu, lutidine) can yield dimers $[\{MePd(L)(\mu\text{-}Cl)\}_2]$ [23]. The bridge-splitting reaction of the dimeric compound $[\{MePd(SMe_2)(\mu\text{-}I)\}_2]$ (accessible from [*trans*-$PdCl_2(SMe_2)$] in high yield [24,43b]) with bidentate ligands, reported by Canty and coworkers, represents another general route to complexes [(L ^ L)PdMeI]. The corresponding chloro and bromo compounds are also accessible via halide exchange [41,42,43a]. [(bipy)PdMeI] has also been obtained conveniently in good yield by oxidative addition of MeI to [Pd(dba)$_2$] in the presence of bipy [42].

For halide abstraction to yield cationic complexes (Eq. (1)), most often silver[2] or alkali metal salts of a very weakly or non-coordinating counterion Y^- are employed. In the presence of an additional ligand L′, complexes [(L ^ L)PdMe(L′)]Y are obtained (e.g. [(P ^ N)PdMe(L′)]Y (L′ = NCCH$_3$, CH$_2$Cl$_2$; $Y^- = OTf^-$, BF_4^-) [20]; [(P ^ P)PdMe(L′)]Y (L′ = NCCH$_3$, PPh$_3$; $Y^- = OTf^-$ [18] or L′ = MeOH, H$_2$O; $Y^- = BF_4^-$) [25]. Concerning the choice of the halide abstracting agent, it is interesting to note that for the α-diimine complexes [(N ^ N)PdMeCl] (N ^ N = ArN=C(R)–C(R)=NAr, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$–) in the presence of the relatively weakly coordinating ligand L′ = diethylether, reaction with NaBAr$_4^F$ (Ar^F = 3,5-(CF$_3$)$_2$-C$_6$H$_3$) results in incomplete halide abstraction, yielding the dimeric monocation $[\{(L^\wedge L)PdMe\}_2Cl]^+$ [14d]. By contrast, in the reaction with a silver salt such as AgSbF$_6$, halide abstraction is complete, resulting in formation of [(N ^ N)PdMe(OEt$_2$)]Y [14d]. With stronger ligands, such as nitriles, complete abstraction can also be achieved with NaBAr$_4^F$ [14f]. The $BAr_4^{F\,-}$ counterion [26] is highly lipophilic, enabling the preparation of cationic complex which are well soluble in organic solvents even at low-temperatures [34]. Preparation of the thallium salt of $BAr_4^{F\,-}$ has also been described recently [27].

Cationic complexes are often prepared by direct halide abstraction without isolation of [(L ^ L)PdMeX]. Care must be taken to avoid the presence of stronger coordinating ligands, e.g. reaction of $[\{MePd(SMe_2)I\}_2]$ with bipy/AgBF$_4$/acetonitrile did not yield the desired [(bipy)PdMe(NCCH$_3$)]BF$_4$ but [(bipy)PdMe(SMe$_2$)]BF$_4$ [43c]. Cationic complexes of bidentate ligands [(L ^ L)PdMe(L′)]Y have been widely applied for mechanistic investigations of migratory insertion reactions of olefins and carbon monoxide [14a,b,f,g,18,20,25,28,34b,c], as well as, as catalyst precursors for the preparation of olefin homo- and copolymers [14a,b,d,f,28g,29,34b]. As discussed previously, facile displacement of L′ by the substrates is a necessary prerequisite. In cationic complexes [(N ^ N)PdMe(L′)]BAr$_4^F$ (N ^ N = ArN=C(R)–C(R)=NAr; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$–) the following sequence of coordination strength of L′ was found: NCCH$_3$ > ethylene > hexene > propene ≫ *p*-methoxystyrene ≫ methyl acrylate > diethylether [14f].

The application of [(cod)PdMe(NCCH$_3$)]Y ($Y^- = SbF_6^-$; $BAr_4^{F\,-}$), prepared by halide abstraction from [(cod)PdMeCl], to the preparation of cationic diimine complexes via ligand exchange for cod has been described recently in a patent application [14d]. Obviously, this precursor allows for the preparation of a cationic complex of a given bidentate ligand in one step. It can be speculated that in comparison to [(cod)PdMeCl] the cod ligand in $[(cod)PdMe(NCCH_3)]^+$ is more amenable to displacement by hard-donor ligands, due to weaker back-binding from the metal center to the cod ligand in the cationic species.

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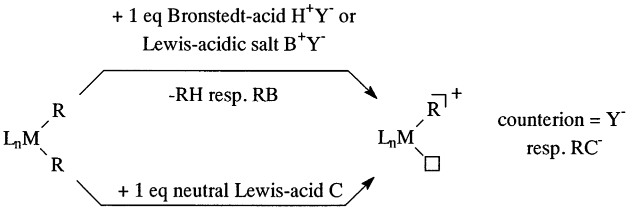
[2] For a possible side reaction cf. Section 4.1.

By comparison to its higher homologue, cationic methyl complexes of nickel with multidentate ligands are relatively scarce [12b,c,14a,30]. Considering preparation of cationic complexes of bidentate ligands via halide abstraction, addition of one equivalent of L–L to the neutral nickel alkyl complexes $[(PMe_3)_2NiMeCl]$ [31] and subsequent halide abstraction with $TlBF_4$ has been reported to yield five coordinate cationic complexes $[(L^\wedge L)(PMe_3)_2NiMe]BF_4$ ($L^\wedge L$ = dppe, dmpe, bipy, phen) [32]. Addition of an excess of dmpe results in formation of $[(L^\wedge L)_2NiMe]BF_4$, but with the less electron-donating ligands bipy and phen decomposition by methyl transfer yielding $[PMe_4]^+$ was observed.

2.2. Preparation from dialkyl complexes

The protonation of dialkyl complexes, or selective abstraction of one alkyl group with a strong Lewis acid, represents a second general route to cationic transition metal alkyl complexes (Scheme 3). By these routes complexes with very weakly coordinating ligands L′ and/or special counterions Y^-, which are not accessible by other methods, can be obtained. In addition, they offer the opportunity of only a gaseous, inert side product being formed, or the complete absence of such, which is advantageous in preparation of defined complexes but also in in situ catalyst systems $[L_nMMe_2]$/acid cocatalyst. This methodology has been applied widely with early metal metallocenes, for the preparation of defined complexes or for in situ catalysts [33]. With metallocenes, dimethylanilinium salts are often used as a proton source, or tritylium salts or Lewis-acidic triaryl boron compounds can be used to abstract one methyl group. Using the solid acid $[H(OEt_2)_2][BAr^F_4]$ [34a], this method has been introduced to the preparation of well-defined cationic late transition metal complexes by Brookhart and coworkers [14a,34].

The dimethyl complexes $[(L^\wedge L)MMe_2]$ are usually prepared by alkylation of a suitable Pd(II), respectively Ni(II) precursor with a main group methyl compound, such as MeLi or a Grignard reagent. In early work by Wilke et al., $[(bipy)NiMe_2]$ was prepared by reaction of $[Ni(acac)_2]$ with $Me_2Al(OEt)$ in the presence of bipy [35]. Preparation of α-diimine complexes $[(N^\wedge N)NiMe_2]$ by alkylation of $[(N^\wedge N)NiBr_2]$ with MeMgI and the analogous reaction of $[Ni(acac)_2]/N^\wedge N/MeMgX$ have been reported by tom Dieck and coworkers [36]. For the latter route, alkylation with Me_2Mg has also been reported [14a]. $[(tmeda)NiMe_2]$ has been obtained from $[(tmeda)MgMe_2]$ [37] and $[(tmeda)Ni(acac)_2]$ [38]. In this compound,



Scheme 3. Reaction of dialkyl complexes with Lewis or Brønsted acids.

which is reported to be stable at room temperature (r.t.) under a protective gas atmosphere as a solid, the tmeda ligands can be displaced by bipy or by the bidentate phosphine dmpe, yielding complexes $[(L^\wedge L)NiMe_2]$ [38]. However, it must be noted that in reaction with $L = PR_3$ ($R = Me$, Ph, OPh), reductive elimination of ethane to complexes $[NiL_4]$ occurs [38]. Similarly, ligand exchange reactions of $[(bipy)NiMe_2]$ with diphosphines $Ph_2P(CH_2)_nPPh_2$ yielded $[(P^\wedge P)NiMe_2]$ for $n = 2$ or 3 whereas for $n = 1$ or 4 reductive elimination occurred [39], which imposes some restrictions on the general applicability of this route.

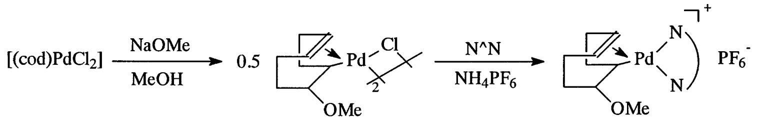
The palladium complexes $[(tmeda)PdMe_2]$ and $[(tmpda)PdMe_2]$ (tmpda = $Me_2N(CH_2)_3NMe_2$) have been prepared by van Koten and coworkers by alkylation of $[(N^\wedge N)PdCl_2]$ with MeLi [24,40]. As with the corresponding nickel complex, in $[(tmeda)PdMe_2]$ the hard-donor based tmeda ligand can be displaced by a variety of ligands, such as bipy [40], phosphines [40], or pyridyl–oxazolines [29a]. Another general route to complexes $[(N^\wedge N)PdMe_2]$, reported by Canty and coworkers, is reaction of [*trans*-$PdCl_2(SMe_2)_2$] with halide free MeLi [41,42], (or $MgMe_2$ [14g]), and subsequent addition of ligand. Canty and coworkers have also proposed displacement of pyradizine from $[(pyridazine)PdMe_2]_n$ as a general route to dimethyl complexes of ligands sensitive to MeLi [24,42,43a]. Palladium dialkyl complexes $[(L^\wedge L)PdR_2]$ ($L^\wedge L$ = dppe, bipy) can also be obtained by reaction of $[Pd(acac)_2]$ with $R_2Al(OEt)$ (e.g. $R = Me$, Et) in the presence of L–L [44]. In general, the palladium dimethyl complexes can be handled at r.t. under a protective gas atmosphere, although storage should occur at low temperature.

In comparison to the thoroughly investigated chemistry of the nickel and palladium dialkyl complexes in general, reactions with Lewis or Brønsted acids of very weakly or non-coordinating counterions have found little attention. As the resulting cationic nickel methyl complexes are very sensitive, they have rarely been isolated [14a]. The polymerization of ethylene by in situ combinations of $[(\alpha\text{-diimine})NiMe_2]$ with different cocatalysts has been described recently [45]; however, only very small amounts of polymers were obtained in this study. By contrast, the preparation and isolation of cationic palladium ether-adducts $[(L^\wedge L)PdMe(OEt_2)][BAr^F_4]$ by reaction of $[(L^\wedge L)PdMe_2]$ with $[H(OEt_2)_2][BAr^F_4]$ has been reported for various ligands $L^\wedge L$ with nitrogen-donors [14a,28e,34c]. An example of the related reaction with alkyl ammonium salts, well known for early metal metallocene catalysts as already alluded to, is the reaction of $[(dmpe)PdMe_2]$ with $[NH_nR_{4-n}]BPh_4$ ($n = 1$–4) [46]. In the resulting cationic complexes, the amine formed coordinates to the metal center. Reaction of $[(tmeda)PdMe_2]$ with $B(C_6F_5)_3$ yielding the cation $[(tmeda)Pd(CD_2Cl_2)Me]^+$ was monitored by ^{1}H-NMR spectroscopy [47]. Reaction of the dibenzylcomplex $[(dippe)Pd(CH_2Ph)_2]$ with $B(C_6F_5)_3$ was reported to yield the (rather unreactive) allylic complex $[(dippe)Pd(\eta^3\text{-}CH_2Ph)_2]^+$ with a $[PhCH_2B(C_6F_5)_3]^-$ counterion, the same cationic product being obtained by reaction of the dibenzyl precursor with $[H(OEt_2)_2][BAr^F_4]$ [48]. From the reaction of the related neopentyl complex $[(dppe)Pd(CH_2CMe_3)_2]$ with one or two equivalents of $[Ph_3C][BF_4]$, $Ph_3CCH_2CMe_3$ was isolated, evidence also for the alkyl abstraction by tritylium salts [49]. Interestingly, reaction of the palladacyclopentane complexes $[(L^\wedge L)Pd(CH_2)_4]$ ($L^\wedge L$ = bipy, dppe) with $[Ph_3C][BF_4]$ results in formation of cationic allyl complexes $[(L^\wedge L)Pd(1\text{-}MeC_3H_4)]^+$, corresponding to a *hydride* abstraction from the butandiyl ligand [50]. In addition to the above routes via alkyl abstraction, $[(tmeda)PdMe(NCCH_3)]OTf$ has been prepared in good yield by the reaction of $[(tmeda)PdMe_2]$ with MeOTf. A Pd(IV) intermediate is formed primarily by oxidative addition of MeOTf, which reductively eliminates ethane [29b,40b].

Di(trimethylsilyl) complexes $[(L^\wedge L)Ni(CH_2SiMe_3)_2]$ can be prepared from $[(py)_2Ni(CH_2SiMe_3)_2]$, the py ligands of which are easily displaced by a variety of ligands (also by tmeda) [51]. The precursor $[(py)_2Ni(CH_2SiMe_3)_2]$, which can be prepared from $[(py)_4NiCl_2]$ and $Mg(CH_2SiMe_3)Cl$ in good yield, is stable at r.t. under a protective gas atmosphere as a solid. In contrast to $[(tmeda)NiMe_2]$, reaction of $[(py)_2Ni(CH_2SiMe_3)_2]$ with PMe_3 has been reported to yield the dialkylcomplex, but with PPh_3 again $[NiL_4]$ is obtained [51]. The (relatively unstable) palladium compound $[(tmeda)Pd(CH_2SiMe_3)_2]$ can also be prepared by reaction of $[(tmeda)PdCl_2]$ with $Mg(CH_2SiMe_3)Cl$ [52]. Reaction of $[(\alpha\text{-diimine})Ni(CH_2SiMe_3)_2]$ with the Brønsted acid $[H(OEt_2)_2][BAr^F_4]$ was reported to result in 'intractable product mixtures' [53].

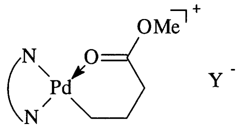
2.3. Complexes with an alkyl group which chelates via a functional group

Alkyl complexes can be stabilized by chelating coordination of a functional group, which is incorporated in the alkyl ligand, i.e. in terms of the general structure **3**, L′ is covalently bound to the R group. Enyl complexes are a representative of such compounds. They can be obtained by addition of nucleophiles to coordinated dienes (Eq. (2)) [54]. The dimer **4** reacts with monodentate ligands to neutral monomeric complexes $[(\sigma,\pi\text{-}C_8H_{12}OMe)PdCl(L)]$. In the presence of a suitable neutral bidentate ligand and a halide abstracting agent, cationic complexes can be obtained directly [55,56]. Concerning applications of cationic complexes with bidentate ligands in catalysis, the utilization of $[(\sigma,\pi\text{-}C_8H_{12}OMe)Pd(L^\wedge L)]PF_6$ ($L^\wedge L$ = bipy; phen) for the copolymerization of olefins with carbon monoxide has been described [56].



4 (2)

In terms of recent developments, it is interesting to note that the 'weakly coordinated' cationic systems obtained by the reaction of $[\{(\sigma,\pi\text{-}C_7H_8OMe)PdCl\}_2]$ with $AgBF_4$ or methylalumoxane (MAO) [57a], or the complex $[(\sigma,\pi\text{-}C_7H_8OMe)Pd(cod)]PF_6$ [58] have been applied to the polymerization of norbornene.



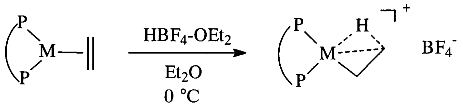
5

Another class of cationic chelate-stabilized alkyl compounds, which have been applied as catalyst precursors and for mechanistic studies, are complexes of the type **5**. The chelate is formed by migratory insertion of methyl acrylate into a Pd–Me bond [14b,f]. The complexes, which are stable in air at r.t., can be prepared in a one-pot reaction from [(L ^ L)PdMeCl], $NaBAr_4^F$ and acrylate (L ^ L = α-diimine). They are readily activated for polymerization of olefins. Corresponding nickel–chelate complexes have been described briefly [14d].

In the above examples, introduction of the cationic charge is achieved via halide abstraction (cf. Section 2.1), but complexes of this type have also been prepared by other routes [14b,d].

2.4. Protonation of olefin complexes

Protonation of an olefin complex by a Brønsted acid, accompanied by increase of the oxidation state of the metal, can also be utilized for the preparation of alkyl complexes [59]. For the synthesis of *neutral* alkyl complexes with monoanionic bidentate ligands this route is well established, exemplified by the preparation of a cyclooctenyl complex via $[Ni^0(cod)_2] + Ph_2PCH_2COOH \rightarrow [(\eta^3\text{-}C_8H_{13})Ni^{II}\{Ph_2PCH_2C(=O)O\text{-}\kappa^2P,O\}]$ (here the Brønsted acidic site is part of a bidentate ligand) [6]. Considering activation for catalysis, it should be noted that reaction of this complex with ethylene resulted predominantly in formation of C_8H_{12}-isomers, i.e. cleavage of the cyclooctenyl group from the metal center does not involve coupling with the olefinic monomer in this case [6].



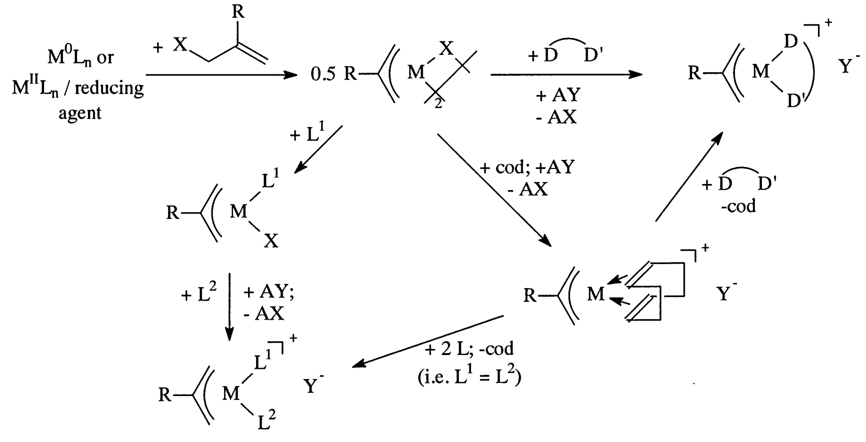
M = Ni, Pd
P^P = $^tBu_2P(CH_2)_nP^tBu_2$ (n = 2, 3)
$^tBu_2P(o\text{-}C_6H_4)P^tBu_2$ (3)

Well-defined *cationic* complexes of nickel and palladium have been prepared by reaction of the ethylene complexes $[(P^\wedge P)M(H_2C{=}CH_2)]$ with $HBF_4{\cdot}Et_2O$ (M = Ni, Pd; Eq. (3)), yielding the agostic cations [(P ^ P)MEt] [60].

3. Cationic allyl complexes

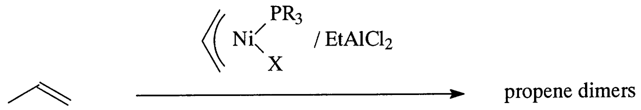
In containing metal–carbon bonds, η^3-allyl complexes also provide a convenient entry into the catalytic cycle of monoolefin-linkage reactions. Much of the pioneering work in this field has relied on these complexes, and allyl complexes may be regarded as the first well-defined organometallic late transition metal complexes used as catalyst precursors for these reactions [61]. An example of early work in catalysis, the dimerization of propene, explored by Wilke et al. is shown in Eq. (4) [7].

It should be noted that the related reactions of conjugated dienes proceed via allyl complexes as intermediates of the catalytic cycle [7,10], and the extensive chemistry of allyl complexes has also received much attention in this context.



e.g. M^0L_n resp. $M^{II}L_n$ / reducing agent = $Ni(cod)_2$; $Ni(CO)_4$; $Na_2PdCl_4/CO/MeOH$
$X = Cl, Br$; $R = H$, Alkyl
$A = Ag, Na, Tl$; $Y^- = BF_4^-, PF_6^-, SbF_6^-, BAr^F{}_4^-$

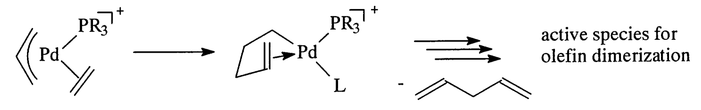
Scheme 4. General routes to allyl complexes.



(4)

General routes to allyl complexes of nickel and palladium are depicted in Scheme 4. The starting compounds [{(allyl)MX}$_2$] can be prepared from allyl halide and [Ni(cod)$_2$] [62], or Na_2PdCl_4 in the presence of CO [63], respectively. Cationic compounds [(allyl)ML$_2$]Y (e.g. $L_2 = cod$, $L = NCCH_3$) are usually prepared from the allyl complexes [{(allyl)MX}$_2$] by halide abstraction with silver or thallium salts in the presence of the appropriate ligand [64]. For neutral bidentate ligands with a strong and a weaker donor ligand, complexes [(allyl)MX(A ~ B-κ^1A)] can be isolated as products of the bridge splitting reaction of the dimeric starting compound, and converted to the cationic complexes [(allyl)M(A ^ B-κ^2A,B)]$^+$ by halide abstraction [21,65a].

Activation of allyl complexes occurs by formal insertion of the monoolefinic substrate into the metal–allyl moiety, ultimately resulting in cleavage of the allyl group from the metal center [12a]. In recent work on cationic palladium complexes with phosphine ligands PR_3, complexes [(η^3-allyl)($H_2C{=}CH_2$)Pd(PR_3)]$^+$ could be observed directly as precursors for olefin–allyl coupling (Eq. (5)) [65].



(5)

For complexes $[(\eta^3\text{-allyl})(H_2C{=}CH_2)Pd(P\sim O\text{-}\kappa^1P)]^+$ with hemilabile P–O ligands containing a strongly coordinating phosphine and a rather weakly binding oxygen donor, the insertion rate was found to decrease when an O-donor of increased binding strength was introduced, due to equilibria $[(\eta^3\text{-allyl})(H_2C{=}CH_2)Pd(P\sim O\text{-}\kappa^1P)]^+ \leftrightarrows [(\eta^3\text{-allyl})Pd(P^\wedge O\text{-}\kappa^2P,O)]^+ + H_2C{=}CH_2$ [65a]. Accordingly, cationic allyl complexes with strongly coordinating bidentate ligands $[(\eta^3\text{-allyl})M(L^\wedge L)]^+$, which do not readily provide a free site for olefin coordination, have long been known to display relatively low, if any catalytic activity (cf. Ref. [12a])[3]. For example, the complex $[(\eta^3\text{-methallyl})Ni(N^\wedge N)]PF_6$ ($N^\wedge N = ArN{=}C(H){-}C(H){=}NAr$, $Ar = 2,6\text{-}^i Pr_2C_6H_3$) has recently been reported [66] to be considerably less active in ethylene polymerization than Brookhart's original catalyst systems [14a] with the same diimine ligand.

To circumvent the disadvantage of slow activation, substituted allyl complexes with electron-withdrawing substituents [67] have been used recently in combination with Lewis acids. For example, activity in olefin polymerization using complexes $[(XC_3H_4)Ni(\text{bidentate ligand})]Y$ ($X = Cl$, MeOC(O), EtOC(O)) as precursors has been claimed to be significantly enhanced by the presence of BAr_3 [14d,102]. Alternately, the use of allyl compounds with aryl or alkyl substituents in the 1-position has been claimed to be advantageous in comparison to the unsubstituted allyl compounds in such catalysts [102].

4. Cationic aryl complexes

In nickel(II) complexes containing an *anionic* bidentate ligand (cf. Section 1), η^1-σ-bound aryl substituents have played an important role in the development of well defined catalyst precursors. In the pioneering work of Keim et al., the phenyl ligand in $[\{Ph_2PC(H){=}C(Ph)O\text{-}\kappa^2P,O\}NiPh(PPh_3)]$ originates from the ylid ligand precursor $Ph_3P = C(H){-}C({=}O)Ph$ [8d,68], In subsequent work, related single component catalyst precursors with aryl substituents have also been prepared by other routes [9a,69]. Neutral palladium complexes with an aryl substituent have also attracted attention due to their occurrence as intermediates in organic synthesis involving coupling reactions of aryl groups [70], such as the Heck reaction [71]. By comparison, applications of *cationic* aryl complexes related to catalysis are less.

In comparison to alkyl complexes, in aryl complexes, particularly with perhalo aryl substituents, the metal–carbon bond is significantly more stable. This may result in lower reactivity of the catalyst precursor's metal–carbon bond towards olefin monomer on the one hand, but higher stability of the precursor may be an advantage. The latter aspect may be relevant especially for the preparation of well-defined nickel complexes, Ni–alkyl compounds being quite susceptible to

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[3] This generalized correlation of experimental observations should not be mistaken with a conclusion (e.g. regarding intermediate involvment of five-coordinate species) on the mechanism of allyl–olefin coupling for individual complexes.

decomposition. However, so far aryl complexes clearly do not possess the same importance as their alkyl counterparts (Section 2) as precursors for cationic catalysts for C–C linkage reactions of olefins. In this section, examples of general routes to their preparation will be reviewed briefly, and reactions relevant to catalysis will be discussed.

4.1. Preparation from neutral monoaryl complexes

As precursors to cationic complexes, neutral nickel halide compounds [$ArXNiL_2$] ($Ar = (CH_3)_nC_6H_{5-n}$, C_6Cl_5, C_6F_5) have been used in general. They can be prepared by reaction of [X_2NiL_2] with magnesium Grignard reagents $X'MgAr$ or with LiAr [72,73]. Oxidative addition of aryl halides to [$Ni(cod)_2$] [74] in the presence of L, or to [NiL_4] [75], can also yield [$ArXNiL_2$]. In [*trans*-$BrMesNi(PPh_3)_2$], the triphenylphosphine ligands can be displaced by bidentate ligands (bipy, phen, dppe) to yield [BrMesNi(L ^ L)] [76].

Halide abstraction from [$ArXNiL_2$] with silver [77,98b], thallium [98a], or alkali metal salts [76,78], of counterions such as BF_4^- or ClO_4^- yields cationic complexes. In the reaction of nickel mono-halide complexes with silver salts, abstraction of a phosphine ligand to form $[Ag(PR_3)_n]^+$ has been reported as a side reaction [77e,78,97a], limiting the general scope of this reaction. Employing [ArXNi(L ^ L)], cationic complexes of bidentate ligands have been prepared [76,77e,98b].

Palladium complexes [L_2PdArI] are conveniently prepared by oxidative addition of aryl iodides to $Pd(dba)_2$ [79a,80]. By this route, van Koten and coworkers obtained complexes [(tmeda)PdPhI] and [(bipy)PdPhI] in high yield [79a]. In the former complex, the tmeda ligand can easily be displaced by bipy [79a] or by bidentate phosphine ligands [79b].

Neutral pentahalophenyl complexes [Ar^XBrPdL_2] can be prepared by reaction of L with the anionic dimer $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$, which is accessible in a two step-synthesis from $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br4]$ and $BrMgC_6X_5$ for X = F [81]. Complexes with bidentate ligands were prepared (X = Cl, F; L = 0.5 dppe, bipy, tmeda, cod). Compounds [(L ^ L)Pd(C_6F_5)Cl] (L ^ L = bipy, phen [82a] or $Ph_2PCH_2CH_2$(2-pyridyl) [83]) have been obtained by displacement of tetrahydrothiophene (tht) from [$\{(tht)Pd(C_6F_5)(\mu\text{-}Cl)\}_2$] with L ^ L. Reaction of [(bipy)Pd(C_6F_5)Cl] with $AgClO_4$ in acetone was reported to yield the cationic complex [(bipy)Pd(C_6F_5)(acetone)]ClO_4, the acetone ligand being lost upon heating to yield [(L ^ L)Pd(C_6F_5)(ClO_4)] [82a]. Halide abstraction from [(L ^ L)PdCl(C_6F_5)] with $NaClO_4$ in the presence of isonitriles yields the complexes [(L ^ L)Pd(C_6F_5)(NCR)]ClO_4 (L ^ L = bipy, tmeda, dppe; R = ^{t}Bu, Cy, *p*-Tol) [82b].

4.2. Bis(aryl) complexes

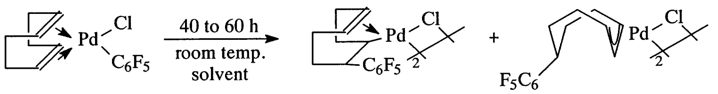
Activation of a bis(aryl) complex of an appropriate multidentate ligand to a catalytically active cationic complex, analogous to the protonation or abstraction of one methyl group from dimethyl complexes (Section 2.2), might be envisioned. In this respect, it can be noted that cleavage of the M–C bond by HCl in complexes

[XArNiL$_2$] has been reported for various aryl groups, whereas in pentachlorophenyl complexes (Ar = C_6Cl_5) the M–C bond was found to be stable under the reaction conditions employed [84]. Concerning the relative rate of protonation of complexes with different Pd–C moieties, the reaction of [(η^1-allyl)(F_5C_6)Pd(dppe)] with HCl predominantly yielded propene. Reaction of [(η^3-allyl)(F_5C_6)Pd(PPh_3)] with HCl, on the other hand, predominantly yielded HC_6F_5 [85]. These results imply a decreasing susceptibility to protonation in the sequence σ^1-CH_2R > perfluoroaryl > η^3-allyl.

Considering preparative accessibility, e.g. bis(pentafluoroaryl) nickel complexes have been prepared for a wide range of bidentate ligands L ^ L by displacement of labile ligands L from [$L_2Ni(C_6F_5)_2$] (L = dioxane, L ^ L = bipy, phen, dppe, en [86]; L = PhCN, L ^ L = α-diimine, iminophosphine [87]). As an example of a bis(aryl) palladium complex, [(bipy)Pd(C_6F_5)$_2$] was obtained by the reaction of [(bipy)PdCl$_2$] with pentafluorophenyllithium in good yield [88]. Reaction of [(dioxane)$_2$Pd(C_6F_5)$_2$] [89] with terpy yielded [(terpy)Pd(C_6F_5)$_2$] in moderate yield, the terpy ligand coordinating in a bidentate fashion [90]. In context of the use of bis(aryl) nickel complexes as catalyst precursors, it is interesting to note that complexes [(arene)Ni(C_6F_5)$_2$] (accessible by vapor codeposition [91a] or more conveniently by 'classic' synthetic methodology via Grignard reactions [91b]) are precursors for olefin dimerization or isomerization, without additional cocatalyst. In this case, the authors propose complexes [(arene)Ni(alkyl)(C_6F_5)] as part of the catalytic cycle, one of the C_6F_5-ligands thus performing the role of a 'controlling' ligand [92]. Initial activation by coupling of one C_6F_5-group in [(arene)Ni(C_6F_5)$_2$] with olefin monomer and cleavage from the metal center is thought to be the overall rate limiting step of catalysis, due to the strong Ni–C_6F_5 bond. Utilization of [(toluene)Ni(C_6F_5)$_2$] for the polymerization of functionalized norbornenes has been described [93].

4.3. Activation of aryl complexes by olefin insertion

Considering suitability of aryl complexes as catalyst precursors, activation via coupling of the aryl moiety with olefin monomer [68,98b] can be expected to be a crucial step. With regard to cationic species containing bidentate ligands, data is lacking to allow for a direct comparison to, e.g. alkyl complexes. Nonetheless, various examples of olefin insertion into M–Ar bonds under mild reaction conditions are known. Reaction of [(bipy)Pd(C_6F_5)Br]/AgClO$_4$/diene was reported to yield cationic complexes [(bipy)Pd(C_6F_5-η^3-allyl)]ClO$_4$ [94]. The neutral acetonitrile complex [(MeCN)$_2$Pd(C_6F_5)Br] was found to react rapidly with dienes at r.t., yielding the dimeric insertion products [Pd(η^3-C_6F_5-allyl)(μ-Br)]$_2$ [95a]. Intramolecular insertion of the neutral complex [(cod)Pd(C_6F_5)Cl] was found to occur slowly at r.t. in solution (Eq. (6)), allowing for isolation of the insertion product [95b]. Reversible insertion of carbon monoxide into the palladium–phenyl bond of the cationic complex [(N ^ N ^ N)PdPh]OTf (N ^ N ^ N = 2,6-bis[(dimethylamino)-methyl]pyridine has been reported [96].



(6)

Cationic pentafluoro- and pentachlorophenyl complexes obtained in situ by reaction of [$(X_5C_6)Ni(PPh_3)_2Br$] with $AgClO_4$ have been reported to be active for ethylene dimerization [97]. For the system [$(F_5C_6)Ni(PPh_3)_2Br$]/two equivalents $AgClO_4$ (proposed to contain an unsaturated species with one phosphine ligand [$(F_5C_6)Ni(PPh_3)(ClO_4)$]), catalysis was reported to proceed upon addition of ethylene without a significant induction period (rate: ca. 300 TO h^{-1} at 0°C, 0.67 atm initial pressure) [97b]. This result indicates a rapid activation by insertion of ethylene into the Ni–Ar^F bond. Cationic complexes [$MesNiL_2(L')$]BF_4 ($L = P^nBu_3$, P^iBu_3, PBz_3; $L' = NCCH_3$ resp. $L = 0.5$ dppe; $L' =$ py resp. $L = 0.5$ Ph_2PCH_2(2-pyridyl); $L' =$ THF) have been employed as one-component catalysts for ethylene dimerization [98]. In this study, the complexes with the bidentate ligands displayed little or no activity, which the authors attribute to the instability of hydride intermediates occurring as part of the catalytic cycle; considering activation of the precursor complexes, substituted styrenes as coupling products of the aryl group with ethylene could be detected [98b].

Transfer of halogenated aryl groups from BAr_3^X to a late transition metal center may prove to be a useful route to the preparation of cationic catalysts. A precedent for this reaction has been observed in early transition metal chemistry [99]. Polyketones with corresponding endgroups have been claimed to result from the copolymerization of olefins with carbon monoxide with the in situ system [$(L{}^\wedge L)Pd(NCPh)_2$]/$B(p\text{-}C_6H_4Cl)_3$ [100].

5. In situ catalyst systems

5.1. Catalyst systems involving addition of Brønsted acids

Brønsted acids have been applied widely in in situ catalyst mixtures for the C–C linkage of olefins. When discussing the reactions occurring in in situ catalyst systems, it must obviously be kept in mind that often they have not been clarified in detail for a particular system. Nonetheless, it is clear that Brønsted acids can fulfill various functions. In combination with metal species containing M–C σ-bonds (e.g. L_nMMe_2), the latter can be protonated by Brønsted acids HY, resulting in cationic complexes if Y is a very weakly or non-coordinating counterion, as already referred to in Section 2.2. A second important function of Brønsted acids are addition-type reactions, the subject of this section. Another function, removal of anions of weaker acids from the metal center, is mentioned in Section 5.3.

In situ reaction of a metal compound in a low oxidation state with a Brønsted acidic component is a well-established route for preparation of C–C linkage catalysts, namely for preparation of nickel(II) catalysts [12a]. A net oxidative addition resulting in formation of a hydride complex may occur. For example, by reaction of the Ni(0) complex [$Ni^0\{P(OEt)_3\}_4$] with Brønsted acids cationic hydride species $[HNi^{II}L_n]^+$ are formed, which were observed spectroscopically [101]. The latter are active for the dimerization and isomerization of olefins [101c]. Reaction of M(0) olefin complexes with a Brønsted acid can also result in the formation of M(II) alkyl complexes, the alkyl moiety being formed by coupling of an olefin ligand with the proton. As previously mentioned (cf. Section 2.4), this route has also been used for the preparation of cationic alkyl complexes with bidentate ligands.

Brønsted acids have also been used for the in situ preparation of cationic catalysts with bidentate ligands for olefin polymerization. The system $[Ni(cod)_2]$/bidentate ligand/$[H(OEt_2)_2][BAr^F_4]$ has been applied to olefin polymerization for a variety of bidentate ligands [14d,102]. If the acid is premixed with the ligand, for sufficiently basic ligands a salt will be formed, which can then be reacted with the nickel component. With respect to the use of diimine ligands in such in situ catalysts, it is interesting to note that reaction of the nickel(0) compound $[(Cy_3P)_2Ni(N_2)Ni(PCy_3)_2]$ with $[BzHN{=}CMe_2]BPh_4$ to the cationic hydride complex $[(H)(BzN{=}CMe_2\text{-}\kappa^1N)Ni(PCy_3)_2]BPh_4$ was reported recently [103]. Concerning the use of $[Ni(cod)_2]$ in combination with Brønsted acids for the in situ preparation of catalysts, the following observations made on isolated neutral complexes are notable: whereas the cylooct-4-en-1-yl complex $[(\eta^1,\eta^2\text{-}C_8H_{13})Ni(hfacac)]$ (hfacac = 1,1,1,3,3,3-hexafluoroacetylacetonate), prepared from $[Ni(cod)_2]$ and hfacacH, is very active for 1-olefin oligomerization, the isomeric compound with a η^3-allyl bound cyclooct-2-en-1-yl ligand, prepared by a different route, is inactive towards 1-butene [104]. On the other hand, enyl to allyl isomerizations are well known [65a,105], and for the similar compound $[(\eta^3\text{-}C_8H_{13})Ni^{II}\{Ph_2PCH_2C({=}O)O\text{-}\kappa^2P,O\}]$, an equilibrium between the 4-en-1-yl and the η^3-allyl form was observed [6]. Thus, for the general case of utilization of the above in situ preparation methods with new multidentate ligands, it may be speculated that formation of inactive η^3-allyl complexes may diminish catalyst activity (cf. Section 3), and that the conditions of catalyst preformation (time, temperature) may have a strong influence.

5.2. Catalyst systems containing alkyl aluminum cocatalysts

In preparation of Ziegler-type catalysts, aluminum alkyls $R_nAl_xCl_{3x-n}$, have found extensive use as cocatalysts. Later, methylalumoxane (MAO) was introduced as a halide-free cocatalyst [106]. Kaminsky's finding that Brintzinger's ansa-metallocenes can be activated for the highly stereospecific polymerization of propylene by MAO [107], as well as the independent work by Ewen utilizing ansa-titanocenes [108], may be considered to have initiated today's strong interest in metallocenes. While the functions of MAO can by no means be regarded as fully understood, there is evidence that activation of metallocene dihalides involves alkylation to the dimethyl complexes, and subsequent abstraction of one methyl group by MAO yielding a cationic metallocene complex $[L_2MCH_3]^+$ [1b,c]. Apart from its special properties as a cocatalyst, MAO is also advantageous on a laboratory scale due to its less hazardous properties in comparison to common aluminum alkyls. In the pioneering work on nickel catalyzed oligomerization reactions of olefins, halide containing alkylaluminum compounds were used as activators in catalysts with monodentate 'controlling' ligands or 'weakly coordinated' catalysts. For example $Et_3Al_2Cl_3$ or $EtAlCl_2$ were used in the activation of precursors such as nickel carboxylates, phosphine adducts of nickel halides, or of halide containing allyl complexes [7,12a].

In recent work, aluminum alkyls, particularly MAO, have also been applied successfully to the activation of nickel catalysts with bidentate ligands. The system [(α-diimine)$NiBr_2$]/MAO resp. modified MAO (e.g. Ni:Al = 1:1000) was found to be highly active in olefin polymerization and oligomerization [14a,e,h,53,109]. The same nickel halides can also be activated by Et_2AlCl [14a,h,45]. Addition of Lewis acids such as $B(C_6F_5)_3$ has been claimed to reduce the amount of aluminum alkyl cocatalyst required in such systems [110]. The complexes [(L ^ L)$NiBr_2$] can be prepared conveniently from the commercially available [(dme)$NiBr_2$] [111] via exchange of dme for the bidentate ligand (dme = 1,2-dimethoxyethane) [14a,36,112]. Exchange for a polymer-bound diimine ligand has also been described in the context of high-throughput catalyst screening [15b]. In analogy to typical procedures used for metallocenes [113], heterogenization of the above nickel systems on silica has been reported [114]. Activation of other diimine nickel compounds, such as allyl complexes [14d,66] or dimethyl complexes [14d,45] (cf. Section 2.2) by MAO have also been described.

It should be noted that MAO has also proven a versatile cocatalyst with other late transition metals. Iron and cobalt complexes [(N ^ N ^ N)MCl_n] with tridentate nitrogen donor ligands are highly active for ethylene polymerization in combination with MAO [5]. The activation of palladium(II) complexes [(P ^ P)PdX_2] with alumoxanes for polymerization reactions of olefins has been claimed [29d,115]. MAO activation of palladium catalysts without 'controlling' ligands has recently been reported to result in highly active catalysts for norbornene polymerization [57].

5.3. In situ systems for the preparation of cationic palladium catalysts

A convenient catalyst precursor which has been used in combination with a variety of different mono- or bidentate ligands is $[Pd(NCCH_3)_4](BF_4)_2$ [116], now available commercially. Sen et al. have applied the compound, respectively its reaction products with monodentate phosphines, as precursor to C–C linkage reactions of olefins, such as the oligomerization of ethylene and α-olefins, the slow copolymerization of ethylene with CO, or the polymerization of styrene [117]. Later, Sen and coworkers [118] and others [119,120], applied the (much more active) catalyst system obtained from $[Pd(NCCH_3)_4](BF_4)_2$ and one equivalent of the bidentate phosphine dppp to the alternating copolymerization of olefins with CO[4]. Using aprotic solvents as a reaction medium, a relatively long induction period was observed, which was strongly reduced by addition of protic solvents [118a,119]. Addition of hydrogen also eliminates the induction period [118a]. Running the

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[4] A similar catalyst system, obtained by reacting $PdCl_2$ with $AgBF_4$ and combining the product with dppp in acetonitrile solvent has been described in an early Shell patent [13a].

reaction in methylene chloride in the presence of only small amounts of methanol or water, high molecular weight propylene–CO copolymers can be obtained [120]. The combination of $[Pd(NCCH_3)_4](BF_4)_2$ with a sterically hindered α-diimine ligand results in an ethylene polymerization catalyst, yielding highly branched amorphous ethylene homopolymers [121]. In this case, addition of small amounts of alcohol to the dry chloroform solvent used had no effect on polymer yield. The related compound $[Pd(NCCH_3)_4](OTf)_2$ has also been applied to olefin–CO copolymerization in combination with bidentate phosphines [13b]. Complexes $[(N\wedge N)PdL_2](BF_4)_2$ ($L = NCCH_3$; OH_2) with bidentate amine ligands are active for the polymerization of norbornene [122]. Very recently, isolated complexes $[(C\wedge C)Pd(NCCH_3)_2](BF_4)_2$, containing a chelating N-heterocyclic carbene ligand, have been employed for the alternating copolymerization of ethylene with carbon monoxide [123]. While $[Pd(NCCH_3)_4](BF_4)_2$ provides a convenient entry to cationic palladium catalysts, little unambiguous proof currently exists as to its mode of *activation*. Concerning the mechanism of chain *propagation*, there is strong evidence for an insertion-type mechanism, i.e. insertion of monomers into Pd–C bonds. Thus, endgroup-analyses of propene–CO oligomers are in accordance with chain initiation from intermediate Pd–H and Pd–OR species, and chain transfer from Pd–alkyl and Pd–acyl complexes [118a]. Also, the similar results obtained in the above reactions of olefins, catalyzed by $[Pd(NCCH_3)_4](BF_4)_2$/L–L or isolated dicationic complexes $[(L\wedge L)Pd(NCCH_3)_2](BF_4)_2$, in comparison to well defined complexes $[(\alpha\text{-diimine})PdMe(OEt_2)]Y$ [14a] or to the in situ system $Pd(OAc)_2$/dppp/HOTs (methanol solvent; vide infra) [13b] suggest that with the $[Pd(NCCH_3)_4](BF_4)_2$-based in situ system chain growth proceeds via an insertion-type mechanism. This assumption is in accordance with previous conclusions by Risse and coworkers on the mechanism of norbornene-polymerization by $[Pd(NCR)_4](BF_4)_2$ without additional ligands [11c,d]. In this case, well defined allyl and alkyl complexes as catalyst precursors also yield comparative results [11b,124], analogously indicating the reaction to proceed via an insertion-type mechanism. Concerning the activation of $[Pd(NCCH_3)_4](BF_4)_2$-based catalysts, a Wacker-type mechanism involving nucleophilic attack by trace impurities of water on coordinated olefin has been proposed [125]. In reactions in aprotic solvents involving CO, formation of a palladium–hydride species via a water gas shift reaction with traces of water has been formulated [118a]. In the presence of alcohol solvents, activation via formation of a Pd–OR species has been proposed [118a]. However, unambiguous experimental proof is lacking in all cases.

Another, related, system for the in situ preparation of cationic palladium catalysts, which has been cited in a large number of patents [13a,126] on the alternating copolymerization of olefins with CO in protic solvents is $Pd(OAc)_2$/ligand/strong acid with a weakly or non-coordinating anion (e.g. $Pd(OAc)_2$/dppp/*p*-toluenesulfonic acid; in methanol solvent). Presumably, a catalyst system of this type is the basis for Shell's commercial process for the production of Carilon™ ethylene–propene–carbon monoxide terpolymers [127]. A mechanistic proposal [13b] suggests the role of the acid being substitution of the acetate ligands for a weakly coordinating anion via protonation to acetic acid, thus providing easily accessible coordination sites. The acid component can also be replaced by transition metal salts of weakly or non-coordinating anions, such as $Cu(OTs)_2$ [13b]. Further activation is thought to occur via a Pd–C(O)OMe species, which results from CO insertion into a palladium methoxide formed via $(L^\wedge L)Pd^{2+} + MeOH \rightarrow (L^\wedge L)Pd{-}OMe^{+} + H^{+}$, or by direct attack of methanol on coordinated CO. Alternately, activation can proceed via a Pd–H species, which has been proposed to be formed in various ways (β-hydrogen elimination from Pd–OMe, via the water gas shift reaction, or by Wacker-type reaction of methanol with ethylene) [13c]. Addition of oxidant promoters, such as benzoquinone, was found to enhance catalyst activity, particularly for bipy-type ligands [13c,126b]. The related system $[(phen)Pd(OTs)_2]$ has been used for the alternating copolymerization of styrene and CO by Consiglio and coworkers [128]. The system $Pd(OAc)_2$/bidentate ligand/strong acid has also been applied in the absence of CO for the dimerization of olefins, using bidentate ligands (dppp, phen, bipy) in alcohol solvents [129]. By comparison, the system $Pd(OAc)_2/HBF_4 \cdot Et_2O/\alpha$-diimine has been reported to be active for ethylene polymerization in chloroform solution, in the absence of protic solvents [121].

6. Concluding remarks

Recent discoveries of a number of new catalyst systems for olefin polymerization based on cationic complexes of late transition metals have stirred excitement in industry and academia alike. Multidentate ligands are a key feature of these new complex catalysts. Recent investigations of the reactivity of such complexes towards unsaturated substrates has increased the understanding of their catalytic behaviour, already providing a remarkably detailed mechanistic understanding in some cases. The availability of synthetic routes to highly reactive, well-defined cationic compounds has been a prerequisite for this work. Cationic methyl complexes are used as well-defined catalyst precursors which are instantaneously activated, and they also occupy a central position in mechanistic investigations. Protonation of neutral dimethyl complexes, or halide abstraction from neutral mono-methyl complexes have proven to be convenient routes to such cationic complexes. In addition, in situ-systems allowing for a large-scale commercial application are known, as well as organometallic complexes with other metal-bound organic groups. In summary, a field of chemistry exciting from the standpoint of fundamental as well as applied research has been opened.

References

[1] (a) G. Fink, R. Muelhaupt, H.H. Brintzinger (Eds.), Ziegler Catalysts, Springer, Berlin, 1995. (b) H.H. Brintzinger, D. Fischer, R. Muelhaupt, B. Rieger, R. Waymouth, Angew. Chem. 107 (1995) 1255; Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (c) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143 and Refs. cited therein.

[2] D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Chemistry, Wiley–VCH, Weinheim, 1998, pp. 541–547.

[3] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. 111 (1999) 448; Angew. Chem. Int. Ed. Engl. 38 (1999) 428.

[4] (a) G.F. Schmidt, M. Brookhart, J. Am. Chem. Soc. 107 (1985) 1443. (b) M. Brookhart, A.F. Volpe, Jr., D.M. Lincoln, I.T. Horvath, J.M. Millar, J. Am. Chem. Soc. 112 (1990) 5634. (c) L. Wang, R.S. Lu, R. Bau, T.C. Flood, J. Am. Chem. Soc. 115 (1993) 6999.

[5] (a) B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049. (b) G.J.P. Britovsek, V. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849. (c) WO98/27124, DuPont, inv.: A.M.A. Bennett, 1998. For ethylene oligomerization by related complexes: (d) B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.

[6] M. Peuckert, W. Keim, Organometallics 2 (1983) 594.

[7] G. Wilke, Angew. Chem. 100 (1988) 189; Angew. Chem. Int. Ed. Engl. 27 (1988) 185.

[8] (a) Ger. Offen. DE 2101422, Shell, invs.: R.S. Bauer, H. Chung, L.G. Cannell, W. Keim, H. van Zwet, 1971. (b) W. Keim, R. Appel, A. Storeck, C. Krueger, R. Goddard, Angew. Chem. 93 (1981) 91; Angew. Chem. Int. Ed. Engl. 20 (1981) 116. (c) W. Keim, Ann. NY Acad. Sci. 415 (1983) 191. (d) W. Keim, F.H. Kowaldt, R. Goddard, C. Krueger, Angew. Chem. 90 (1978) 493; Angew. Chem. Int. Ed. Engl. 1 (1978) 466. (e) K.A. Ostoja-Starzewski, J. Witte, Angew. Chem. 99 (1987) 76; Angew. Chem. Int. Ed. Engl. 26 (1987) 63. (f) K.A. Ostoja-Starzewski, J. Witte, K.H. Reichert, G. Vasiliou, in: W. Kaminsky, H. Sinn (Eds.), Transit. Met. Organomet. Catal. Olefin Polym., Springer, Berlin 1988, pp. 349–360. (g) U. Klabunde, S.D. Ittel, J. Mol. Cat. 41 (1987) 123.

[9] (a) C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149. (b) WO98/30609, DuPont, invs.: L.K. Johnson, A.M.A. Bennett, S.D. Ittel, L. Wang, A. Parthasarathy, E. Hauptman, R.D. Simpson, J. Feldman, E.B. Coughlin, 1998.

[10] (a) R. Taube, J. Gehrke, P. Boehme, K. Scherzer, J. Organomet. Chem. 410 (1991) 403. (b) R. Taube, J.-P. Gehrke, J. Organomet. Chem. 327 (1987) 419.

[11] (a) US Patent 5468819, BFGoodrich, invs.: B.L. Goodall, G.M. Benedikt, L.H. McIntosh III, D.A. Barnes, 1995. (b) B.L. Goodall, D.A. Barnes, G.H. Benedikt, L.H. McIntosch, Proceedings of the 6th International Business Forum on Specialty Polyolefins (SPO 1996) Schotland Business Research, 1996, pp. 121–142. Also cf. related earlier work: (c) C. Mehler, W. Risse, Makromol. Chem., Rapid Commun. 12 (1991) 255. (d) C. Mehler, W. Risse, Macromolecules 25 (1992) 4226. (e) EP-A 445755, Idemitsu, invs.: H. Maezawa, J. Matsumoto, A. Hideki, S. Asahi, 1991.

[12] Review with emphasis on catalyst preparation and activation: (a) B. Bogdanovic, Adv. Organomet. Chem. 17 (1979) 105. Emphasis on organometallic chemistry: (b) G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 6, Pergamon, Oxford, 1982. (c) G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry II: A Review of the Literature 1982–1994, vol. 9, Elsevier, Oxford, 1995. Emphasis on catalysis: (d) W. Keim, A. Behr, M. Röper, Comprehensive Organometallic Chemistry, vol. 8, pp. 371–462. (e) W. Keim, Angew. Chem. 102 (1990) 251; Angew. Chem. Int. Ed. Engl. 29 (1990) 235.

[13] (a) EP 121965, Sh ell, inv.: E. Drent, 1984. (b) E. Drent, J.A.M. Van Broekhoven, M.J. Doyle, J. Organomet. Chem. 417 (1991) 235. (c) E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663.

[14] (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414. (b) L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267. (c) C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11 664. (d) WO 96/23010, DuPont/UNC-Chapel Hill, invs.: L.K. Johnson, C.M. Killian, S.D. Arthur, J. Feldman, E. McCord, S.J. McLain, K.A. Kreutzer, M.A. Bennett, E.B. Coughlin, S.D. Ittel, A. Parthasarathy, D. Tempel, M. Brookhart, 1996. (e) C.M. Killian, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005. (f) S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888. (g) D. Tempel, M. Brookhart, Organometallics 11 (1998) 2290. (h) S.A. Svejda, M. Brookhart, Organometallics 18 (1999) 65.

[15] (a) W.H. Weinberg, B. Jandeleit, K. Self, H. Turner, Curr. Opin. Solid State Mater. Sci. 3 (1998) 104. (b) T.R. Boussie, C. Coutard, H. Turner, V. Murphy, T.S. Powers, Angew. Chem. 110 (1998) 3472; Angew. Chem. Int. Ed. Engl. 37 (1998) 3272. (c) K.D. Shimizu, M.L. Snapper, A.H.

Hoveyda, Chem. Eur. J. 4 (1998) 1885. (d) M.T. Reetz, M.H. Becker, K.M. Kuhling, A. Holzwarth, Angew. Chem. 110 (1998) 2792; Angew. Chem. Int. Ed. Engl. 37 (1998) 2647.

[16] (a) S.H. Strauss, Chem. Rev. 93 (1993) 927. (b) W. Beck, K. Kuenkel, Chem. Rev. 88 (1988) 1405.

[17] (a) EP 380162, Shell, invs.: P.W.N.M. van Leeuwen, C.F. Roobeek, 1989. (b) R.E. Rulke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, Inorg. Chem. 32 (1993) 5769.

[18] G.P.C.M. Dekker, C.J. Elsevier, K. Vrieze, P.W.N.M. Van Leeuwen, Organometallics 11 (1992) 1598.

[19] R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, R. Benedix, Recl. Trav. Chim. Pays-Bas 113 (1994) 88.

[20] G.P.C.M. Dekker, A. Buijs, C.J. Elsevier, K. Vrieze, P.W.N.M. van Leeuwen, W.J.J. Smeets, A.L. Spek, Y.F. Wang, C.H. Stam, Organometallics 11 (1992) 1937.

[21] I. Brassat, U. Englert, W. Keim, D.P. Keitel, S. Killat, G.P. Suranna, R. Wang, Inorg. Chim. Acta 280 (1998) 150.

[22] H.A. Ankersmit, N. Veldman, A.L. Spek, K. Eriksen, K. Goubitz, K. Vrieze, G. van Koten, Inorg. Chim. Acta 252 (1996) 203.

[23] F.T. Ladipo, G.K. Anderson, Organometallics 13 (1994) 303.

[24] P.K. Byers, A.J. Canty, H. Jin, D. Kruis, B.A. Markies, J. Boersma, G. van Koten, Inorg. Synth. 32 (1998) 162.

[25] I. Toth, C.J. Elsevier, J. Am. Chem. Soc. 115 (1993) 10388.

[26] H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, Bull. Chem. Soc. Jpn. 57 (1984) 2600.

[27] R.P. Hughes, D.C. Lindner, A.L. Rheingold, G.P.A. Yap, Inorg. Chem. 36 (1997) 1726.

[28] (a) F. Ozawa, T. Hayashi, H. Koide, A. Yamamoto, J. Chem. Soc. Chem. Commun. (1991) 1469. (b) B.A. Markies, K.A.N. Verkerk, M.H.P. Rietveld, J. Boersma, H. Kooijman, A.L. Spek, G. van Koten, J. Chem. Soc. Chem. Commun. (1993) 1317. (c) R. van Asselt, E.E.C.G. Gielens, R. Ruelke, K. Vrieze, C.J. Elsevier, J. Am. Chem. Soc. 116 (1994) 977. (d) B.A. Markies, D. Kruis, M.H.P. Rietveld, K.A.N. Verkerk, J. Boersma, H. Kooijman, M.T. Lakin, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 117 (1995) 5263. (e) F.C. Rix, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 1137. (f) K. Nozaki, N. Sato, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara, N. Koga, J. Am. Chem. Soc. 119 (1997) 12779. (g) M.J. Green, G.J.P. Britovsek, K.J. Cavell, F. Gerhards, B.F. Yates, K. Frankcombe, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1998) 1137. (h) G.A. Luinstra, P.H.P. Brinkmann, Organometallics 17 (1998) 5160.

[29] (a) M. Brookhart, M.I. Wagner, G.G.A. Balavoine, H.A. Haddou, J. Am. Chem. Soc. 116 (1994) 3641. (b) S. Stroemberg, M. Oksman, L. Zhang, K. Zetterberg, Acta Chem. Scand. 49 (1995) 689. (c) W. Keim, H. Maas, J. Organomet. Chem. 514 (1996) 271. (d) WO98/56839, BFGoodrich, invs.: B.L. Goodall, L.H. McIntosh, 1998.

[30] (a) L. Sacconi, P. Dapporto, P. Stoppioni, P. Innocenti, C. Benelli, Inorg. Chem. 16 (1977) 1669. (b) P. Stoppioni, P. Dapporto, L. Sacconi, Inorg. Chem. 17 (1978) 718.

[31] H.F. Klein, H.H. Karsch, Chem. Ber. 105 (1972) 2628.

[32] M. Bochmann, I. Hawkins, M.B. Hursthouse, R.L. Short, J. Chem. Soc. Dalton Trans. (1990) 1213.

[33] (a) WO91/09882, Exxon, invs.: G.G. Hlatky, D.J. Upton, H.W. Turner, 1990. (b) C. Sishta, R.M. Hathorn, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 1112. (c) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 113 (1991) 3623. (d) R.F. Jordan Adv. Organomet. Chem. 32 (1991) 325.

[34] (a) M. Brookhart, B. Grant, A.F. Volpe Jr., Organometallics 11 (1992) 3920. (b) M. Brookhart, F.C. Rix, J.M. DeSimone, J.C. Barborak, J. Am. Chem. Soc. 114 (1992) 5894. (c) F.C. Rix, M. Brookhart, P.S. White, J. Am. Chem. Soc. 118 (1996) 4746.

[35] G. Wilke, G. Herrmann, Angew. Chem. 78 (1966) 591; Angew. Chem. Int. Ed. Engl. 5 (1966) 581.

[36] M. Svoboda, H. Tom Dieck, J. Organomet. Chem. 191 (1980) 321.

[37] (a) T. Greisser, J. Kopf, D. Thoennes, E. Weiss, J. Organomet. Chem. 191 (1980) 1. (b) W. Kaschube, K.-R. Poerschke, K. Angermund, C. Krüger, G. Wilke, Chem. Ber. 121 (1988) 1921.

[38] W. Kaschube, K.R. Poerschke, G. Wilke, J. Organomet. Chem. 355 (1988) 525.

[39] J. Kohara, T. Yamamoto, A. Yamamoto, J. Organomet. Chem. 192 (1980) 265.

[40] (a) W. de Graaf, J. Boersma, D. Grove, A.L. Spek, G. van Koten, Recl. Trav. Chim. Pays-Bas 103 (1988) 299. (b) W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 8 (1989) 2907.

[41] P.K. Byers, A.J. Canty, Inorg. Chim. Acta 104 (1985) L13.

[42] P.K. Byers, A.J. Canty, Organometallics 9 (1990) 210.

[43] (a) P.K. Byers, A.J. Canty, B.W. Skelton, A.H. White, J. Organomet. Chem. 336 (1987) C55. (b) P.K. Byers, A.L. Canty, L.M. Engelhardt, A.H. White, J. Chem. Soc. Dalton Trans. (1986) 1731. (c) P.K. Byers, A.J. Canty, B.W. Skelton, A.H. White, J. Organomet. Chem. 393 (1990) 299.

[44] (a) T. Ito, H. Tsuchiya, A. Yamamoto, Bull. Chem. Soc. Jpn. 50 (1977) 1319. (b) F. Ozawa, T. Ito, Y. Nakamura, A. Yamamoto, J. Am. Chem. Soc. 102 (1980) 6457.

[45] D. Pappalardo, M. Mazzeo, C. Pellecchia, Macromol. Rapid Commun. 18 (1997) 1017.

[46] (a) A.L. Seligson, W.C. Trogler, Organometallics 12 (1993) 744. (b) A.L. Seligson, W.C. Trogler, J. Am. Chem. Soc. 113 (1991) 2520.

[47] S.Y. Desjardins, A.A. Way, M.C. Murray, D. Adirim, M.C. Baird, Organometallics 17 (1998) 2382.

[48] M.D. Fryzuk, G.K.B. Clentsmith, S.J. Rettig, J. Chem. Soc. Dalton Trans. (1998) 2007.

[49] P. Diversi, D. Fasce, R. Santini, J. Organomet. Chem. 269 (1984) 285.

[50] P. Diversi, G. Ingrosso, A. Lucherini, S. Murtas, J. Chem. Soc. Dalton Trans. (1980) 1633.

[51] E. Carmona, F. Gonzalez, M.L. Poveda, J.L. Atwood, D.R. Rogers, J. Chem. Soc. Dalton Trans. (1981) 777.

[52] M.A. Bennett, A.J. Canty, J. Felixberger, L.M. Rendina, L. Sunderland, A.C. Willis, Inorg. Chem. 32 (1993) 1951.

[53] T. Schleis, T.P. Spaniol, J. Okuda, J. Heinemann, R. Muelhaupt, J. Organomet. Chem. 569 (1998) 159.

[54] (a) M. Green, R.I. Hancock, J. Chem. Soc. A (1967) 2054. (b) C.T. Bailey, G.C. Lisensky, J. Chem. Educ. 62 (1985) 896.

[55] R. Pietropaolo, F. Cusmano, E. Rotondo, A. Spadaro, J. Organomet. Chem. 155 (1978) 117.

[56] EP-A 728791, Enichem, invs.: B. Milani, G. Mestroni, A. Sommanzzi, F. Garbassi, 1996.

[57] (a) B.S. Heinz, F.P. Alt, W. Heitz, Macromol. Rapid Commun. 19 (1998) 251. (b) M. Arndt, M. Gosmann, Polym. Bull. 41 (1998) 433.

[58] US Patent 5569730, BF Goodrich, invs.: B.L. Goodall, G.M. Benedikt, L.H. Mcintosh III, D.A. Barnes, L.F. Rhodes, 1996.

[59] Reaction of late transition metal olefin complexes with Brønsted acids and properties of resulting cationic agostic complexes: (a) M. Brookhart, D.M. Lincoln, M.A. Bennett, S. Pelling, J. Am. Chem. Soc. 112 (1990) 2691. (b) M. Brookhart, E. Hauptman, D.M. Lincoln, J. Am. Chem. Soc. 114 (1992) 10 394. Mechanistic investigation of the reaction of [Ni(cod)$_2$] with hexafluoroacetylacetone, yielding a neutral complex: (c) B. Akermark, J. Martin, J.-E. Nystrom, S. Stromberg, M. Svensson, K. Zetterberg, M. Zuber, Organometallics 17 (1998) 5367.

[60] F.M. Conroy-Lewis, L. Mole, A.D. Redhouse, S.A. Litster, J.L. Spencer, J. Chem. Soc. Chem. Commun. (1991) 1601.

[61] P.M. Maitlis, P. Espinet, M.J.H. Russell, Comprehensive Organometallic Chemistry, vol. 6, 1992, pp. 385–446.

[62] (a) DE 1194417 (1963) Studienges. Kohle m.b.H., inv.: G. Wilke. (b) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroener, W. Oberkirch, K. Tanaka, E. Steinruecke, D. Walter, H. Zimmermann, Angew. Chem. 78 (1966) 157; Angew. Chem. Int. Ed. Engl. 5 (1966) 151. Preparation of [Ni(cod)$_2$]: (c) R.A. Schunn, S.D. Ittel, M.A. Cushing, Inorg. Synth. 28 (1990) 94.

[63] Y. Tatsuno, T. Yoshida, Seiotsuka, Inorg. Synth. 19 (1979) 220.

[64] (a) D.J. Mabbott, B.E. Mann, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1977) 294. (b) R.B.A. Pardy, I. Tkatchenko, J. Chem. Soc. Chem. Commun. (1981) 49. (c) D.A. White, Inorg. Synth. 13 (1972) 61.

[65] (a) S. Mecking, W. Keim, Organometallics 15 (1996) 2650. (b) G.M. DiRenzo, P.S. White, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 6225.

[66] R.F. de Souza, R.S. Mauler, L.C. Simon, F.F. Nunes, D.V.S. Vescia, A. Cavagnolli, Macromol. Rapid Commun. 18 (1997) 795.

[67] L.S. Hegedus, S.D. Wagner, E.L. Waterman, K. Siirala-Hansen, J. Org. Chem. 40 (1975) 593.
[68] W. Keim, A. Behr, B. Gruber, B. Hoffmann, F.H. Kowaldt, U. Kuerschner, B. Limbaecker, F.P. Sistig, Organometallics 5 (1986) 2356.
[69] (a) S.Y. Desjardins, K.J. Cavell, H. Jin, B.W. Skelton, A.H. White, J. Organomet. Chem. 515 (1996) 233. (b) S.Y. Desjardins, K.J. Cavell, J.L. Hoare, B.W. Skelton, A.N. Sobolev, A.H. White, W. Keim, J. Organomet. Chem. 544 (1997) 163.
[70] F. Diederich, P.J. Stang (Eds.), Metal-catalyzed cross-coupling reactions, Wiley–VCH, Weinheim, 1997.
[71] A. de Meijere, F.E. Meyer, Angew. Chem. 106 (1994) 2473; Angew. Chem. Int. Ed. Engl. 33 (1994) 2379.
[72] J. Chatt, B.L. Shaw, J. Chem. Soc. (1960) 1718.
[73] M.D. Rausch, F.E. Tibbetts, Inorg. Chem. 9 (1970) 512.
[74] (a) D.R. Fahey, J.E. Mahan, J. Am. Chem. Soc. 99 (1977) 2501. (b) T. Yamamoto, S. Wakabayashi, K. Osakada, J. Organomet. Chem. 428 (1992) 223.
[75] M. Hidai, T. Kashiwagi, T. Ikeuchi, Y. Uchida, J. Organomet. Chem. 30 (1971) 279.
[76] W. Seidel, Z. Chem. 25 (1985) 411.
[77] (a) M. Wada, Inorg. Chem. 14 (1975) 1415. (b) M. Wada, K. Oguro, Y. Kawasaki, J. Organomet. Chem. 178 (1979) 262. (c) M. Wada, K. Sameshima, J. Chem. Soc. Dalton Trans. (1981) 240. (d) F. Caballero, P. Royo, J. Organomet. Chem. 137 (1977) 229. (e) J.M. Coronas, O. Rossell, J. Sales, J. Organomet. Chem. 121 (1976) 265.
[78] J.M. Coronas, C. Polo, J. Sales, Inorg. Chim. Acta 48 (1981) 87.
[79] (a) B.A. Markies, A.J. Canty, W. de Graaf, J. Boersma, M.D. Janssen, M.P. Hogerheide, W.J.J. Smeets, A.L. Spek, G. van Koten, J. Organomet. Chem. 482 (1994) 191. (b) W. de Graaf, J. van Wegen, J. Boersma, A.L. Spek, G. van Koten, Recl. Trav. Chim. Pays-Bas 108 (1989) 275.
[80] T.L. Wallow, F.E. Goodson, B.M. Novak, Organometallics 15 (1996) 3708.
[81] (a) R. Uson, J. Fornies, J.A. Nalda, M.J. Lozano, P. Espinet, A.C. Albeniz, Inorg. Chim. Acta 156 (1989) 251. (b) R. Uson, J. Fornies, F. Martinez, M. Tomas, J. Chem. Soc. Dalton Trans. (1980) 888.
[82] (a) R. Uson, J. Fornies, P. Espinet, R. Navarro, Inorg. Chim. Acta 82 (1984) 215. (b) R. Uson, J. Fornies, P. Espinet, A. Garcia, A. Sanau, Transit. Met. Chem. 8 (1983) 11.
[83] J.A. Casares, P. Espinet, K. Soulantica, I. Pascual, A.G. Orpen, Inorg. Chem. 36 (1997) 5251.
[84] (a) J.M. Coronas, J. Sales, J. Organomet. Chem. 94 (1975) 107. (b) M. Anton, J.M. Coronas, G. Muller, J. Sales, M. Seco, Inorg. Chim. Acta 36 (1979) 173. (c) A. Uchino, A. Yamamoto, S. Ikeda, J. Organomet. Chem. 24 (1970) C63.
[85] H. Kurosawa, A. Urabe, K. Miki, N. Kasai, Organometallics 5 (1986) 2002.
[86] A. Arcas, P. Royo, Inorg. Chim. Acta 31 (1978) 97.
[87] G. Sanchez, J.L. Serrano, F. Ruiz, G. Lopez, J. Fluor. Chem. 91 (1998) 165.
[88] M.D. Rausch, F.E. Tibbetts, J. Organomet. Chem. 21 (1970) 487.
[89] G. Garcia, G. Lopez, Inorg. Chim. Acta 52 (1981) 87.
[90] E.W. Abel, K.G. Orrell, A.G. Osborne, H.M. Pain, V. Sik, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc. Dalton Trans. (1994) 3441.
[91] (a) K.J. Klabunde, B.B. Anderson, M. Bader, Inorg. Synth. 19 (1979) 72. (b) S.-T. Lin, R.N. Narske, K.J. Klabunde, Organometallics 4 (1985) 571.
[92] S.-K. Choe, H. Kanai, K.J. Klabunde, J. Am. Chem. Soc. 111 (1989) 2875.
[93] WO97/33198, BFGoodrich, invs.: B.L. Goodall, S. Jayaraman, R.A. Shick, L.F. Rhodes, 1997.
[94] A.C. Albeniz, P. Espinet, J. Organomet. Chem. 452 (1993) 229.
[95] (a) A.C. Albeniz, E.P. Espinet, C. Foces-Foces, F.H. Cano, Organometallics 9 (1990) 1079. (b) A.C. Albeniz, P. Espinet, Y. Jeannin, M. Philoche-Levisalles, B.E. Mann, J. Am. Chem. Soc. 112 (1990) 6594.
[96] B.A. Markies, P. Wijkens, J. Boersma, A.L. Spek, G. van Koten, Recl. Trav. Chim. Pays-Bas 110 (1991) 133.
[97] (a) Y. Ishimura, K.-I. Maruya, Y. Nakamura, T. Mizoriki, A. Ozaki, Chem. Lett. (1981) 657. (b) Y. Ishimura, K.-I. Maruya, Y. Nakamura, T. Mizoroki, A. Ozaki, Bull. Chem. Soc. Jpn. 56 (1983) 818.

[98] (a) R. Ceder, G. Muller, J. Sales, J. Vidal, D. Neibecker, I. Tkatchenko, J. Mol. Cat. 68 (1991) 23. (b) R.M. Ceder, J. Cubillo, G. Muller, M. Rocamora, J. Sales, J. Organomet. Chem. 429 (1992) 391.

[99] (a) R. Gomez, M.L.H. Green, J.L. Haggitt, J. Chem. Soc. Chem. Commun. (1994) 2607. (b) J.D. Scollard, D.H. McConville, S.J. Rettig, Organometallics 16 (1997) 1810.

[100] EP-A 704471, BP Chemicals Ltd., invs.: N.A. Cooley, P.G. Lodge, P.K.G. Hodgson, J.P. McNally, 1995.

[101] (a) C.A. Tolman, J. Am. Chem. Soc. 92 (1970) 4217. (b) C.A. Tolman, J. Am. Chem. Soc. 94 (1972) 2994. (c) C.A. Tolman, J. Am. Chem. Soc. 92 (1970) 6777.

[102] WO 97/02298, DuPont, invs.: L.K. Johnson, J. Feldman, K.A. Kreutzer, S.J. McLain, A.M.A. Bennett, E.B. Coughlin, D.S. Donald, L.T.J. Nelson, A. Parthasarathy, X. Shen, W. Tam, Y. Wang, 1997.

[103] M. Aresta, E. Quaranta, A. Dibenedetto, P. Giannoccaro, I. Tommasi, M. Lanfranchi, A. Tiripicchio, Organometallics 16 (1997) 834.

[104] (a) W. Keim, A. Behr, G. Kraus, J. Organomet. Chem. 251 (1983) 377. (b) W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert, G. Schmitt, J. Fleischhauer, U. Meier, J. Mol. Catal. 6 (1979) 79.

[105] (a) H. Lehmkuhl, A. Rufinska, R. Benn, G. Schroth, R. Mynott, Liebigs Ann. Chem. (1981) 317. (b) M. Parra-Hake, M.F. Rettig, J.L. Williams, R.M. Wing, Organometallics 5 (1986) 1032.

[106] (a) A. Andresen, H.-G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.-J. Vollmer, Angew. Chem. 88 (1976) 689; Angew. Chem. Int. Ed. Engl. 15 (1976) 630. (b) H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99. (c) J. Bliemeister, W. Hagendorf, A. Harder, B. Heitmann, I Schimmel, E. Schmedt, W. Schnuchel, H. Sinn, L. Tikwe, N. von Thienen, K. Urlass, H. Winter, O. Zarncke, Ziegler Catalysts, Springer, Berlin, 1995 pp. 57–82.

[107] (a) W. Kaminsky, K. Kuelper, H.H. Brintzinger, F.R.W.P. Wild, Angew. Chem. 97 (1985) 507; Angew. Chem. Int. Ed. Engl. 24 (1985) 507. (b) F.R.W.P. Wild, M. Wasiucionek, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 288 (1985) 63.

[108] J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355.

[109] C. Pellecchia, A. Zambelli, M. Mazzeo, D. Pappalardo, J. Mol. Catal. A: Chem. 128 (1998) 229.

[110] WO 98/03559, DuPont, invs.: S.J. McLain, J. Feldman, 1998.

[111] L.G.L. Ward, Inorg. Synth. 13 (1972) 154.

[112] H. tom Dieck, M. Svoboda, T. Greiser, Z. Naturforsch. 36b (1981) 823.

[113] (a) C. Jenny, P. Maddox, Curr. Opin. Solid State Mat. Sci. 3 (1998) 94. (b) M.R. Ribeiro, A. Deffieux, M.F. Portela, Ind. Eng. Chem. Res. 36 (1997) 1224. (c) M.O. Kristen, Topics Catal. 7 (1999) 89.

[114] (a) WO 97/48736, Exxon, invs.: G.A. Vaughan, J.A.M. Canich, P.T. Matsunaga, D.E. Gindelberger, K.R. Squire, 1997. (b) S. Mecking, Macromol. Rapid. Commun. 20 (1999) 139.

[115] EP 590942, BP Chemicals, invs.: J.H. Brophy, N.A. Cooley, M.J. Green, 1993.

[116] (a) R.F. Schramm, B.B. Wayland, J. Chem. Soc. Chem. Commun. (1968) 898. (b) R.R. Thomas, A. Sen, Inorg. Synth. 26 (1989) 128.

[117] (a) A. Sen, T.W. Lai, J. Am. Chem. Soc. 104 (1982) 3520. (b) A. Sen, T.-W. Lai, J. Am. Chem. Soc. 103 (1981) 4627.

[118] (a) Z. Jiang, G.M. Dahlen, K. Houseknecht, A. Sen, Macromolecules 25 (1992) 2999. (b) A. Sen, Acc. Chem. Res. 26 (1993) 303.

[119] (a) A.X. Zhao, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 30 (1992) 2735. cf. (b) J.A.M. van Broekhoven, M.J. Doyle, E. Drent, J. Polym. Sci. Part A: Polym. Chem. 31 (1993) 2879.

[120] A.S. Abu-Surrah, R. Wursche, B. Rieger, G. Eckert, W. Pechhold, Macromolecules 29 (1996) 4806.

[121] J. Feldman, S.J. McLain, A. Parthasarathy, W.J. Marshall, J.C. Calabrese, S.D. Arthur, Organometallics 16 (1997) 1514.

[122] A.S. Abu-Surrah, B. Rieger, J. Mol. Catal. A: Chem. 128 (1998) 239.

[123] M.G. Gardiner, W.A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239.

[124] (a) A.L. Safir, B.M. Novak, Macromolecules 28 (1995) 5396. (b) A. Reinmuth, J.P. Mathew, J. Melia, W. Risse, Macromol. Rapid Commun. 17 (1996) 173. (c) B.S. Heinz, W. Heitz, S.A. Krügel, F. Raubacher, J.H. Wendorff, Acta Polym. 48 (1997) 385.

[125] B.M. Novak, A.L. Safir, Polym. Prepr. 37 (1996) 335.

[126] Selected patents: bis(diphenylphosphine)-ligands with OMe-substituents in *o*-position of the aryl groups: (a) EP 296687, Shell, invs.: J.A. van Doorn, R.L. Wife, 1988. Bidentate nitrogen donor ligands: (b) EP 229408, Shell, inv.: E. Drent, 1986. Bidentate ligands with various other donor atoms: (c) EP-A 280374, Shell, invs.: J.A. van Doorn, E. Drent, J.J.M. Snel, 1988. (d) EP 345847, Shell, invs.: J.A. van Doorn, E. Drent, 1989. (e) EP 343734, Shell, invs.: J.A. van Doorn, A.H. Kramer, J.J.M. Snel, 1989. $H[B(O_2C_6H_4)_2]$ as acid component: (f) EP-A 314309, BP Chemicals, invs.: S.L. Brown, A.R. Lucy, 1989. Gas phase polymerization: (g) EP 501576, Shell, invs.: E. Drent, J.J. Keijsper, 1992.

[127] (a) N. Alperowicz, Chem. Week July (1995) 22. (b) Anonymous, Chem. Eng. News, May (1999) 11.

[128] M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U.W. Suter, Angew. Chem. 103 (1991) 992; Angew. Chem. Int. Ed. Engl. 30 (1991) 989.

[129] (a) EP-A 170311, Shell, inv.: E. Drent, 1986. (b) E. Drent, Pure Appl. Chem. 62 (1990) 661.