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Early transition metal complexes containing aminopyridinato ligands — coordination chemistry, organometallic chemistry and catalysis*)

Summary — Early transition metal complexes containing aminopyridinato ligands have been reported only rarely. Such ligands combine a number of virtues which make them unique in the early transition metal chemistry. Besides the great variety of substitution patterns enabling us to fine tune electronic and steric features, they impress us with the flexibility in the binding mode covering the whole range from a pure amido metal bond up to a delocalized N_{amido}-C_{ipso}-$N_{pyridine}$-M four members ring. Coordination chemistry, organometallic chemistry and some selected applications in homogeneous catalysis including olefin polymerization are reviewed.

Key words: transition metal complexes containing aminopyridinato ligands, coordination chemistry, organometallic chemistry, selected applications in homogeneous catalysis, olefin polymerization.

The early transition metal chemistry is dominated by the cyclopentadienyl moiety employed as a ligand or by metallocenes used as reactive metal centers. There are two main reasons, first, the outstanding stability (in the sense of being kinetically inert) of the ligand metal bonds despite their organometallic character and, secondly, the history of the ligands, which started with the discovery of the fascinating structure of ferrocene by G. Wilkinson and E. O. Fischer [1] in the early fifties including the great potential of the experience gathered over the years. Nevertheless, there is a strong tendency in the early transition metal chemistry to develop alternative ligand systems to have more specific tools for special problems in that chemistry. We are following this tendency by focusing the interest on aminopyridinato ligands. Aminopyridinato ligands are derived from deprotonated α-aminopyridines. Such ligands have become attractive to us mainly for the following three reasons:

First, the flexibility of the binding mode of such ligands is a unique feature considering the anionic ligands capable of forming a stable ligand metal bond with early transition metals. The binding situation might cover the interior range from a simple metal amido bond without pyridine coordination (Fig. 1, left) as well as a strained η^2-coordination involving a typical metal amido and a common metal pyridine bond (middle) up to the delocalized binding mode indicated by equal metal nitrogen bond distances (right).

Secondly, the large variety of substitution patterns make such ligands attractive. By just considering a „simple" aminopyridinato ligand electron density withdrawing or pushing substituents can be introduced at the pyridine ring to fine tune ligand properties. Sterical shielding as well as electronic influence can be controlled by varying the substituents connected to the potential amido nitrogen. The opportunity to fine tune the

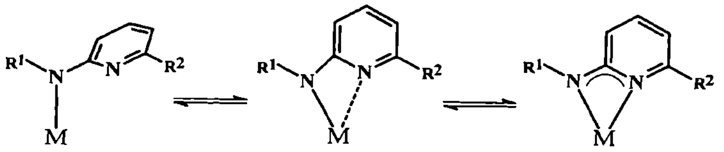

Fig. 1. The binding mode of aminopyridinato ligands (M = metal)

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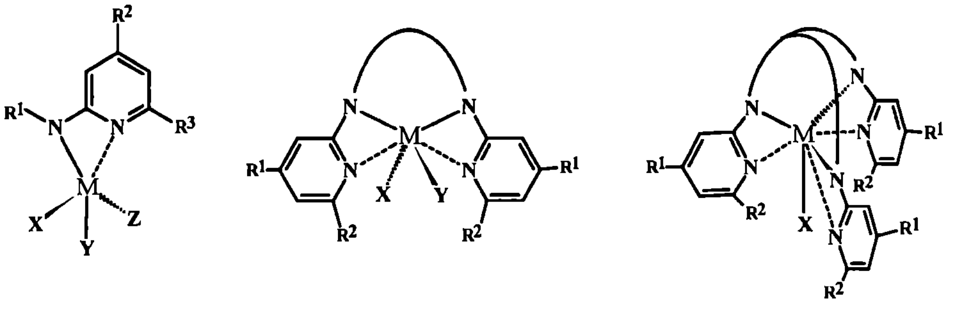


Fig. 2. Simple-, ansa- and superchelated aminopyridinato complexes

reactivity of metal complexes *via* ligand modifications is especially important with regard to catalytic applications.

By connecting two aminopyridines, a well defined bisanionic ligand system (after double deprotonation) is opened up (Fig. 2, middle). The handle build up in the metal complexes that contain such a ligand arrangement makes the name *ansa*-aminopyridinato complexes obvious [2]. Furthermore, a problem in the application of chelating bisamido type ligands is the co-coordination *via* the amido nitrogen lone pair which gives rise to dimerization. It might be overcome in *ansa*-aminopyridinato complexes by the pyridine binding in front of the amido nitrogen. The variety of substitution patterns mentioned in the case of a „simple" aminopyridinato ligand can be applied to fine tune the ligand environment of *ansa*-aminopyridinato complexes as well. It is even conceivable to connect three α-aminopyridines *via* the potential amido nitrogen and thus to acquire a trisanionic hexadentate ligand (after triple deprotonation) able to form mononuclear complexes with early transition metals [3] (Fig. 2, right).

Thirdly, an attractive feature in terms of application of such a ligand system is that just very few publications have reported on the use of deprotonated α-aminopyridines with the desired η^2-coordination mode in the early transition metal chemistry [4]. The first complexes were reported by Cotton (1984), a ruthenium(II) compound, and by Gambarotta (1991), a vanadium(II) complex, showing that aminopyridinato ligands might be able to stabilize unusual oxidation states, a crucial step in metal mediated catalytic transformations [4].

This paper sets out to describe

(i) the coordination chemistry of highly nitrogen coordinated early transition metal complexes (Group 3—6);

(ii) the organometallic chemistry of Group 3 and Group 4 metal complexes that contain aminopyridinato ligands;

(iii) catalysis, *e.g.*, olefin polymerization and ring opening polymerization of small ring lactams.

RESULTS AND DISCUSSION

Coordination chemistry

The coordination chemistry of the aminopyridinato ligands is mainly determined by two facts. First, the steric bulk of the ligands which is very large if the maximum steric angle [5] ranging between 120° and 144° (*cf.* Fig. 3) is considered, but very small if to look perpendicular to that direction. The ligands appear to be flat.

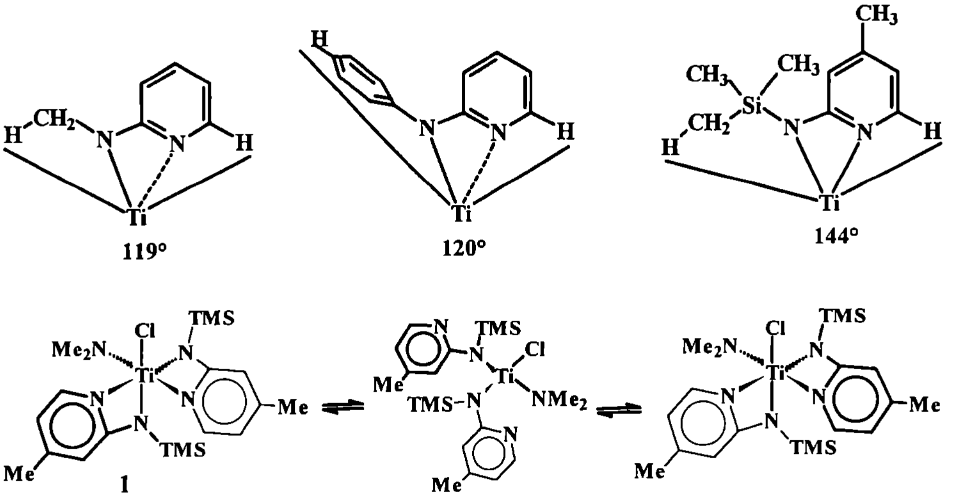
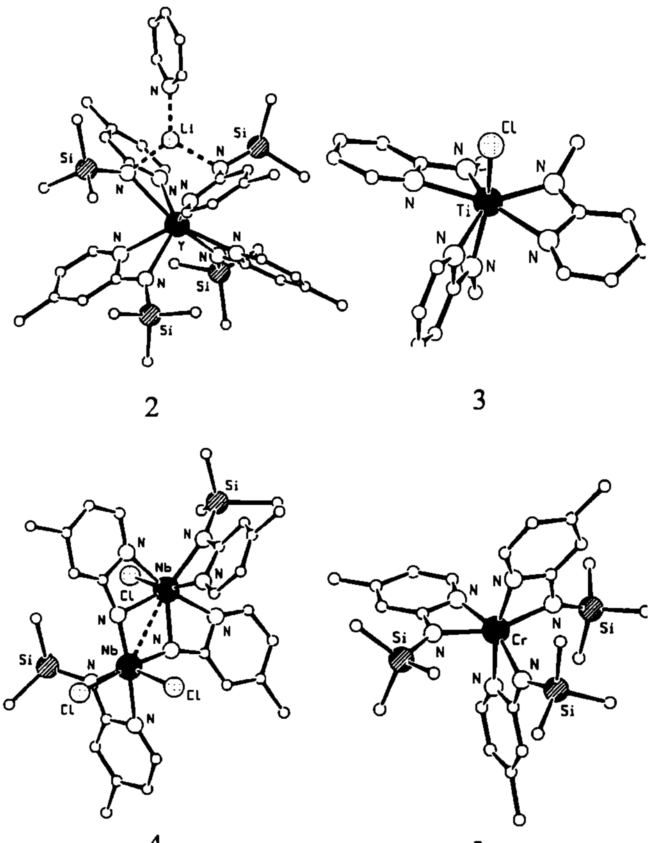


Fig. 3. Maximum steric properties of aminopyridinato ligands and the exchange process in such complexes (TMS = Me_3Si, Me = CH_3)

Furthermore, exchange processes occur most likely *via* the metal pyridine bond cleavage. For example, the barrier of the symmetric exchange process of the titanium complex **1** (Fig. 3) was determined to be ~13 kcal/mol. The two facts give rise to the tendency to form highly nitrogen coordinated early transition metal complexes with an unusual coordination geometry. For each of the Groups 3—6 one example is given (Fig. 4).



2 3

4 5

Fig. 4. Examples of highly nitrogen coordinated aminopyridinato complexes of Group 3, 4, 5 and 6 metals

The Group 3 example is an yttrium „ate" complex (**2**) *tetrakis*-coordinated including lithium coordination in the second ligand sphere. The **2** is used as an anionic ligand for bimetallic chemistry or as a transfer reagent to form late transition metal aminopyridinato complexes. The best general way to prepare Group 3 complexes is salt elimination. The Group 4 metal example is a *tris*(aminopyridinato)-coordinated titanium monochloro complex (**3**). Such complexes have an interesting photochemical behavior. They may be reduced to paramagnetic species by UV radiation. The best way to prepare compounds of the titanium group is amine elimination. The Group 5 example is a homobinuclear niobium complex (**4**). The **4** contains imidopyridinato bridges as well as a strained coordinated aminopyridinato ligand. Such compounds are accessible *via* abstraction of trimethylsilyl chloride. The Group 6 example is a *tris*-coordinated chromium complex (**5**), one of the rare chromium(III) species that are six-coordinated without having the very common octahedral coordination geometry. Something about the binding mode of aminopyridinato ligands can be learned from such coordination chemical studies.

Figure 5 compares aminopyridinato ligands with the most related bonding situation as found in amidinato metal complexes [6]. The binding parameters are averaged using 9 (aminopyridinato) and 12 (amidinato) X-ray crystal structure analyses, respectively. The standard deviations are not usual ones resulting from an X-ray analysis. They are the standard deviations of a sample mean and thus allow to imagine the flexibility of the corresponding bond. The standard deviations in the metal nitrogen range are much higher in the case of aminopyridinato ligands and may indicate the higher flexibility that can be explained by partial distribution of the anionic function between the two nitrogen (the amido and the pyridine) atoms. The second interesting observation is the highly strained N_{amido}-C_{ipso}-$N_{pyridine}$ angle which might lead to an unexpected reactivity of such aminopyridinato complexes. Furthermore, a typical metal pyridine bond distance and the metal amido bond longer by ~0.1 Å, are observed for the aminopyridinato ligands as contrasted with the equal metal nitrogen distances seen for the amidinato ligand system.

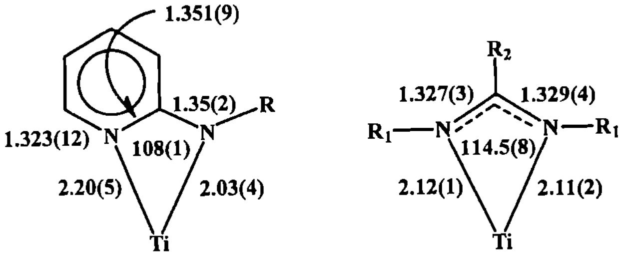


Fig. 5. A comparison of aminopyridinato with amidinato complexes

Organometallic chemistry

In order to learn something about the aminopyridinato complexes in terms of stabilization of metal carbon bonds, a crucial step with regard to the application of those complexes in olefin polymerization, some results on the preparation of organometallic complexes are reported. The zirconium monochloride **6** is a qualified starting material for organometallic chemistry because, in the zirconium chemistry, the chloride is known to be a good leaving group and the three trimethylsilyl groups of the ligands set surround the sensitive metal carbon bond in a protective manner. The **6** is prepared *via* amine elimination as well as *via* salt elimination [7]. The success of the salt elimination reaction contrasts with the synthesis of similar titanium complexes where such an approach has failed [5]. The reactions of **6** with a

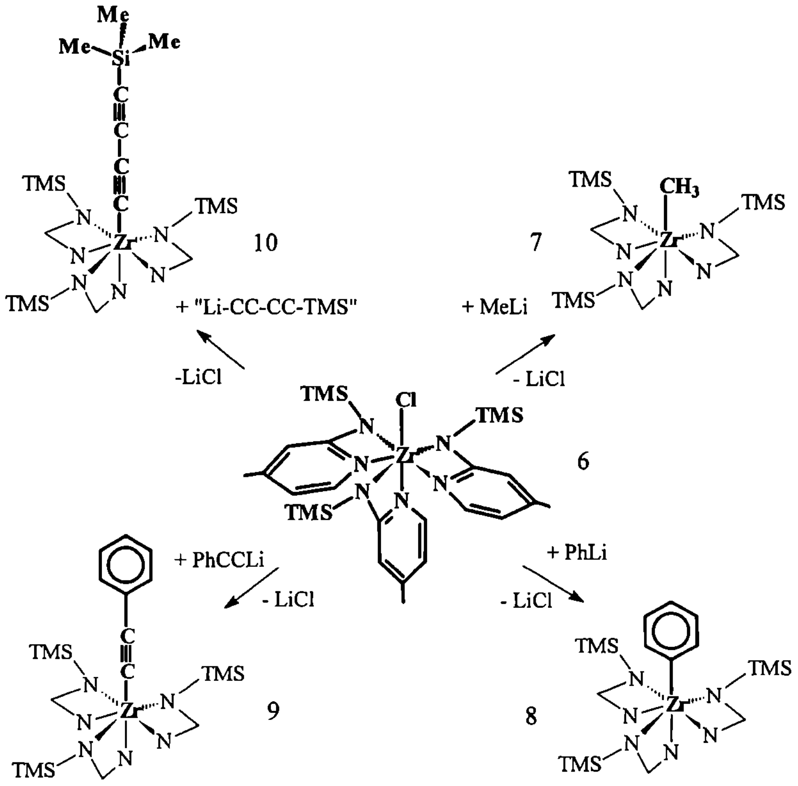


Fig. 6. Alkyl-, aryl-, alkinyl and butadiynyl complexes

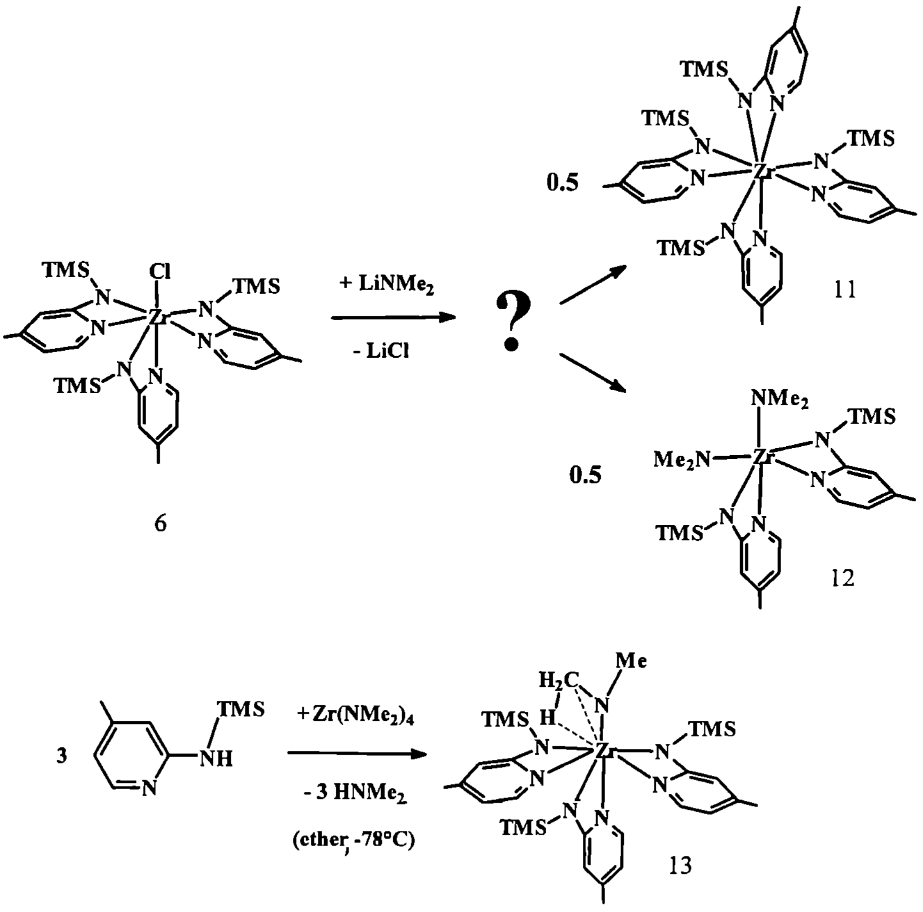


Fig. 7. Synthesis of ***13***

variety of organolithium compounds give rise to σ-alkyl (**7**), -aryl **8**), -alkinyl (**9**) and -butadiynyl (**10**) complexes (Fig. 6).

X-Ray crystal structure analyses of such compounds indicate an adaptation of the ligand arrangement of the three aminopyridinato ligands, depending on the steric demand of the ancillary coordinated „organic" substrate. Less bulky substrates, *e.g.*, the alkinyl moiety, afford a propeller-like organization of the aminipyridinato ligands [8]. Thus, the three trimethylsilyl groups of the aminopyridinato ligands protect the sensitive zirconium carbon bond which might be considered as the reason for the stability of these complexes. To bind steric demanding substrates, *e.g.*, the phenyl moiety, one of the ligands has to turn down and the propeller-like arrangement is left [9]. The instability of the compounds increases. The reaction of **6** with lithium dimethylamide affords two compounds in the 1:1 ratio, a tetrakis(aminopyridinato) complex (**11**) and a *bis*(dimethylamido) complex (**12**) (Fig. 7).

By following the course of the reaction by NMR spectroscopy, the desired mono(dimethylamido) complex (**13**) could be detected as an intermediate. It was prepared by a different route. The structure of this complex indicates an agostic interaction of one of the methyl groups of the dimethylamido moiety. Because the interaction could not be observed by ^{1}H-NMR, the packing effect had to be ruled out. As seen in Fig. 9, no steric pressure is made by any of the aminopyridinato ligands to force the asymmetric binding mode of the dimethyl amido ligand. Thus, the reason for the interaction could be the electron deficiency at the zirconium center caused by the aminopyridinato ligands. Such an agostic interaction is proposed as a key intermediate in the aminomethylation of nonactivated olefins catalyzed by early transition metal amido complexes [10].

In order to have better defined systems and to start with a bisanionic ligand set that provides access to mononuclear complexes, two aminopyridines were connected *via* a two-and a three-atom moiety, respectively, and after double deprotonation they formed *ansa*-aminopyridinato complexes with a variety of early transition metals (*cf.* Fig. 9). An analogy to the metallocenes might be drawn. A number of different dichloro as well as dialkyl Group 4 metal complexes and a number of Group 3 metal complexes were prepared with regard to applications in catalysis, *e.g.*, olefin polymerization.

Catalysis

Despite the fact that metallocenes brought up a variety of highly active olefin polymerization catalysts [11] and that amido metal complexes are not so stable (kinetically inert) as are metallocenes, there are still open questions in this area of research which motivate the use of novel ligand systems. By way of illustration, olefin polymerization in a living matter or incorporation of functionalized olefins into the polymer chain to increase the compatibility with more polar polymer systems is mentioned. Living polymerization would allow to prepare block copolymers with totally novel characteristics. It is well known from the metallocene chemistry that a highly electrophilic metal center with a metal carbon bond and an empty coordination spot for olefin coor-

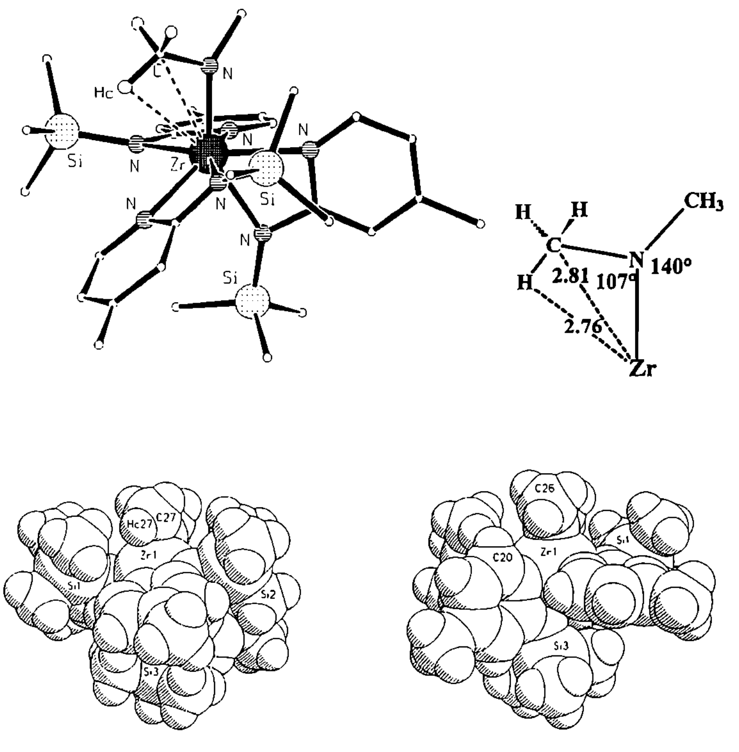


Fig. 8. Agostic interaction of the dimethylamido moiety in 13

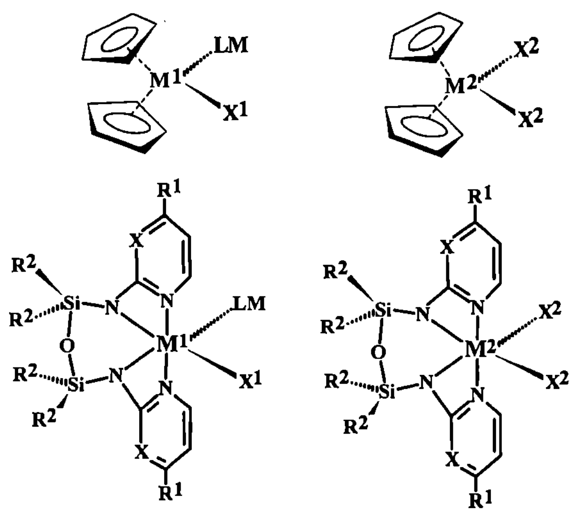


Fig. 9. ansa-Aminopyridinato complexes of Group 3 and 4 metals (x = N or C-H; LM = coordinated THF; X^1 = Cl; X^2 = Cl or alkyl; R = alkyl)

dination in the neighborhood are required. Thus, the Group 4 metal dichloro complexes with a cissoid arrangement of the two chloro ligands may, in principle, impart polymerizability following activation with aluminum alkyls.

The reaction of aminopyridine **14** with $(Me_2N)_2TiCl_2$ leads to an octahedral titanium dichloro complex (**15**) containing the ancillary amine, the amido and the aminopyridinato ligands. Synthesis of a corresponding zirconium complex has failed [7]: different compounds were obtained. The use of $(Et_2N)_2ZrCl_2$ and aminopyridine **16** which means more bulky amine, amido and aminopyridinato ligands has afforded a similar zirconium complex (Fig. 10). X-Ray crystal structure analyses of both compounds disclosed the cissoid arrangement of the two chloro ligands [12].

Polymerization results are interesting because the titanium complex **15** is remarkably active in the oligomerization of higher olefins whereas the zirconium compound **17** does not polymerize higher olefins by using the same activation protocols. Table 1 summarizes oligomerization results obtained with 1-butene.

Table 1. 1-Butene oligomerization using 15 as precatalyst

Run	Cocatalyst	Al/Ti	Temp. °C	Activity kg oligo/ /(g Ti·h)	$\overline{M}_n$ [a)] g/mol	Olefins [b)] %
1 [c)]	MAO	500	25	59.5	388	18
2	i-$Bu_3Al/B(C_6F_5)_3$ [e)]	38	10	33.6	3100 [g)]	none
3 [d)]	$Et_3Al_2Cl_3$	40	70	45.2	850 [f)]	none

[a)] By vapor pressure osmometry; [b)] by GC-FTIR and ^{1}H-NMR; [c)] in toluene (all other experiments in hexane); [d)] titanium complex incorporated in a $MgCl_2$ matrix by coprecipitation from a mixture of i-Bu_2Mg and CCl_4 in hexane; [e)] modified with $B(C_6H_5)_3$ (mole ratio Ti/B = 1:1); [f)] about 40—50% of the saturated oligomers in the C_{10}—C_{22} fraction are products of carbometallation; [g)] 6—8 g of a rubber-like polybutene isolated in 20 h ($\overline{M}_n$ = 8580 by GPC) with an unusually broad molecular mass distribution of $\overline{M}_w/\overline{M}_n$ = 125.

MAO (methylalumoxane), $(i\text{-Bu})_3Al$, and ethylaluminum sesquichloride were found to be the best cocatalyst systems. If $(i\text{-Bu})_3Al$ is used, addition of $B(C_6F_5)_3$ in the 1:1 ratio with respect to titanium is required. Ethylaluminum sesquichloride proved to be a productive cocatalyst in the heterogeneous polymerization process. The resulting oligomers are invariably atactic. The flexible nature of the ligand set may well allow for a high degree of freedom, randomness, and thus an atactic polymer is produced under the presumed chain-end control regime.

The experience showing titanium complexes to be more active as compared with zirconium complexes and the opportunity to have a better defined system by using

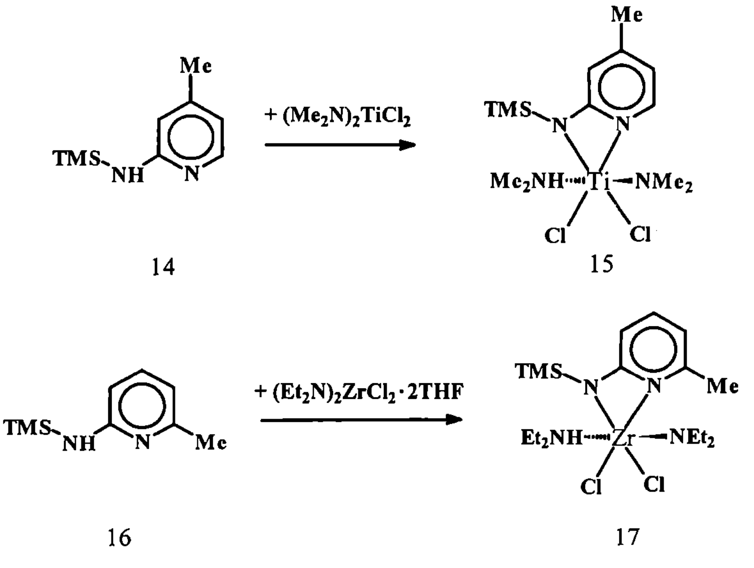


Fig. 10. Synthesis of octahedral Group 4 metal complexes containing a cissoid arrangement of two chloro ligands

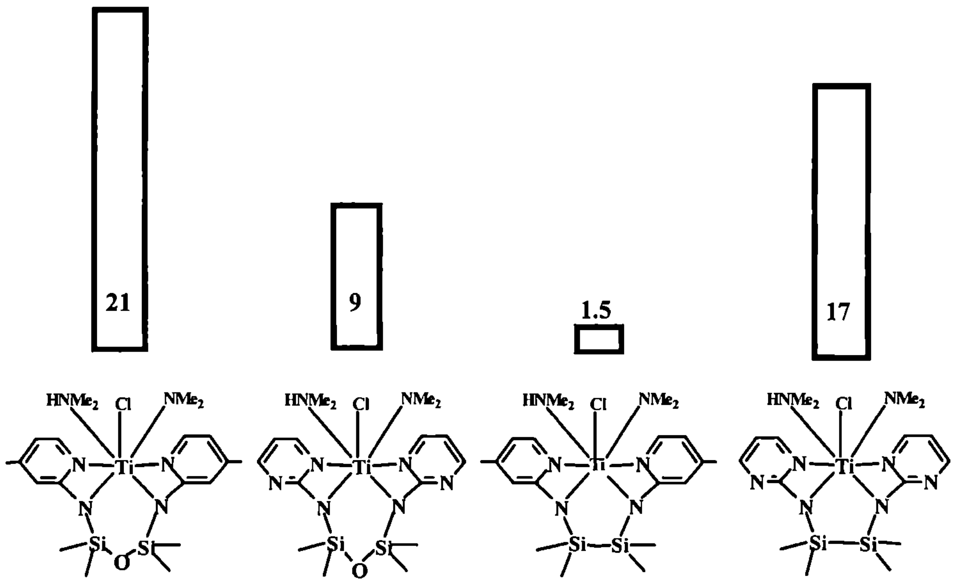


Fig. 11. Ethylene polymerization results using ansa-aminopyridinato complexes as precatalysts [activities in kg polymer/(mol catalyst·bar·h)]

ansa-aminopyridinato titanium complexes has led to the examination of such titanium complexes in ethylene polymerization and to the structure-activity relationship. Figure 11 shows selected complexes correlated with their ethylene polymerization activity. MAO (2000 equiv) was used as a cocatalyst. The variation in the length of the handle (two or three atoms) and the change of basicity by using pyrimidine instead of pyridine, does not give a clear picture as to which ligand moieties increase or decrease the polymerization activity.

The application of aminopyridinato complexes in catalytic transformation reactions was investigated in ring opening reactions of lactams with regard to the mechanistic point of view and to information about activity-increasing circumstances resulting from the ligand set, *viz.*, *bis*(dimethylamido)titanium complexes containing ancillary aminopyridinato ligands initializing ring opening of small ring lactams. Larger ring systems such as ε-caprolactam stop, following the activation step (Fig. 12). Well-defined compounds can be isolated and X-ray analysis of one of these complexes has shown the coordination mode of the caprolactamato ligand to be pseudo delocalized with almost equal Ti-O (2.172(2) Å) and Ti-N (2.139(2) Å) distances.

NMR investigations of the polymerization process as well as information derived from the X-ray analysis has led to the proposal of an anionic mechanism [13].

The activity of a variety of *bis*(dimethylamido)titanium complexes that contain ancillary aminopyridinato ligands, was compared with that to polymerize 2-azetidinone. The highest productivity was observed for the complexes bearing the lowest steric demand of the ami-

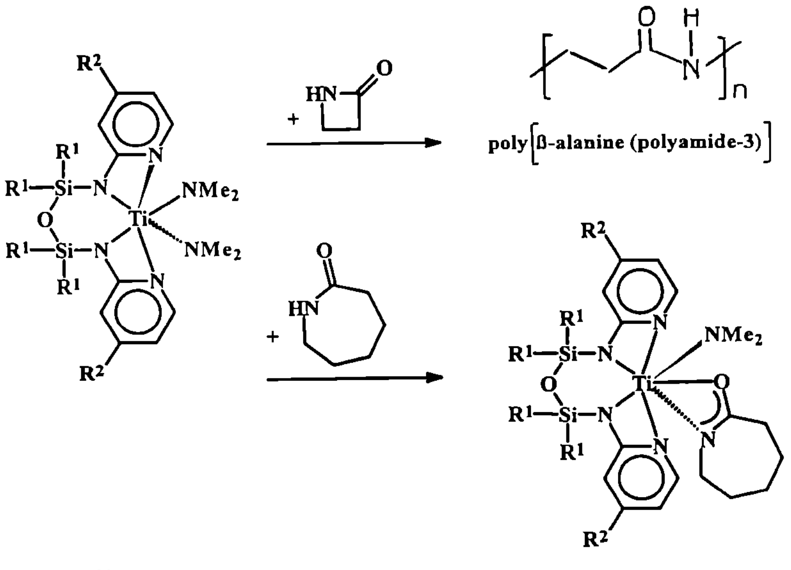


Fig. 12. Ring opening and activation of lactams

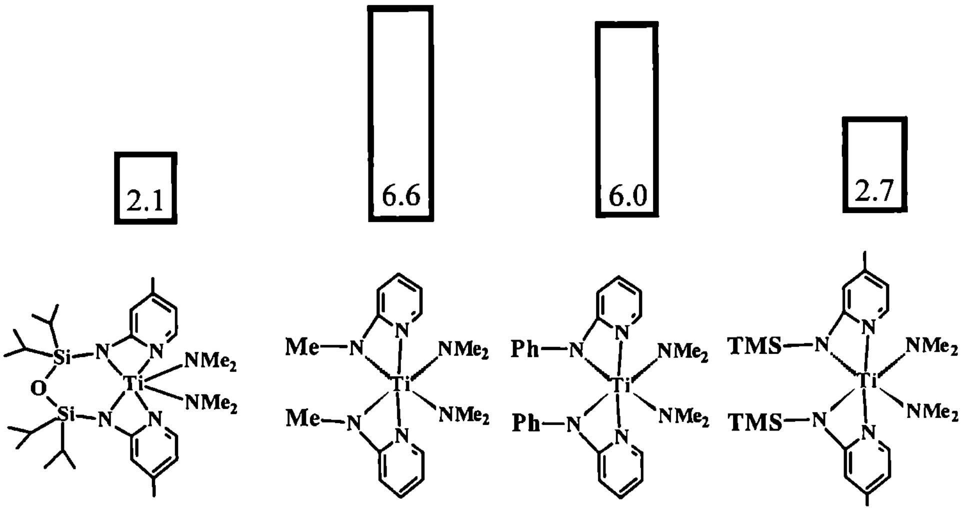


Fig. 13. Activity data [kg polymer/(mol catalyst·h)] of ring opening polymerization of 2-azetidinone initiated by titanium complexes

nopyridinato ligand as seen in Fig. 13 and might be correlated with the best access to the titanium center to initiate ring opening.

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