The Strained η^2-N_{Amido}−$N_{Pyridine}$ Coordination of Aminopyridinato Ligands

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Dedicated to Prof. Dr. Uwe Rosenthal

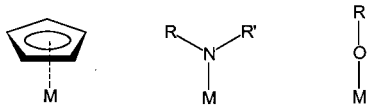
Keywords: N ligands / Catalysis / Coordination modes / Lanthanides / Transition metals

This review gives an account of the syntheses and structures of group-3 (including lanthanides), -4 and -5 metal complexes stabilised by strained η^2-coordinated aminopyridinato ligands. Reactivity studies and catalytic applications of the coordination compounds are discussed.

Introduction

General Remarks

Considerable efforts are being expended in organometallic chemistry on modifying the reactivity of metal−carbon bonds through choice of appropriate coligands. The information thus obtained is now being extensively used in, for example, homogeneous catalysis.[1] Coligands such as the cyclopentadienyl (Cp) fragment and phosphanes (Scheme 1) have hitherto played the dominant role as anionic and neutral donor functions, respectively.[2]



Scheme 1. The three most important ligand types for the stabilisation of early transition metal ions in medium to high oxidation states (R, R′ = alkyl, aryl or silyl)

In addition to these classic examples for the control of complex reactivity, exhaustive efforts over the last decade have been devoted to the development of novel ligands. As well as Cp ligands (Scheme 1, left), alkoxy (right) and amido ligands[3] (centre) have proven to be suitable for the stabilisation of early, electron-poor transition metal ions in medium to high oxidation states. Of these two alternatives, the amido ligand is especially interesting since it offers a

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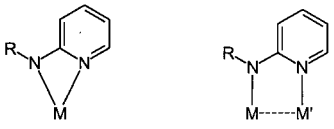
Rhett Kempe was born in Dresden in 1964. He studied chemistry at the Universität Leipzig including research stays in Jena (Prof. D. Walther) and Stuttgart (Prof. H.-G. von Schnering) and received his PhD degree (organonickel chemistry) under the supervision of Prof. J. Sieler (1989). During a DAAD postdoctoral research fellowship at MIT (1992/1993) with Prof. R. R. Schrock he became interested in N_2 activation. After a period at the MPI für Kohlenforschung in Mülheim (1993/1994) he began to study for his habilitation in the Max-Planck-Gesellschaft Group "Complex Catalysis" led by Prof. U. Rosenthal. The habilitation (metal−amido chemistry) followed at the Universität Rostock in 1998. He worked as a group leader in the Institut für Organische Katalyseforschung Rostock (IfOK) for two years and moved in 2000/2001 as a visiting scientist to the University of Melbourne (Prof. R. Robson's group). He became a Professor of Inorganic Chemistry at the University of Oldenburg in 2001 and was appointed to a Chair of Inorganic Chemistry at the University of Bayreuth in 2002. His research interests include the development of novel catalyst systems and he is working at the interface between coordination chemistry and homogeneous catalysis. He is an author of more than 170 publications and was awarded the Karl-Winnacker-Stipendium (1998) and the Heisenberg-Stipendium (2000).

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

greater variety in ligand and complex design because of the possibility for double substitution at the donor atom.

The foundations of amido transition metal chemistry were laid in the 1960s and 1970s and are associated with names such as Bürger, Wannagat, Bradley, and Lappert. The motivation for these investigations was mainly the exploration of the reactivity of metal−amido bonds in comparison to the metal−carbon bond. Disappointingly, the metal−amido bond is kinetically inert and thermodynamically more stable than the corresponding metal−carbon bond, and thus synthetically far less interesting. Today in metal−amido chemistry the stable metal−amido bond is exploited to produce well-defined reaction centres in transition metal complexes. In this way the reactivity of the resulting compounds can be specifically tailored.[4]

Aminopyridinato ligands (Scheme 2) are an important class of amido ligands and are derived from deprotonated 2-aminopyridines.[5]

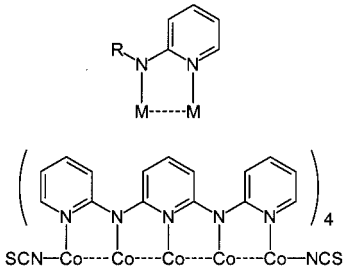


Scheme 2. Binding modes of aminopyridinato ligands (R = alkyl, aryl or silyl; M = transition metal, M′ = late transition metal)

They are interesting due to the flexibility of their binding modes. This microreview encompasses the early transition metal coordination chemistry of aminopyridinato ligands as well as the reactivity of their complexes.

Di- and Multimetallic Compounds

In addition to early transition metal coordination chemistry, deprotonated 2-aminopyridine ligands have been used to stabilise di- and multimetallic compounds (Scheme 3).[6]

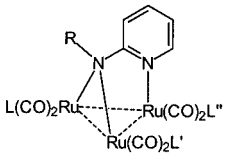


Scheme 3. Dimetallic complexes (top) and an example of a multinuclear cobalt compound (bottom) stabilised by deprotonated 2-aminopyridine ligands (R = H, alkyl or aryl; M = Ag, Cd, Co, Cr, Cu, Ir, Mo, Ni, Os, Pd, Pt, Rh, Ru, W and Zn)

Such complexes have been extensively described for Co,[7] Cr,[8] Cu,[7a,7b,9], Mo,[8a,10] Ni,[7e,9b,11] Rh,[12] and Ru[12i,13] and are known for Ag,[9e,9i,14] Cd,[15] Ir,[16] Os,[17] Pd,[18] Pt,[18] W,[8a,10d,19] and Zn.[9e,20]

Cluster Chemistry

The syntheses and reactivities of Ru[21] and Os[22] cluster compounds coordinated by deprotonated 2-aminopyridines (Scheme 4) have been reported.



Scheme 4. Examples of cluster compounds stabilised by deprotonated 2-aminopyridines (R = H, alkyl or aryl, L, L′, L′′ = additional ligand, for instance CO, PPh_3 or alkyne)

Main-Group Metal Complexes

The structural variety of aminopyridinato main-group metal complexes[23,60] makes their coordination chemistry a fascinating field and must be mentioned in any discussion of such ligands. This chemistry, as well as that of the multimetallic and cluster compounds, are not reviewed in this article.

Early Work and Contributions to the Renaissance of (Amido)metal Chemistry

The first strained η^2-coordinated aminopyridinato complex (Scheme 2, left) was published by Cotton et al.,[24] and only a few compounds[9e,25,26] had been investigated prior to 1996. The first early transition metal complex, a vanadium compound, was published by Gambarotta et al. in 1991.[26] Four years later, aminopyridinato ligands started to become extensively used to stabilise early transition metal ions in medium or high oxidation states. These studies can be seen in the context of the renaissance of metal−amido chemistry[4] which was initiated by the search for alternatives to the well-known Cp ligands. An interest in these systems soon grew due to the unique chemistry of these ligands, which is mainly a result of the close proximity of the amido and pyridine functions. In addition, these ligands may be easily derivatised to fine-tune metal complex reactivity.

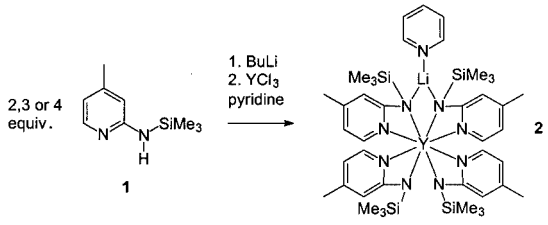
Lanthanide Chemistry Including Sc and Y

The steric bulk of aminopyridinato ligands is rather small in comparison to the related cyclopentadienyl ligands[27] and the closely related silyl-substituted amidinates.[28,29] Therefore the chemistry of aminopyridinato ligands differs dramatically from these two types in cases such as group-3 or lanthanide chemistry where steric bulk is important for the stabilisation of reactive transition metal complexes.[30]

Simple Aminopyridinato Ligands and Their Transfer Reactions

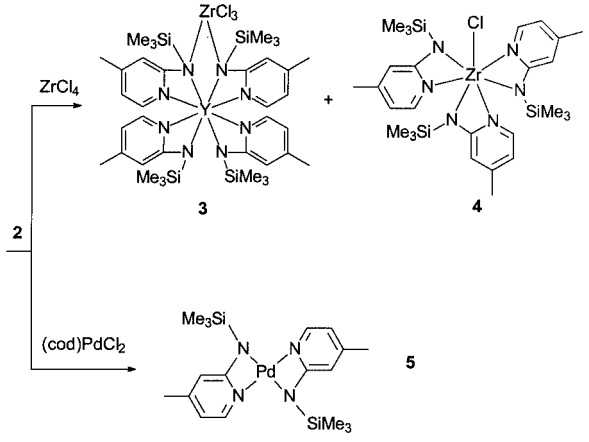
The reactions of deprotonated aminopyridines such as **1** (Scheme 5) with lanthanide trihalides gave the ate complexes such as **2**.[31] Monochloro compounds were formed

if 2 equiv. of cyclopentadienyl ligands[32] or silyl-substituted amidinates[33,28,29] were used instead of **1**.



Scheme 5. Synthesis of extensively N-coordinated ate complexes

Compound **2** can be considered as a sterically demanding lithium amide and was thus expected to react with transition metal chlorides. The reaction with $ZrCl_4$ and [(cod)$PdCl_2$] (COD = 1,5-cyclooctadiene) afforded the aminopyridinato complexes **4** and **5**, respectively (Scheme 6). The isolation of **3**, a Y−Zr dimetallic complex, indicates that such reactions proceed via heterodimetallic intermediates. Complex **5** is a rare example of a homoleptic (amido)-palladium compound.[34] In addition to the ligand transfer method, **5** was also synthesised by a salt elimination reaction at low temperature in THF (THF = tetrahydrofuran).[31] Since lanthanide ate complexes react with late metal chlorides, such salt metathesis reactions might be the key to the synthesis of heterodimetallic compounds combining lanthanides and group-8 to -10 metals. The ligand transfer reaction must be avoided in order to stabilise intermediates such as **3**.

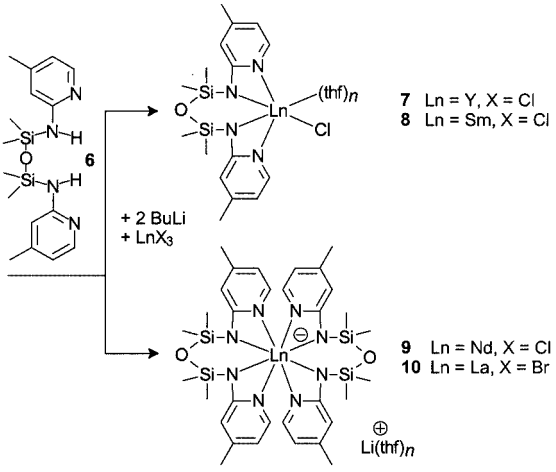


Scheme 6. Ligand transfer reactions

Bis(aminopyridinato) Ligand Complexes

Some of the limitations of simple aminopyridinato ligands can be overcome by using bis(aminopyridinato) ligands such as deprotonated **6**.

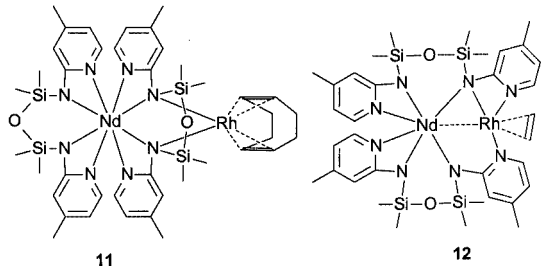
Reaction of bis(lithiated) **6** (generated in situ) with $LnCl_3$ gave different products depending on the size of the lanthanide ion. For Ln = Y and Sm, the monochloro complexes **7** and **8** were formed (Scheme 7). These could be further functionalised with $LiCH(SiMe_3)_2$, $(C_4H_9)_4NBH_4$ and $NaBH_4$ to give the corresponding bis[$CH(SiMe_3)_2$] and bis(BH_4) ate complexes.[35] Similar reactions as used to synthesise **7** and **8** afforded **9** and **10** for the larger Nd and La ions (Scheme 7). The aminopyridinato ate complex **10** was investigated as an initiator in the ring opening polymerisation of ε-caprolactone and δ-valerolactone, with particular interest focusing on the relationship between the monomer/initiator ratio and the molecular weight of the polyester, as well as the production of high molecular weight products. In both cases an almost linear relationship between the monomer/initiator ratio and the molecular weight was observed.[35] The high efficiency of the system was shown by carrying out the polymerisation in neat ε-caprolactone at room temperature. A solid polyester block (300000 g/mol, M_w/M_n = 2.3) was formed after 3 min. Ring-opening polymerisation of lactones is a useful method to produce biodegradable aliphatic polyesters,[36] and well-defined polymers of this type have possible applications as surgical sutures and in drug delivery systems.[37] The production of polymers with a well-defined molecular weight as well as a narrow molecular weight distribution is needed for such applications, since the polymer decomposition process depends on the length of the polymer chains.



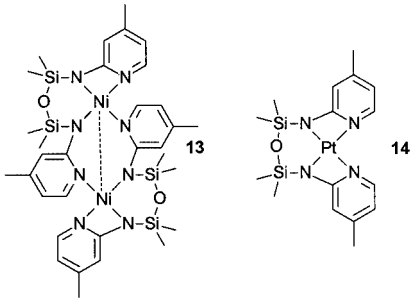
Scheme 7. Synthesis of bis(aminopyridinato) complexes

The reaction of **9** with [(cod)$RhCl]_2$ and $[(C_2H_4)_2RhCl]_2$ gave rise to the dimetallic compounds **11** and **12**, respectively (Scheme 8).[38] Both compounds are rare examples of early late heterobimetallics (ELHB) in which lanthanides and group-9 metals are combined. Investigations of the nature of the interactions between the two metals are underway.[39] The very short distance between Nd and Rh in **12** is consistent with a direct metal−metal bond, the only other example being the Lu−Ru bond in $[Cp_2(THF)Lu-RuCp(CO)_2]$ [2.955(2) Å].[40]

The reaction of **9** or **10** with [(dme)$NiCl_2$] and [(cod)$PtCl_2$] (DME = dimethoxyethane) gave the dimeric nickel complex **13** and a mononuclear platinum complex **14** (Scheme 9).[41] Both compounds are rare examples of late metal amido complexes.

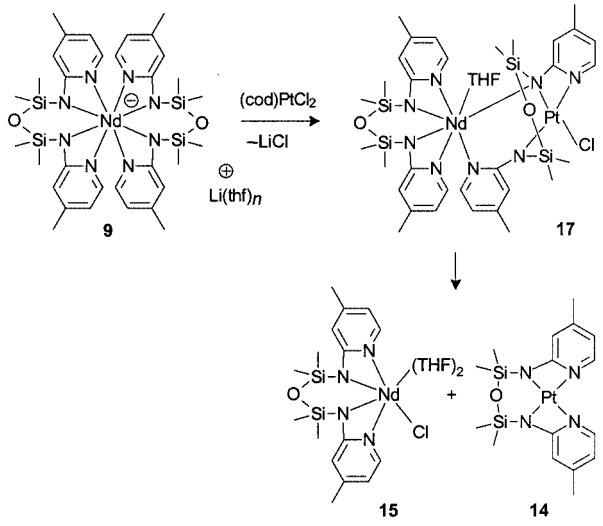


Scheme 8. Nd−Rh dimetallic complexes; Nd−Rh distances are 3.2283(15) Å for **11** and 2.9744(15) Å for **12**



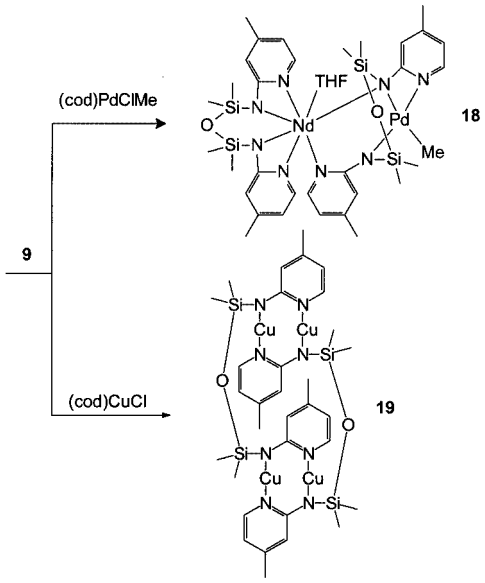
Scheme 9. Synthesis of **13** and **14** by ligand transfer

The mechanism shown in Scheme 10 was proposed for the synthesis of **14**. The neodymium ate complex **9** reacts with [(cod)$PtCl_2$] and the heterodimetallic intermediate **17** is formed. Transient **17** decomposes to give **14** and **15**. In addition to **14**, the monochloro complex **15** and LiCl were also isolated as by-products.



Scheme 10. Proposed mechanism for the formation of **14**

The reaction of **9** with [(cod)PdClMe][42] afforded the dimetallic compound **18** which can be considered as a model compound for the intermediate **17**. If **9** or **10** were treated with [(cod)$PdCl_2$] the formation of Pd black was observed. Ligand transfer also gave the tetrameric copper complex **19** (Scheme 11).



Scheme 11. Synthesis of **18** and **19**

The compounds **13**, **14** and **19** are rare examples of group-10 and -11 amido complexes.[43,44] Activation of **13** with $EtAlCl_2$ (Al/Ni = 150) in hexane at room temperature generated an efficient ethylene oligomerisation catalyst. The obtained oligoethylenes contained mainly internal double bonds (Schulz−Flory distribution, TOF = 2400 h^{-1}). When $Et_3Al_2Cl_3$ was used as a co-catalyst and CH_2Cl_2 as the solvent, highly branched oligomers with a very narrow molecular weight distribution [M_n = 230 g/mol (relative to polystyrene standards), M_w/M_n = 1.14] were produced. According to NMR investigations, the oligomers are identical with results recently published by Sen et al. The catalyst system based on **13** has significantly higher activity.[45]

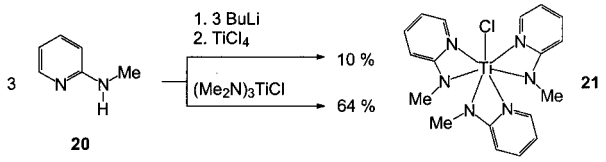
The ligand transfer reactions that led to **5**, **13**, **14** and **19** can be explained in terms of modification of the reactivity of the corresponding lithium amides by coordination at the lanthanide centres. Thus, the reduction potential is lowered but the lithium amides are still active enough to react with transition metal chlorides. Unstable Ln−Ni, Ln−Pt and Ln−Cu heterodimetallic complexes can be assumed as intermediates in the ligand transfer reactions. These intermediates are important for the formation of the polycyclic and multinuclear structures of the resulting complexes such as **13** and **19**.

Bis(aminopyridinato) ligands are useful to prepare heterodimetallic compounds with metal−metal distances smaller then 3 Å. The nature of possible interactions between the lanthanides and the group-9 or -10 metals is not yet clear. Unfortunately, the synthesis of ate complexes using deprotonated **6** is limited to larger Ln ions, and the ligand transfer could only be avoided for selected examples of group-9 and -10 metals. Ligand variations might be the key to overcome these restrictions, as was shown by the recent use of (aminopyridinato)(Cp) ligands.[46]

Titanium, Zirconium and Hafnium

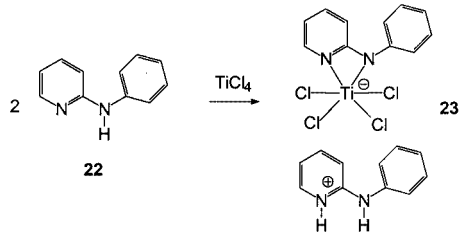
Titanium and Zirconium Complexes that Contain Alkyl-, Aryl- and Silyl-Substituted Ap (Ap = Aminopyridinato) Ligands

The exploration of group-4 metal coordination chemistry of selected aminopyridinato ligands began in 1996.[47,48] The investigators were interested in replacing Cp ligands with special amido-type ligands and studying the reactivities of the resulting complexes. It was emphasised that traditional synthesis protocols such as salt metathesis failed in the case of titanium. For instance, the lithiation of the preligand **20** with BuLi and subsequent reaction with $TiCl_4$ or $[TiCl_4(THF)_2]$ afforded **21** in only very low yield (Scheme 12).



Scheme 12. Synthesis of **21** by salt metathesis and amine elimination

The poor yield was thought to be due to reduction of the titanium centre by the lithiated Ap ligands. Two solutions were found, namely "direct synthesis" (Scheme 13) and amine elimination (Scheme 12). Direct synthesis involves treatment of an alkyl- or aryl-substituted aminopyridine (for instance **22**) with $TiCl_4$ in either boiling toluene or without solvent at temperatures above 100 °C.

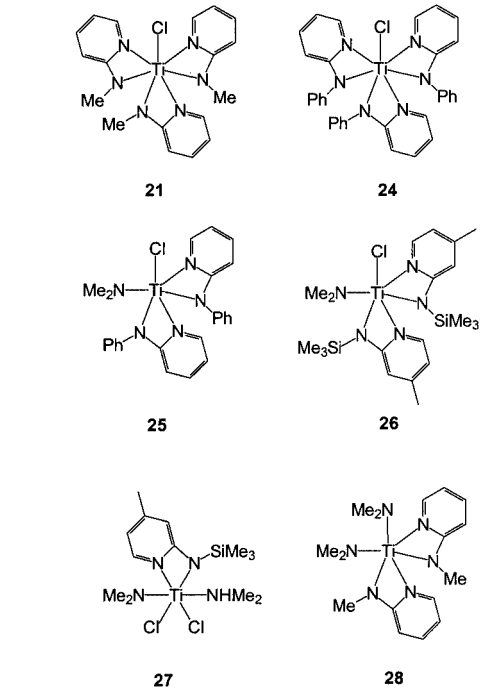


Scheme 13. "Direct synthesis": reaction of an aminopyridine with $TiCl_4$

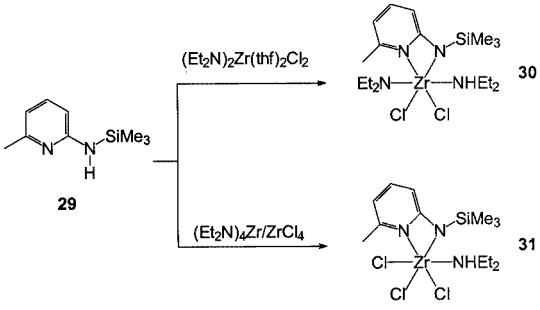
Amine elimination has been useful for the synthesis of many titanium complexes. The reaction of **1**, **20** and **22** with $(Me_2N)_3TiCl$[49] or $(Me_2N)_2TiCl_2$ [49] afforded **21**, **24**, **25**, **26**[48] and **27**.[50] Reaction of **20** with $(Me_2N)_4Ti$ gave **28**.[51]

Compound **27** showed very high[52] activities for the polymerisation of propene and 1-butene if activated with MAO, triisobutylaluminium/$B(C_6F_5)_3$ or ethylaluminium sesquichloride.[50] Remarkably the corresponding zirconium complex **30** (Scheme 15) was inactive. Compound **30** is accessible by amine elimination starting from $[(Et_2N)_2Zr(THF)_2Cl_2]$[53] and **29**.

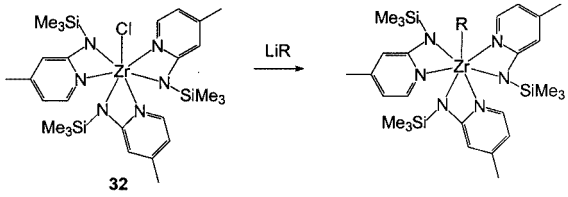
The use of in situ-generated mixed (amido)(chloro)zirconium complexes instead of the well-defined starting material $(Et_2N)_2Zr(THF)_2Cl_2$ leads to by-products such as **31**.[54] Besides amine elimination and salt metathesis, "direct synthesis" has proven to be efficient for the synthesis of zirconium complexes. In situ lithiation of **1** and subsequent reaction with $ZrCl_4$ gave **32**.[55] The propeller-like arrangement of the three Ap ligands in **32** provides a sterically well-protected reactive pocket. This allows the stabilisation of a variety of alkyl-,[55] aryl-,[55,56] alkynyl-[55,57] and butadiynylzirconium[58] complexes (Scheme 16).



Scheme 14. Ap titanium complexes by amine elimination starting from $(Me_2N)_3TiCl$, $(Me_2N)_2TiCl_2$ and $(Me_2N)_4Ti$

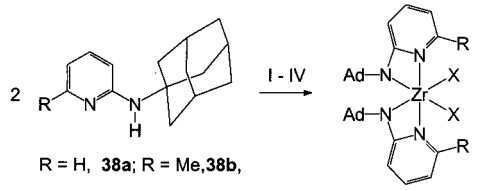


Scheme 15. Synthesis of **30** and **31**



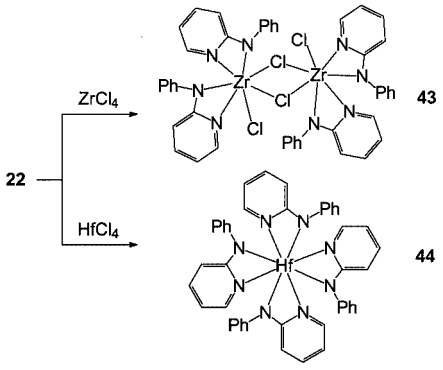
Scheme 16. Synthesis of alkyl-, aryl-, alkynyl- and butadiynylzirconium complexes [R = Me (**33**), Ph (**34**), C≡CPh (**35**), C≡CSiMe$_3$ (**36**), C≡CC≡CSiMe$_3$ (**37**)]

Better control of the zirconium/ligand stoichiometry and structures of bis(aminopyridinato) complexes is possible by introduction of sterically demanding alkyl substituents (e.g. adamantyl) on the ligands. Scott et al. reported the synthesis and structure of bis(Ap)zirconium complexes by salt metathesis, amine and alkyl elimination reactions (Scheme 17).[59]



Scheme 17. Synthesis of bis(aminopyridinato)zirconium complexes [I: 2 BuLi, $ZrCl_4$; II: $(Me_2N)_4Zr$; III: $(PhCH_2)_4Zr$; IV: (*tert*-butyl$CH_2)_4Zr$; **39a/39b** R = H/Me, X = Cl; **40a/40b** R = H/Me, X = NMe_2; **41a/41b** R = H/Me, X = CH_2Ph; **42a/42b** R = H/Me, X = CH_2-*tert*-butyl]

The activation of **39a** with MAO afforded a catalyst that showed moderate[52] activity in ethylene polymerisation. A bis(aminopyridinato) complex of zirconium has been described previously. Polamo et al. reported the "direct synthesis" of **43** by treating **22** with $ZrCl_4$.[60] A similar reaction of **22** with $HfCl_4$ gave the homoleptic complex **4** (Scheme 18).[61] This work shows that the "direct synthesis" is not a consistent method and does not allow control of the metal/ligand stoichiometry.

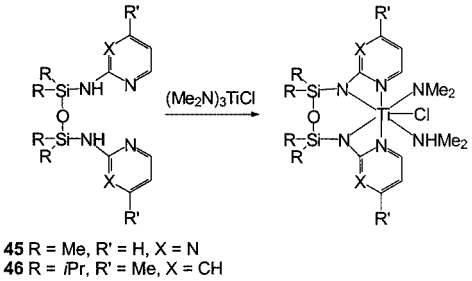


Scheme 18. Synthesis of **43** and **44**

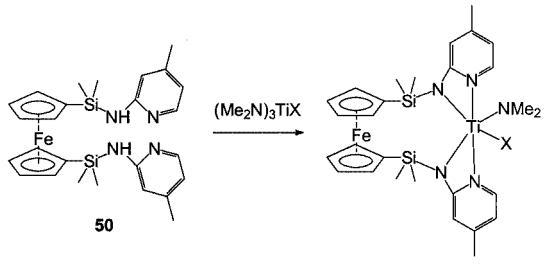
Bis(aminopyridinato)titanium Complexes

As mentioned above (see group-3 and lanthanide chemistry) two aminopyridine moieties may be easily connected and this leads to better tuned reactive sites of the corresponding transition metal complexes. The reaction of the siloxane-bridged bis(aminopyridine) **6**, **45** and **46** with $(Me_2N)_3TiCl$ yielded mixed (amido)(chloro) complexes **47**−**49** (Scheme 19).[62]

Olefin polymerisation studies of **47**−**49** have been carried out. Activation of the complexes with MAO gave rise to low[52] activities in ethylene polymerisation and no activity was observed for higher olefins. Structural studies of the precatalysts showed planar coordination of the bis(aminopyridinato) ligands and the ligands thus "cut" the complexes into two parts. This results in a separation of the coordination site of the growing alkyl chain and the coordination site for olefins during the polymerisation process. Such a separation leads to a high insertion barrier and a correspondingly slow polymerisation process. In addition to siloxane bridges, a ferrocene moiety was also introduced as a connector.[63] The reaction of **50** with $(Me_2N)_4Ti$ and $(Me_2N)_3TiCl$ afforded the heterodimetallic complexes **51** and **52** (Scheme 20).



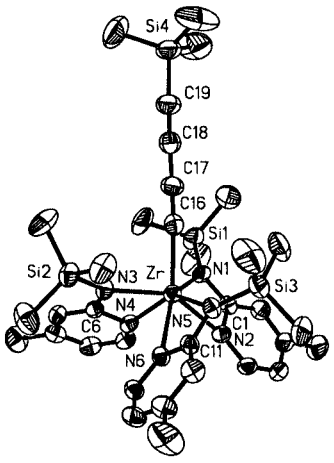
Scheme 19. Synthesis of the bis(aminopyridinato)titanium complexes **47** (R = Me, R′ = Me, X = CH), **48** (R = Me, R′ = H, X = N) and **49** (R = *i*Pr, R′ = Me, X = CH)



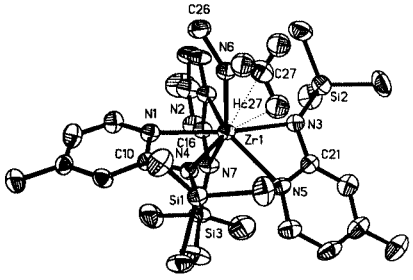
Scheme 20. Synthesis of heterodimetallic complexes **51** (X = NMe_2) and **52** (X = Cl)

Ligand/Substrate Communication

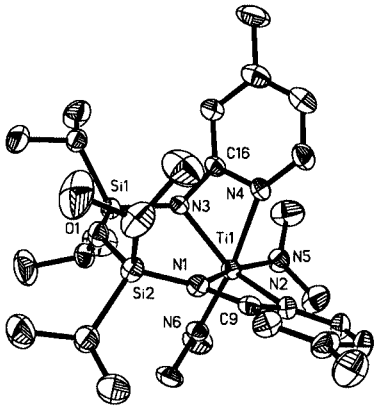
Ligand/substrate communication (steric repulsion between a ligand core and an ancillary coordinated substrate as well as electronic interactions of both via the metal centre) is a fundamental component of all metal-mediated transformation reactions, especially catalysis. While the design of a reactive metal centre is well understood in many cases,[1] understanding of the opposite influence, how substrate binding changes the coordination mode of a certain ligand core, is poor. Owing to the high flexibility of the binding modes of aminopyridinato ligands, their corresponding metal complexes may act as model systems to study ligand substrate communication because the ligands are sensitive to the steric and electronic requirements of the ancillary coordinated substrates. Comparison of the σ-butadiynylzirconium complex **37** with the dimethylamido compound **53** and the *ansa*-(aminopyridinato)titanium complexes accommodating dimethylamido (**54**) and ε-caprolactamato moieties (**55**) shows how the flexible Ap ligands can meet substrate requirements.[58] Molecular structures of the aforementioned compounds are shown in Scheme 21.



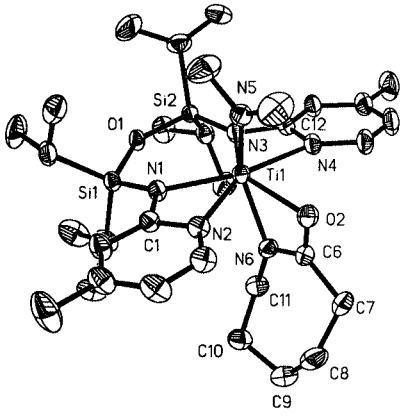
37



53



54



55

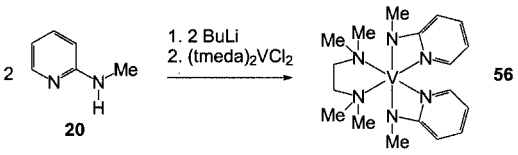
Scheme 21. Crystal structures of **37**, **53**, **54** and **55**

The propeller-like arrangement of the three aminopyridinato ligands in **37** may cause a kinetic stabilisation. The zirconium−carbon bond is sterically shielded by the three bulky trimethylsilyl groups of the ligands. This coordination mode seems to be favoured with regard to electronic considerations and is accomplished as long as the steric demand of the ancillary coordinated substrate does not dictate a rearrangement. If the substrate is sterically demanding like the dimethylamido moiety (see complex **53**), the aminopyridinato-coordinated metal centre easily alters its coordination mode. This alteration is facilitated by the extraordinary flexibility of the ligand system. It opens up a large coordination site to provide sufficient space even for an agostic interaction of the methyl group of the dimethylamido moiety. Such an interaction is proposed as an intermediate in the early transition metal catalysed aminomethylation of non-activated olefins.[64] An adaptation of the coordination mode of the ligand core can also be observed by comparing **54** and **55**. Compound **54** is a six-coordinate complex, and in order to achieve an octahedral coordination geometry the aminopyridinato ligand must become twisted. Thus, two different binding modes of the ligand core can be observed. The coordination number must be raised from six to seven to bind the caprolactamato ligand, and the pyridine moiety situated "out of plane" in **54** is turned "in the plane" in **55** to offer the additional coordination site. The ligand thus becomes planar. In addition to the geometric rearrangement, the binding mode of the formerly "out-of-plane" ligand arm is switched to the delocalised form[65] (almost equal Ti−N bond lengths). Steric and electronic changes are necessary to meet the requirements of the caprolactamato moiety.

The Vanadium Triad

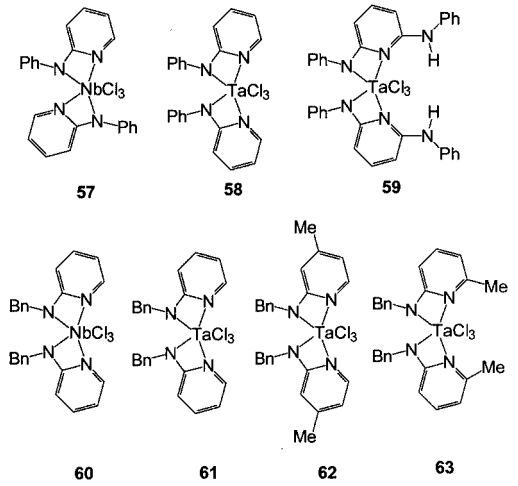
Niobium and Tantalum Complexes and Their Application in Polymerisation Reactions

The first well-characterised early transition metal aminopyridinato complex was reported by Gambarotta et al.[26] The reaction of $[(tmeda)_2VCl_2]$ (tmeda = tetramethylethylenediamine) with in situ lithiated **20** gave **56** (Scheme 22).



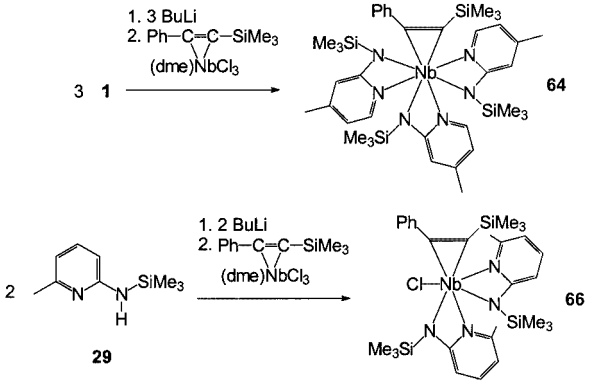
Scheme 22. Synthesis of **56**

A more detailed investigation of the group-5 metal coordination chemistry was started by Polamo et al. He applied the "direct synthesis" method to prepare a variety of niobium and tantalum complexes in high oxidation states (Scheme 23).[60,66−68]



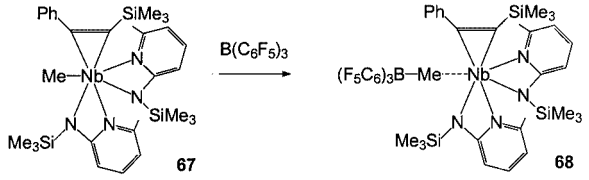
Scheme 23. Trichloro complexes of Nb and Ta prepared by "direct synthesis"

The syntheses of **57**−**59** were carried out in toluene and the compounds **60**−**63** were generated "solvent-free" using molten preligands (aminopyridines) as solvent. All compounds have been characterised by X-ray crystallography and adopt a pentagonal-bipyramidal molecular structure in the solid state. Very high[52] ethylene polymerisation activities were observed for **59** and **61** if the complexes were activated with MAO.[69] The catalyst system based on **61** gave up to 5000 $kg_{PE}/(mol_{Ta}h)$ and that based on **59** up to 23900 $kg_{PE}/(mol_{Ta}h)$. Experiments were carried out for 7 min, with longer polymerisation times leading to dramatically reduced activities. While the exact nature of the catalysts is not known, some analogy to group-4 metallocene chemistry can be drawn,[70] and mechanistic studies on high oxidation state (alkyne)bis(aminopyridinato)niobium complexes underline this analogy.[71] Treatment of $[(dme)NbCl_3(PhC{\equiv}CSiMe_3)]$[72] with 3 equiv. of in situ lithiated **1** gave the orange-red alkylniobium complex **64** (Scheme 24). The niobacyclopropene ring in **64** is extremely stable and does not react with ketones, styrene oxide, alkynes and olefins. This converses the high reactivity for the (alkyne)metallocene complexes of the titanium triad.[73]



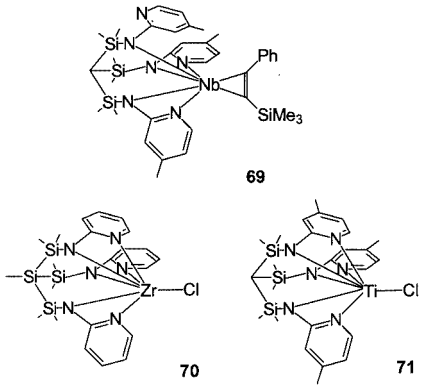
Scheme 24. (Alkyne)niobium complexes

Complexes containing two amido ligands are accessible by using the sterically more demanding deprotonated **29** (Scheme 24). The otherwise analogous reaction (first line in Scheme 24) led to **66**. NMR spectra of **66** indicated a dynamic behaviour which could be explained by alkyne rotation, with the barrier to rotation being $\Delta G^{\neq} = 80$ kJ/mol. The reaction of **66** with MeLi led to **67**, a methyl complex where the methyl group could be partially abstracted by $B(C_6F_5)_3$ (Scheme 25).



Scheme 25. Partial abstraction of a methyl group by $B(C_6F_5)_3$

Complex **68** is a zwitterionic compound and a single component ethylene polymerisation catalyst. The partial abstraction of the methyl group and the structural parameters of **68** are similar to what has been observed for group-4 metallocenes.[74] Thus, an analogy in terms of the generation of ethylene polymerisation catalysts can be drawn between high oxidation state group-5 metal Ap compounds and group-4 metallocenes. The synthetic procedure described in Scheme 24 could also be used to synthesise the niobium alkyne **69**.[75] Complex **69** polymerised acetylene without the formation of benzene as a by-product. The first metal complex of a tris(aminopyridinato) ligand (**70**) was reported by Gade et al.[76] Complexes of such ligands are rarely described (see **69**, **70** and **71** in Scheme 26).

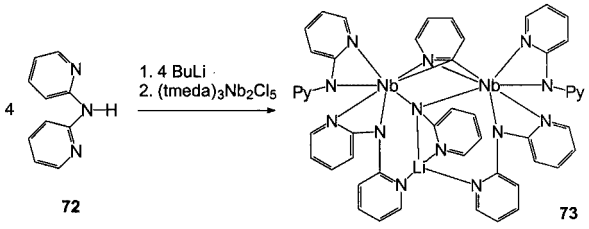


Scheme 26. Complexes stabilised by tris(aminopyridinato) ligands

Complex **71** was synthesised by amine elimination. Owing to the steric crowding in **69**, one of the three pyridine moieties does not coordinate to the niobium centre, in contrast to the hexadentate coordination of **71**. Tris(aminopyridinato) ligands are variable in their denticity, a phenomenon which is characteristic of many Ap compounds during substrate binding and release, but seldom observed in molecular structures determined by X-ray crystallography.

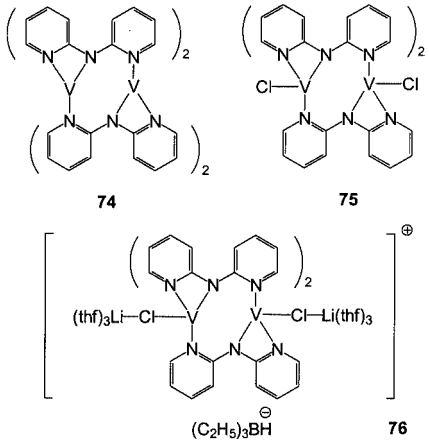
Low Oxidation State Chemistry

Oxidative addition of C−X bonds (X = N, P, O, S, halogen) performed by transition metal complexes is an area of research which is of interest not only from a fundamental point of view, but also because of the many possible applications of such reactions. Aminopyridinato ligands can either stabilise reactive group-5 metal complexes in low oxidation states or be involved in bond cleavage processes. Compound **56** (Scheme 22) is an example of a group-5 complex in a low oxidation state. The reaction which led to **56** proceeded as expected and no C−X bond activation was observed. C−N bond cleavage took place if $(tmeda)_3Nb_2Cl_5$ was treated with the lithium salt of **72** (Scheme 27).[77]



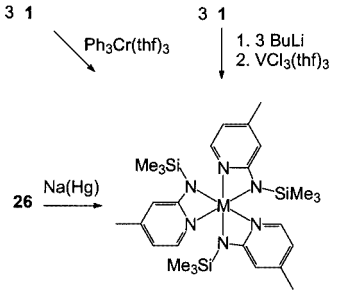
Scheme 27. C−N bond cleavage of an aminopyridinato moiety

The reaction of "$VCl_2{\cdot}n$THF" [generated in situ by the reduction of $VCl_3(THF)_3$ with $NaB(C_2H_5)_3H$] and lithiated **72** yielded **74** if a mixture of THF and toluene was used as solvent at reflux temperature. A similar reaction carried out in THF at 0 °C gave **76**. C−Cl bond cleavage was observed during the reaction of **76** with CH_2Cl_2. Compound **75** was the product of this transformation (Scheme 28).[78]



Scheme 28. Products of the reaction of "$VCl_2{\cdot}n$THF" with lithiated **72**

Complexes shown in Scheme 27 and Scheme 28 are dinuclear compounds. Deprotonated **72** acts as a tridentate ligand and its linear arrangement of the three N donor functions does not stabilise mononuclear complexes. A mononuclear homoleptic tris(aminopyridinato)vanadium complex was synthesised from lithiated **1** (in situ) and $[VCl_3(THF)_3]$ (Scheme 29).[79]



Scheme 29. Mononuclear tris(aminopyridinato)M^{III} complexes (**77**: M = V; **78**: M = Ti; **79**: M = Cr)

Compound **79** is a rare example of an aminopyridinato group-6 metal complex in which the Ap ligands coordinate in a strained η^2-fashion.[25,80]

Conclusions and Outlook

Aminopyridinato ligands can coordinate a variety of early transition metal complexes in the strained η^2-fashion. This binding mode initiates a special reactivity. Thus, it has become possible to stabilise heterodinuclear compounds with unusual metal−metal combinations including short metal−metal distances as well as highly active olefin polymerisation catalysts. The exploration of the catalytic and stoichiometric reactivity of many of the complexes synthesised so far was started only recently and a lot of exiting "chemistry" can be expected in the near future, covering

fields like small molecule activation, homogenous catalysis and the synthesis and reactivity of multinuclear complexes.

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