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Principal trends in the chemistry of amidinate complexes of main-group and transition elements

D A Kissounko, M V Zabalov, G P Brusova, D A Lemenovskii

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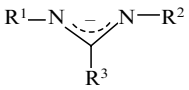
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Abstract. Principal trends in modern organometallic chemistry of transition and main group elements containing amidinate ligands are analysed. The nature of element – amidinate ligand bonding inferred from the X-ray structural data and computational studies is discussed. Synthesis and reactivity of Group 1 – 15 metal amidinate complexes are reviewed. Particular emphasis is drawn to the use of amidinate complexes as catalysts for olefin polymerisation and organic synthesis. Prospects in the development in this area of chemistry are suggested. The bibliography includes 151 references.

I. Introduction

Over the past decade there has been a growing interest in non-metallocene main group and transition metals complexes as catalysts for olefin polymerisation and organic synthesis.[1] The rational for a closer attention to such systems is often explained as the lack of new groundbreaking chemical transformations for analoguos metallocene complexes, which have been extensively studied since the mid-1950s. Hence, there is an essencial need for other ancillary ligands, which would provide new types of organometallic complexes exhibiting unusual electronic and structural properties.

Complexes with allylic ligands and their heteroanalogues, *viz*., NNN- (triazene) and PNP- (phosphazene) ligands are typically referred as non-metallocene derivatives. These compounds are widely used in such important area as asymmetric catalysis.[2–4] Over the past decade the considerable attention has also been paid to NCN-analogues of allylic group, *viz*., to amidinate ligands:



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The particular interest to amidinate is caused primarily by the commercial availability of a wide range of synthetic precursors — carbodiimides. Also of significant importance is the simplicity of preparation of amidinate complexes. Moreover, amidinate ancillary ligand is known to enchance the thermodynamic stability of a corresponding complex; thus, many cationic intermediates, which are unstable for related metallocene analogues, were isolated for amidinate derivatives. The ability to study such intermediates has greatly improved the knowledge of reaction mechanisms in such vital area as cationic olefin polymerisation.[5]

Synthesis and properties of amidinate complexes published prior to 1994 were comprehensively discussed in earlier reviews.[6–9] However, despite the growing number of publications in this field over the past decade, there has been only a single review article dealing with ruthenium amidinate complexes.[10] Hence, this justifies the need for an updated review on organometallic amidinate complexes. The present review is divided into two parts. The first part is devoted to a discussion of metal – amidinate ligand bonding inferred from X-ray diffraction data and computational studies. The other one deals with the chemical behaviour of amidinate complexes. The latter also contains detailed discussion of applications of amidinate derivatives in organic synthesis and catalysis. Future developments in the research of amidinate complexes are analysed in Conclusion.

Due to the limited space available, the metal complexes with neutral analogues of amidinate systems, *i.e*., amidine ligands, are out of scope of the present review. Information about these compounds can be found in earlier reviews.[11–13]

II. Structures of amidinate complexes

To date, the structures of amidinate complexes of different elements are reasonably well studied. Amidinate ligands behave as two- or (more often) four-electron donors depending on the nature of the central atom.[7] Therefore, this system might be referred to as a hetero-analogue of the well known allylic ligand. However, the presence of molecular orbitals n^+ and n^- (Fig. 1) where the electrons of the nitrogen lone pairs are mostly localised results in significant difference in coordination modes of the amidinate and allylic fragments to metals.

Analysis of bonding of amidinate ligands with Group 14 elements (Si, Ge, Sn, Pb) as well as of the structure of a non-coordinated amidinate anion has been performed by detailed quantum-chemical calculations (by the extended Hückel method and by MP2/ECP-31G*).[14] It was found that the N – C bond in a coordinated ligand is significantly longer (by $\sim$0.1 Å) and the NCN bond angle is smaller in comparison with those in the non-coordinated anion. The decrease in the NCN bond angle occurs in

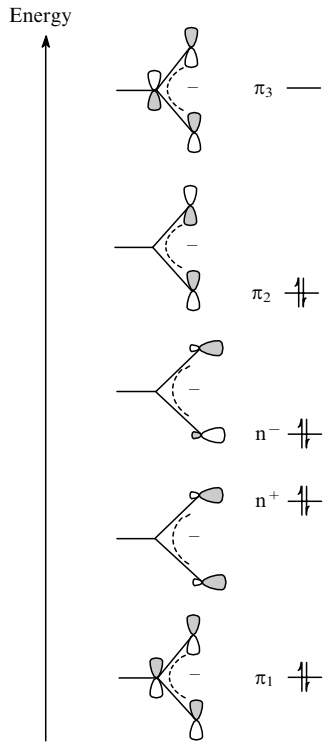
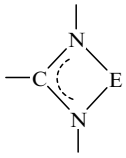


Figure 1. Molecular orbital diagram for the amidinate anion.

parallel to the decrease in the atomic radius of the corresponding element (Pb < Sn < Ge < Si). The calculated bond lengths and bond angles in amidinate complexes of Group 14 elements are listed below.

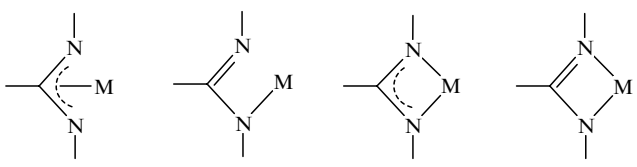


E	The C=N bond length /Å	The NCN angle /deg
—	1.252	125.7
Si	1.349	106.2
Ge	1.348	108.6
Sn	1.347	111.6
Pb	1.347	113.9

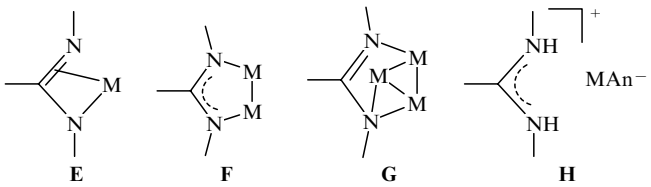
It should be noted that no calculations of this type have been documented for transition metal complexes. The only publication [15] reports DFT calculations of ethylene molecule coordination parameters in titanium and zirconium bis(amidinate) complexes. However, no data on the geometrical parameters of the amidinate ligand itself are given and only bond angles NTiN and NZrN (128.3° and 127.8°, respectively) are presented.

Eight types of coordination of the amidinate ligand to metals can theoretically be predicted based on its electronic and spatial structures (structures **A**–**H**).

It should be noted that no η^3-coordinated amidinate ligands (structure **A**, an analogue of the π-allylic system) and structures **E** have been reported so far. The other structural types have been discussed.[8,9]



A **B** **C** **D**



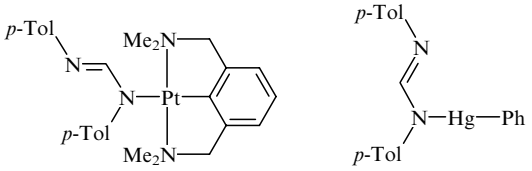
E **F** **G** **H**

M is metal, An is anion.

The main sources of information about the structures of amidinate complexes are single crystal X-ray structural studies and the spectroscopic data (IR, NMR, *etc.*). Typically, the MN(1)CN(2) metallacycle in amidinate complexes of transition and main-group elements is non-planar. In the **C**- and **D**-type structures, this ring usually adopts the 'folded envelope' conformation with dihedral angles between the MN(1)C and MN(2)C planes varying over a wide range (from 5° to 45°) (see Refs 8 and 9). The degree of pyramidalisation (ΣQ_N) of the nitrogen atoms in the amidinate ligand is yet another important criterion of non-planarity of the MN(1)CN(2) metallacycle. This parameter is the sum of all bond angles of a nitrogen atom and is opposite to planarity. A decrease in ΣQ_N value, for example, due to a decrease in the bulk of substituents corresponds to higher degree of nitrogen pyramidalisation and, therefore, to greater deviation of the MN(1)CN(2) metallacycle geometry from planarity. The mean values of the degree of pyramidalisation of nitrogen atoms in amidinate complexes are in the range of 335–360° (see Refs 8 and 9).

A short description of complexes of each known structural type is given below. The selection of examples of the structures **B**–**D** and **F**–**H** is entirely random. We just tried to emphasise the features of each coordination type as clearly as possible. Further in the text (see Section III), schematic depiction of complexes **B**–**G** implies a real structure determined objectively.

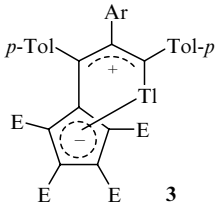
Very few examples of the structural type **B** with monodentate σ-amidinate ligands are known to date. Thus the Pt–N distance in platinum complex **1** is equal to 2.132(6) Å and the NCN bond angle is 113.4(5)° (see Ref. 16).



1 **2**

p-Tol = 4-MeC_6H_4.

Yet another stable compound of this type is σ-organomercury complex **2** with unusual dynamic properties in solution.[17] Also, type **B** compounds were postulated (based on the IR spectra) to serve as intermediates in the insertion of CO into the M–N bond of rhodium amidinate complexes to yield the corresponding carbamide complexes.[18] Unusual zwitter-ionic thallium amidinate complexes of the general formula **3** with formally positively charged amidinate groups have recently been obtained by Minkin and co-workers.[19]

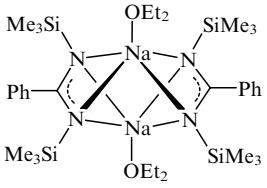


3

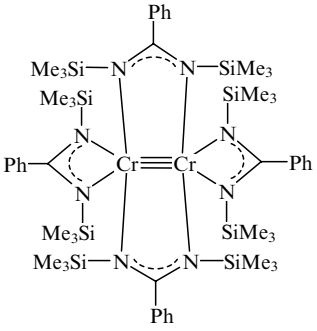
E = CO_2Me; Ar = 1-naphthyl, 2-ClC_6H_4, 2-Cl-6-MeC_6H_3.

According to X-ray diffraction data, the thallium atom in these complexes is σ-coordinated to the nitrogen atom and therefore these complexes may be regarded as type **B** compounds. The Tl – N distance is equal to 2.833(6) Å (for Ar = 2-Cl-6-MeC_6H_3). The distinctive features of complexes **3** include also η^5-coordination of thallium with the π-system of the cyclopentadienyl ring and Z-configuration of the amidinate ligand. The C – N bond lengths are equal to 1.374(10) and 1.283(10) Å, the NCN bond angle is 119.8(7)°.

Most of known amidinate complexes belong to the structural type **C**. Dimers **4** (see Ref. 20) and **5** (see Ref. 21) are the most typical examples of such complexes of the main-group and transition elements, respectively.

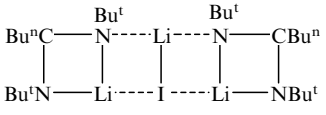


4



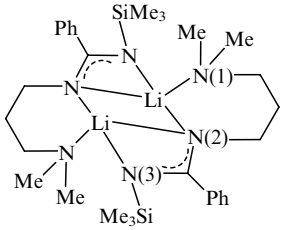
5a

The Na – N distances in compound **4** are equal to 2.617(5), 2.482(5), 2.426(5) and 2.725(5) Å; all NCN bond angles are 121.0(5)°. The Cr – N distances in complex **5a** amount to 2.100(4), 2.096(3), 2.092(4) and 2.095(3) Å; both NCN bond angles are equal to each other [116.4(4)°] as in the case of compound **4**. The derivatives of other alkali and alkaline-earth metals often form stable dimeric associates in crystals.[8,9] The 'ladder'-type aggregates are also known, in which dimerisation of amidinate salt is inhibited by co-crystallisation with inorganic salts MX (M is an alkali metal, X is an inorganic acid anion, for example Cl, I, Br) or with alkalis. Thus associate **6** was obtained by co-crystallisation of Li[$Bu^tNC(Bu^n)NBu^t$] with LiI from a solution in THF.[22]

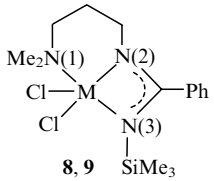


6

Monomeric amidinate complexes with 'constrained' geometry can also be mentioned. In 2000, Lappert and co-workers[23] synthesised lithium complex **7**, which was transformed into aluminium (**8**) and gallium (**9**) amidinate derivatives.



7



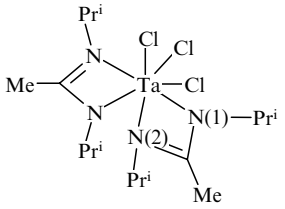
M = Al (**8**), Ga (**9**)

Complexes **8** and **9** are monomeric due to additional coordination of the nitrogen atom of the $CH_2CH_2NMe_2$ fragment by the central atom of the main-group metal. Usually, in the case of such additional coordination, the M – NMe_2 bond lengths became effectively equal to the M – N bond lengths in normal amidinate complexes. The structural parameters of compounds **7**–**9** are listed below.

Parameter	Compound		
	7 (M = Li)	**8**	**9**
Bond lengths /Å			
M – N(1)	2.050(3)	2.0929(16)	2.1407(18)
M – N(2)	2.015(3)	1.9053(15)	1.9592(15)
M – N(3)	1.989(3)	2.0182(16)	2.1130(17)
Bond angle N(2)CN(3) /deg	119.0(2)	111.20(15)	112.27(16)

The NCN bond lengths in these complexes are within a standard range of the values for all amidinate ligands,[8,9] which is common for all coordination types (**C**, **D**, **F** and **G**). A detailed structural analysis of a series of tris(amidinate) complexes of transition metals (Cr, Fe, Co, Ru) of type **C** is given by Cotton *et al.*[24]

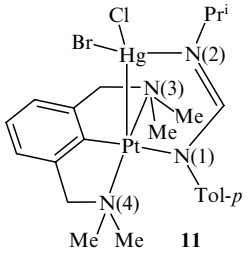
Non-symmetrically coordinated amidinate ligand represents the structural type **D**. In this case both nitrogen atoms are bonded to metal, but one forms formally a M – N σ-bond while another is coordinated by its lone electron pair. Quite a few complexes of this coordination type are known. Complex **10** can be taken as an example.[25]



10

According to the X-ray data, the pairs of Ta – N distances are equal to 2.098(14), 2.196(16) and 2.058(15), 2.180(20) Å. The NCN bond angles are within expected values and are equal to 109.4(16)° and 105.4(20)°. Dihedral angles between TaN(1)C and TaN(2)C, where C is the central carbon atom in the NCN fragment of the amidinate ligand, are equal to 10.7° and 15.5°. The mean value of ΣQ_N = 346.9° indicates significant pyramidalisation of nitrogen atoms.

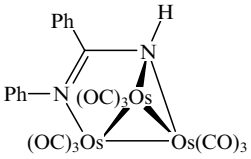
Structures **F** are relatively common for amidinate complexes possessing metal – metal bond. For instance, the platinum atom in bimetallic complex **11** (see Ref. 26) has a square-planar coordination with distances Pt – N equal to 2.155(9), 2.097(9) and 2.080(1) Å for nitrogen atoms N(1), N(3) and N(4) respectively.



11

HgBrCl occupies an apical position relative to the plane of the platinum atom and two nitrogen atoms of the bis(dimethylaminomethyl)phenyl substituent with the Pt – Hg distance equal to 2.8331(7) Å. The amidinate ligand itself is bonded to mercury atom through the nitrogen atom of the NPr^i fragment, the Hg – N(2) bond length is 2.16(1) Å. The five-membered NCNHgPt ring is non-planar and the HgClBrN fragment is rotated such as to avoid staggered conformation of M – N bonds. In this case, the dihedral angle N(2) – Hg – Pt – N(1) is equal to 16.5(4)° and the NCN bond angle [125.0(1)°], in contrast to those found in most amidinate complexes, is larger than the theoretical value (120°). The ΣQ_N parameter for both nitrogen atoms is 360° indicating virtually planar trigonal configuration of nitrogen atoms in the amidinate ligand.

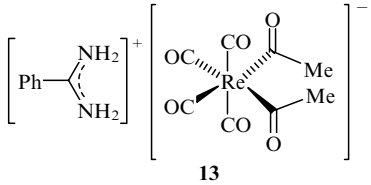
The structural type **G** is rather rare and has only been found in cluster complexes. For example, the amidinate ligand in the osmium cluster $[Os_3(\mu\text{-}H)(CO)_9]\{NPhC(Ph)NH\}$ **12** (see Ref. 27) is formally a five-electron donor. According to data from ^1H NMR spectroscopy, a bridging hydrogen atom is present in complex **12**; however, its position could not be located from X-ray diffraction analysis.



12

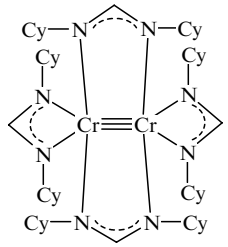
The Os–N bond lengths in metal complex **12** are equal to 2.198(23), 2.193(23) Å for osmium atoms linked to the nitrogen atom by a coordinated bond and to 2.141(22) Å for the σ-bond Os–N. Remarkably, the NCN bond angle [121.7(25)°] is slightly larger than the theoretical value, as it was also observed in complex **11**. Over the last decade, no new complexes of type **G** have been synthesised and therefore they are not discussed in the present review.

Structures **H** are of the most uncommon type of metal amidinate derivatives. In this case the protonated amidinate cation is a counter-ion of an organometallic anion, *i.e.*, there is no bonding between the amidinate moiety and the metal atom. Ionic complex **13** (see Ref. 28) is an example of such compound. Nitrogen atoms in salt **13** are virtually planar, the ΣQ_N parameter is 358°.

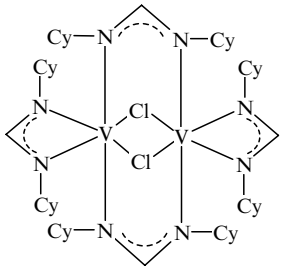


13

In closing this Section, it can be noted that the use of sterically hindered amidinate ligands often imparts unusual structural features to the molecules. For instance, the metal–metal distances in complexes **5b** (see Ref. 29) and **14** (see Ref. 30) are very short [r_{Cr-Cr} = 1.913(3), r_{V-V} = 1.698(2) Å] due to the presence of bulky cyclohexyl substituents at the nitrogen atoms.



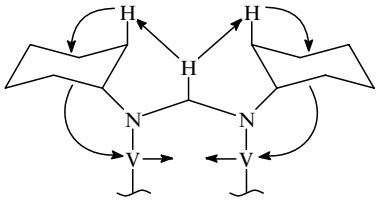
5b



14

Cy = cyclo-C_6H_{11}.

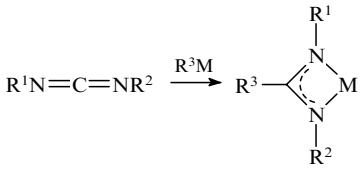
Presumably,[30] strong repulsion between the axial hydrogen atoms of the cyclohexane rings forces the two metal atoms to approach each other (a fragment of complex **14** is shown below). As a result, the equilibrium van der Waals radii of hydrogen atoms are equal to ~1.89 Å.



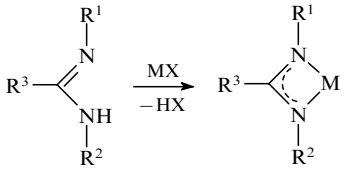
III. Synthesis and chemical properties of amidinate complexes

A large number of amidinate complexes of transition and main-group metals are currently known. In this Section synthesis and chemical properties of these compounds as well as their industrial applications are discussed. For the sake of convenience, the data are divided in two parts dealing separately with main-group and transition metals. The derivatives of the elements of Groups 1 to 15 of the Periodic Table are discussed.†

Four main approaches to the synthesis of amidinate complexes are known. The first one is the insertion of a σ-alkyl group (usually, the methyl group) of an organometallic fragment of the M–R type into the C=N double bond of carbodiimides. This method is fairly popular, since these reactions usually proceed under mild conditions and produce the corresponding amidinate derivatives in high yields.

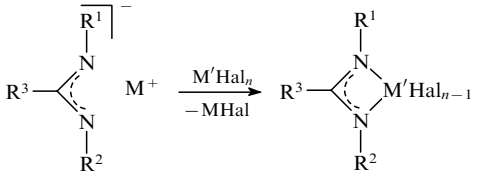


The second approach involves deprotonation of amidine ligands by organometallic compounds containing σ-alkyl (M–R) or σ-amide ($M-NR_2$) groups. This method is mainly used for the synthesis of alkali and alkaline-earth metal amidinates and derivatives of transition metals of Groups 3–5.



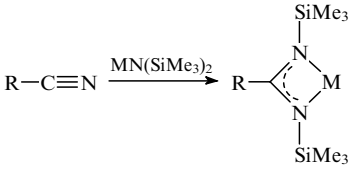
X = Alk, NMe_2.

The most widespread method of synthesis of amidinate complexes of transition and main-group elements is the reaction of anionic amidinate salts of alkali and alkaline-earth metals with halides of Group 3–15 elements.



Finally, the reaction of metal bis(trimethylsilyl)amides with alkyl or aryl cyanides has to be mentioned as a general method of synthesis of 1,3-bis(trimethylsilyl)amidinate complexes.

† The 'long-period' version of the Mendeleev Periodic Table, in which the Groups of elements are indicated by Arabic numerals from1 to 18, is used.



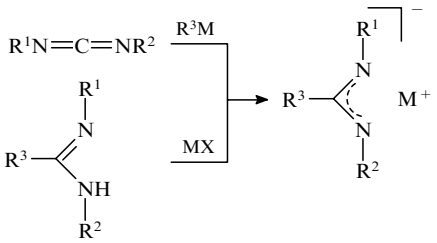
R = Alk, Ar.

Below we discuss the general methods of synthesis of amidinate complexes as well as specific reactions for each group of elements. The structures of all compounds mentioned in this Section are established by physicochemical analytical methods (IR- and UV-spectroscopy, NMR spectroscopy, mass spectrometry and in some cases by X-ray crystallography).

1. Amidinate complexes of main-group elements

a. Group 1 elements (Li, Na and K)

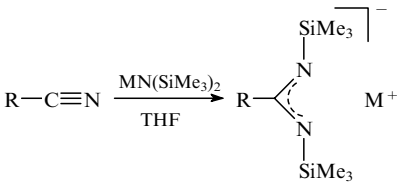
Alkali metal (mainly, lithium and sodium) amidinate derivatives attract attention as starting compounds in the synthesis of other amidinate complexes. Two major methods of synthesis of such compounds are known. The first one is the addition of an organometallic compound R–M (M = Li, Na) to the N=C double bond of carbodiimides.[31–33]



R^1, R^2, R^3 = Alk, Ar; M = Li, Na, K; X = Bu^n, $N(SiMe_3)_2$.

An alternative way is the deprotonation of amidines by an organometallic base, for example, by Bu^nLi, $NaN(SiMe_3)_2$ or $KN(SiMe_3)_2$.[34–36] Usually such reactions proceed in quantitative yields.

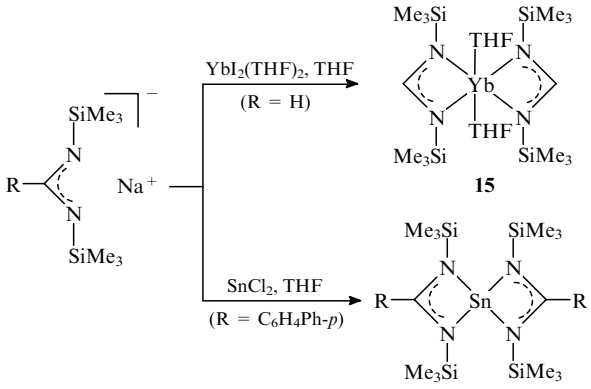
The reaction of carbonitriles with alkali metal bis(trimethylsilyl)amides is a convenient method of synthesis of 1,3-bis(trimethylsilyl)amidinate complexes.[9,37–40]



R = Alk, Ar; M = Li, Na, K.

Particular synthetic aspects for these compounds and their applications for the preparation of a series of 1,3-bis(trimethylsilyl)amidinate complexes of transition and main-group elements are described in detail in a review.[9]

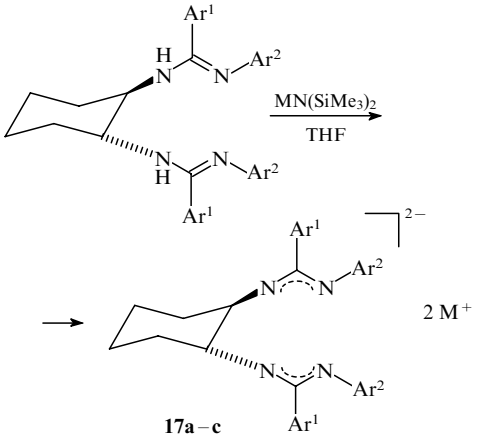
Amidinate complexes of Group 1 metals react with organic electrophiles yielding substituted amidines, and their reactions with metal halides afford the corresponding amidinate complexes. Preparation of complexes **15** and **16** is an example of the use of alkali metal amidinate complexes in the synthesis of the corresponding derivatives of transition and main-group elements.[41,42]



R = H, C_6H_4Ph-*p*.

These reactions will be discussed in detail in appropriate Sections. Studies on the synthesis of different amidinate complexes of Group 1 metal derivatives are summarised in reviews.[6–9] This method is still widely used. A new development of this method is the synthesis of sterically hindered and/or chiral amidinate derivatives of alkali metals. These compounds can further be transformed into the corresponding transition metal complexes with a potential practical application in asymmetric catalysis.[43]

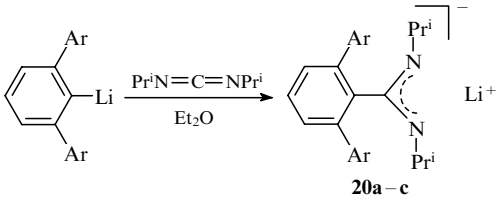
In 2002 chiral bis(amidinate) complexes **17a–c** were obtained by direct metallation of amidines by lithium, sodium and potassium bis(trimethylsilyl)amides.[44]



$Ar^1 = Ar^2 = C_6H_4Me$-*p*: M = Li (**a**), K (**c**);
$Ar^1 = C_6H_4Bu^t$-*p*, $Ar^2 = C_6H_4OMe$-*p*, M = Na (**b**).

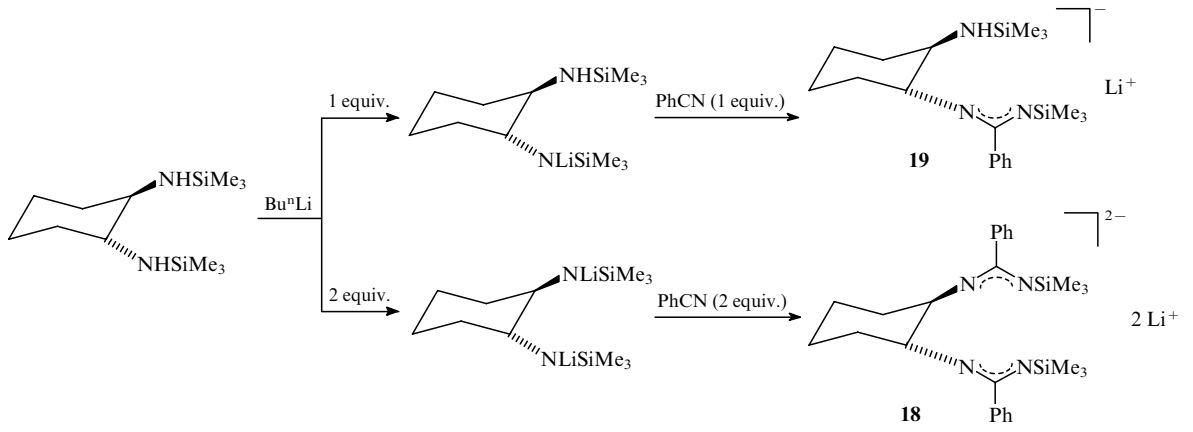
Similar trimethylsilyl derivatives **18** were obtained[35] by the addition of N-anions formed on treatment of bis(trimethylsilylamines) with 2 equiv. of butyllithium to the benzonitrile C≡N bond. Lithium monoamidinate complex **19** is formed in this reaction if equimolar amounts of the base and nitrile are used (Scheme 1).

Sterically hindered amidinate complexes **20a–c** were synthesised recently by the reaction of the corresponding aryllithium derivatives with diisopropylcarbodiimide.[34]



Ar = Ph (**a**), $C_6H_4Bu^t$-*p* (**b**), 2,4,6-$Me_3C_6H_2$ (**c**).

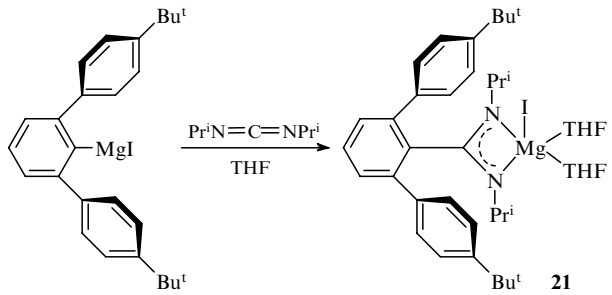
Scheme 1



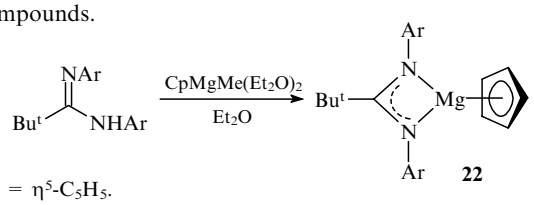
b. Group 2 elements (Mg, Ca, Sr and Ba)

Amidinate complexes of Group 2 elements are less studied than their alkali metal analogues. Data on the synthesis of these complexes published before 1994 were summarised in a review.[9] No papers on the preparation of calcium, strontium and barium amidinate complexes have been published since 1994 and very few articles on the synthesis of the corresponding magnesium derivatives appeared. It has to be noted that no beryllium amidinate complexes are known so far.

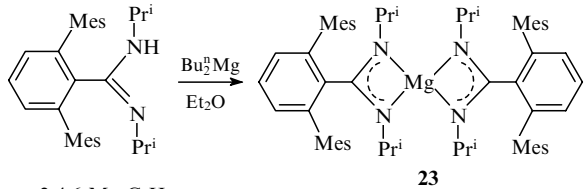
As for amidinate complexes of Group 1 metals, three general methods are used for the synthesis of organomagnesium derivatives. The first two methods afford the products in high yields (>80%). Thus complex **21** was synthesised[34] by addition of sterically hindered arylmagnesium iodide to the N=C double bond of diisopropylcarbodiimide. This complex was isolated and characterised as a THF solvate.



Mono- (**22**)[45] and bis(amidinate) (**23**)[34] complexes were obtained by deprotonation of amidines with organomagnesium compounds.

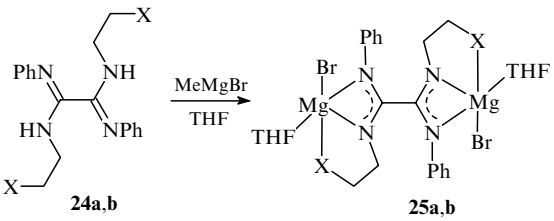


Cp = η^5-C_5H_5.



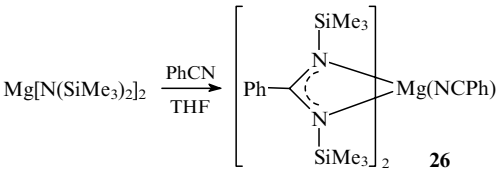
Mes = 2,4,6-$Me_3C_6H_2$.

Similar method was used in the synthesis[46] of dinuclear magnesium complexes **25a**,**b** from bisamidines **24a**,**b**.

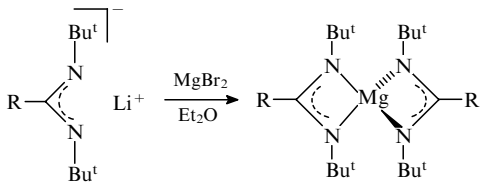


X = OMe (**a**), NMe_2 (**b**).

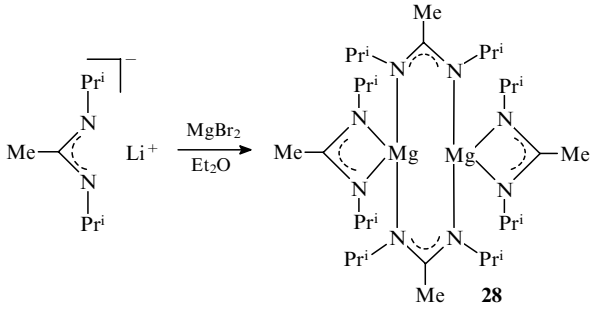
The addition of magnezium hexamethyldisylazide to the multiple C≡N bond of benzonitrile results in the formation of magnesium 1,3-bis(trimethylsilyl)amidinate complex **26**.[47]

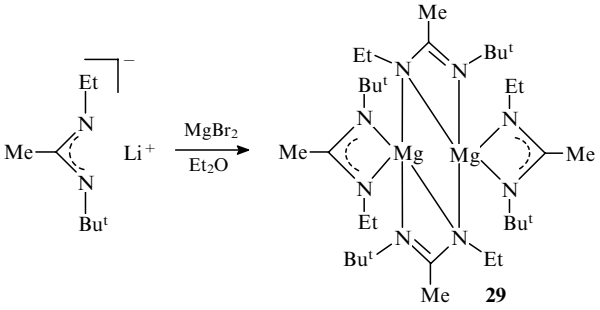


Magnesium amidinate complexes can also be obtained by amidinate ligand exchange between lithium amidinate and magnesium halide.[48] These reactions are usually carried out in ether and the driving force of the process is the formation of insoluble salt LiX (X = Cl, Br). Depending on the character of the substituents at the nitrogen atoms of the amidinate ligand, either mononuclear (**27a**,**b**) or dinuclear (**28**, **29**) magnesium complexes are formed.



27a,**b**: R = Me (**a**), Ph (**b**)





Currently synthesis of sterically hindered ligands (for example, as in type **21** and **23** complexes) is the most intensively developing area in the chemistry of amidinate complexes of Group 2 metals. These derivatives were successfully used for the preparation of transition metal-based asymmetric catalysts.[43] For the same reason, the complexes with 'constrained' geometry (**25a**,**b**) are also of interest. In addition, magnesium amidinate derivatives **22** and **25a**,**b** are used as volatile organomagnesium compounds in CVD (Chemical Vapour Deposition) technology.[45,46]

c. Group 12 elements (Zn, Cd and Hg)

Unusual structural properties are the main reasons for the interest in zinc, cadmium and mercury amidinate derivatives. For example, the most unusual coordination types **B**,[17] **F**[26] and **G**[8] of the amidinate ligand are common for these compounds. A detailed discussion of the data on the synthesis, structure and properties of amidinate complexes of Group 12 elements is reviewed.[8]

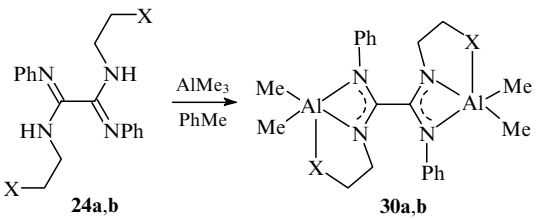
Due to the high toxicity of such elements as cadmium and mercury, no chemical studies on the amidinate complexes of Group 12 elements have been carried out since 1994. Therefore, this group of compounds is not discussed in the present review.

d. Group 13 elements (B, Al, Ga, In and Tl)

Among the amidinate complexes of Group 13 metals, aluminium derivatives, which are used as olefin polymerisation catalysts, are of prime importance.[49–52] At present, gallium, indium and thallium amidinate complexes are of limited theoretical and practical interest; very few papers[23,53–57] have been published on this subject since 1994. Only one paper[60] dealing with the synthesis of new boron amidinate derivatives has been published since the discovery of organoboron amidinate complexes by Lappert and co-workers[58,59] in the early seventies. Difficulties encountered with the isolation of these boron compounds due to large amounts of by-products have been noted in all the three papers.

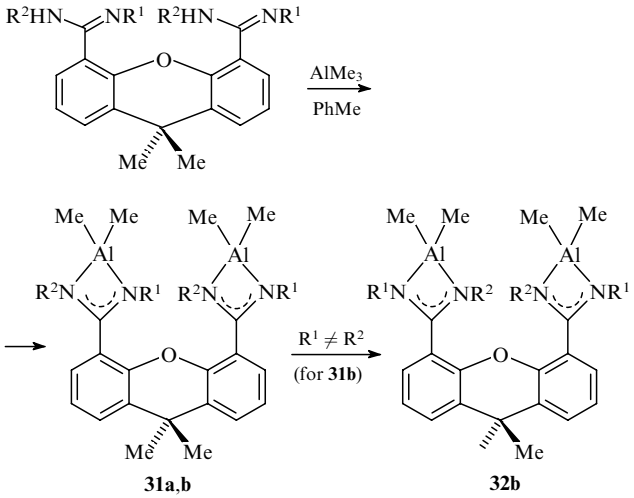
There are four major methods of synthesis of amidinate complexes of Group 13 elements.

The first one is the deprotonation of amidines by organoaluminium compounds, in most cases by trimethylaluminium. Complexes **30a**,**b** with 'constrained' geometry were obtained from bis(amidines) **24a**,**b** by this method.[45]



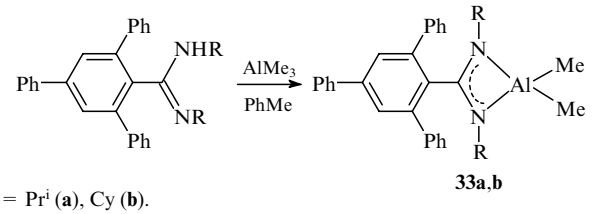
X = OMe (**a**), NMe_2 (**b**).

Bis(amidinate) complexes **31a**,**b** were synthesised similarly in moderate yields (35% – 60%).[61] If the amidine nitrogen atoms of compound **31** carry different substituents, this complex exists in solution as two structural isomers **31b** and **32b**. Depending on the mutual orientation of the amidinate ligands, these isomers are of either C_s- (**31b**) or C_2-symmetry (**32b**). According to data from NMR spectroscopy (EXCHSY-experiment),[61] the rotational barrier is very low and equal to 0.00(4) kcal mol^{-1}.



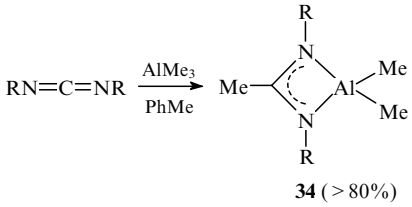
$R^1 = R^2 = Pr^i$ (**a**); R^1 = Et, $R^2 = Bu^t$ (**b**).

This method was successfully used for the synthesis (in satisfactory yields) of dialkylgallium amidinate derivatives[56] and organoaluminium complexes **33a**,**b** with bulky amidinate ligands.[62]



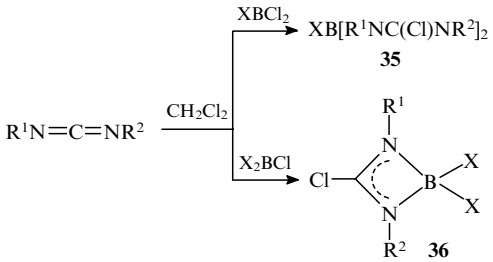
R = Pr^i (**a**), Cy (**b**).

The second method is the addition of trialkylaluminium derivatives to the N=C double bond in carbodiimides.[63,64] These reactions proceed under mild conditions (ambient temperature) and in high yields.



R = Pr^i, Cy, 2,6-$Pr^i_2C_6H_3$, 1-adamantyl.

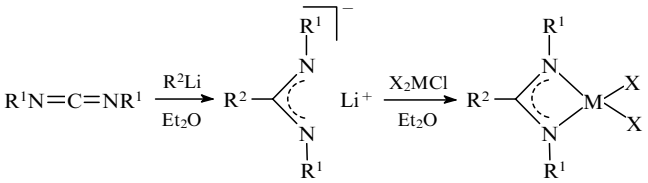
The addition of a B – Cl fragment to the carbodiimide double bond is a modification of this method. This reaction has been used by Lappert and co-workers[58,59] for the synthesis of boron amidinate complexes **35** and **36**.



R^1, R^2 = Ar; X = Cl, OAlk.

Unfortunately, the absence of X-ray diffraction data precludes unambiguous determination of the coordination mode of amidinate ligands in complexes **35** and **36**.

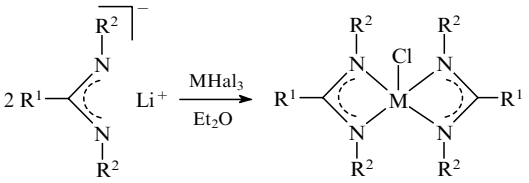
The third most widely used method of synthesis of amidinate complexes of Group 13 elements is the reaction of lithium amidinates with the corresponding metal halides. Dialkyl derivatives (X = Alk) of aluminium (**34**),[63–65] gallium (**37**), indium (**38**) and thallium (**39**) were obtained by this method from the corresponding dialkylmetal chlorides used as halides.[65]. Aluminium and gallium trichlorides were used as the starting compounds in the synthesis of the corresponding dichloroamidinate complexes **40**[63,64] and **41**.[54]



34, **37**–**41**

M = Al (**34**, **40**), Ga (**37**, **41**), In (**38**), Tl (**39**);
X = Alk (**34**, **37**–**39**), Cl (**40**, **41**); R^1 = Alk, $SiMe_3$; R^2 = Alk.

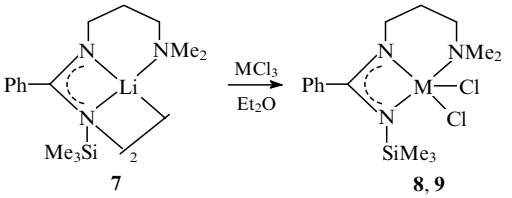
Aluminium, gallium and indium bis(amidinate) complexes, *viz*., compounds **42**–**44**, respectively, are formed in the reaction with a double excess of the starting amidinate salt.[53,54,63]



42–**44**

42: M = Al; R^1 = Me, Bu^t; R^2 = Pr^i, Cy;
43: M = Ga; R^1 = H, Me; R^2 = Me, Bu^t, Ph;
44: M = In, R^1 = Bu^t, R^2 = Cy.

Aluminium and gallium amidinate complexes with 'constrained' geometry (**8** and **9**) were synthesised similarly.[23]

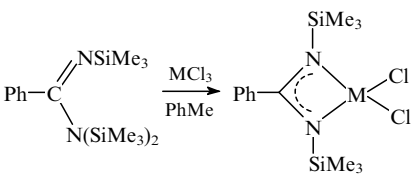


7 **8**, **9**

M = Al (**8**, 85%), Ga (**9**, 78%).

The yields of the complexes obtained by three above-mentioned methods vary from moderate to high (40%–90%).

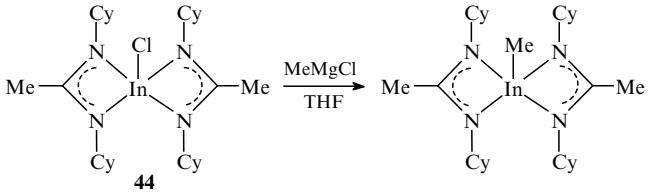
Finally, the fourth method is metathesis of N–Si bonds in trimethylsilyl-substituted amidines and M–X bonds in Group 13 metal halides. This method was successfully used for the synthesis of corresponding dichloroamidinate derivatives of boron (compound **45**), aluminium (**46**), gallium (**47**), indium (**48**) and thallium (**49**).[60] All reactions proceeded under mild conditions and resulted in high yields of the target products.



45–**49** (> 80%)

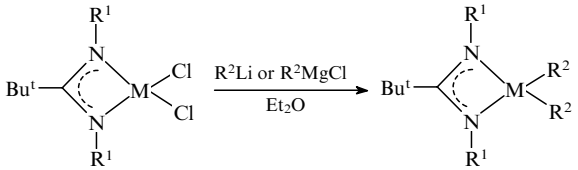
M = B (**45**), Al (**46**), Ga (**47**), In (**48**), Tl (**49**).

Complexes of monoalkyl and dialkyl derivatives of the elements of this Group can also be obtained by the reaction of the corresponding mono- and dichlorides with alkylmagnesium compounds. For instance, treatment of indium chloride amidinate complex **44** with methylmagnesium chloride results in the substitution of the methyl group for the chlorine.[53]



44

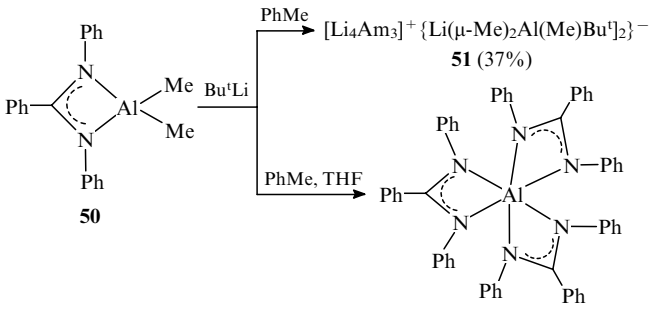
A series of dialkylaluminium[63] and -gallium[54] amidinate complexes were synthesised by this method.



34, **37**

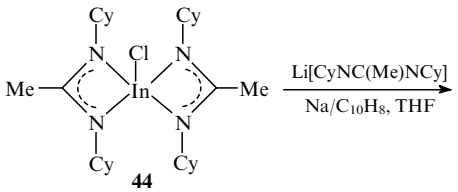
34: M = Al; R^1 = Pr^i, Cy; R^2 = Bn, CH_2Bu^t;
37: M = Ga; R^1 = Pr^i, Bu^t, Cy; R^2 = Me, Et, Bn.

It should be noted that amidinate complexes of Group 13 elements are not Lewis acids. Thus treatment of aluminium derivative **50** with *tert*-butyllithium in toluene resulted in displacement of the amidinate ligand out of the coordination sphere of aluminium and the formation of compound **51**,[66] *i.e*., a complete destruction of the original complex occurred. The cationic fragment $(Li_4Am_3)^+$ of the product **51** is a lithium–nitrogen cluster. Another unusual product was obtained in the reaction of *tert*-butyllithium with compound **50** in a mixture of toluene–THF.[10] Alongside with unidentified compounds, an aluminium tris(amidinate) complex was formed.

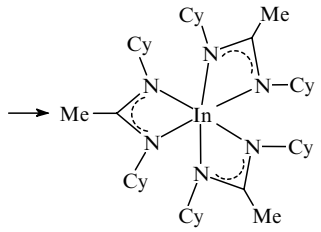


50

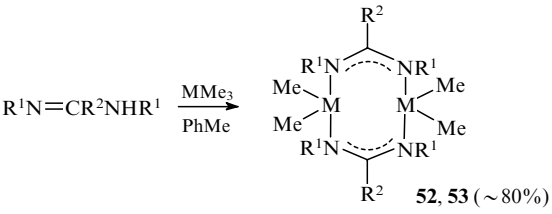
The reaction of bis(amidinate) derivatives with the corresponding lithium amidinate is yet another method of synthesis of tris(amidinate) complexes. Indium tris(amidinate) complex was obtained by this way from chloride **44**.[53]



44



Dinuclear gallium and indium complexes with bridging amidinate ligand are known. Thus compounds **52** and **53** were obtained in the reaction of amidines with trimethylgallium [56] and -indium.[57]

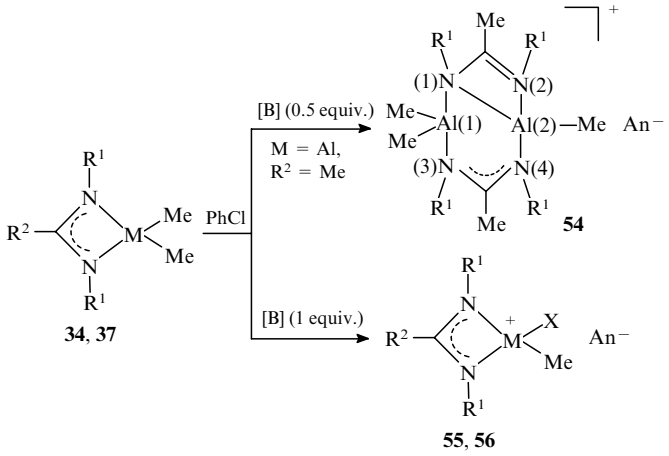


52, **53** (~80%)

52: M = Ga; $R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Ph$;
53: M = In, $R^1 = Cy$, $R^2 = H$.

Catalysis of olefin polymerisation is the main application of amidinate complexes of Group 13 elements. Cationic monoalkyl complexes with central aluminium atom are the most active in these processes.[49, 50, 55] Their gallium analogues were also studied.[55] Such cationic complexes were obtained in quantitative yields by dealkylation of aluminium (**34**) and gallium (**37**) derivatives with arylboron reagents — $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2]$. $[B(C_6F_5)_4]$ or $B(C_6F_5)_3$.

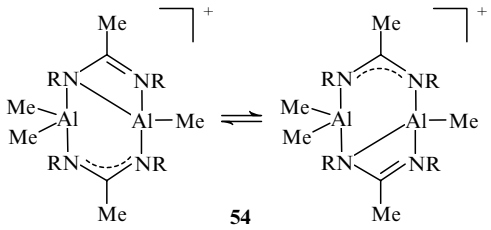
Either bi- (**54**) or mononuclear (**55**, **56**) aluminium and gallium complexes are formed in these reactions depending on the amount of the reagent used (0.5 or 1 equiv.). If the equimolar amount of $[PhNHMe_2][B(C_6F_5)_4]$ is used as a cationic activator, the products contain the group $X = NMe_2Ph$ in the organometallic cation.



34, **37** **54** **55**, **56**

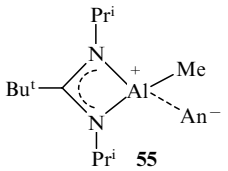
M = Al (**34**, **54**, **55**), Ga (**37**, **56**); $R^1 = Pr^i$, Cy; R^2 = Me, Bu^t;
[B] = $[Ph_3C][B(C_6F_5)_4]$, X is absent, An = $[B(C_6F_5)_4]$;
[B] = $B(C_6F_5)_3$, X is absent, An = $[MeB(C_6F_5)_3]$;
[B] = $[PhNHMe_2][B(C_6F_5)_4]$, X = NMe_2Ph, An = $[B(C_6F_5)_4]$.

Two amidinate ligands in dinuclear complexes **54** coordinate aluminium atoms differently.[49] One of them is bound to two aluminium atoms in the μ-η^1,η^1-mode (structure **F**, Section II). Another ligand coordinates one aluminium atom in the mixed μ-η^2,η^1-mode (structure **D**) and forms a donor-acceptor bond with the second one, *i.e.*, coordinates metal atom in the η^1-mode. The Al—N distances in amidinate complex **54** ($R^1 = Pr^i$, An = $[B(C_6F_5)_4]$) are 1.979 [Al(2)—N(1)], 1.927 [Al(2)—N(2)] and 2.027 Å [Al(1)—N(1)].[55] Complexes **54** are dynamically active in solution, which was confirmed by ^1H NMR spectroscopy.[55] The dynamic equilibrium observed can be expressed as follows:



54

Cationic complexes **55** ($R^1 = Pr^i$, $R^2 = Bu^t$) were used as catalysts of ethylene polymerisation.[49] Their efficiency appeared to be dependent on the character of the anion An^- and temperature.



55

Thus the catalytic activity of compound **55** {An = $[MeB(C_6F_5)_3]$} at 23 °C in CD_2Cl_2 is low. Raising the temperature to 60 °C (polymerisation in toluene) results in a significant enhancement of the activity (up to 700 g mol^{-1} h^{-1} atm^{-1});‡ the polyethylene (PE) produced had the following properties: the number average molecular mass (M_n) was equal to 176 100, the ratio $M_w/M_n = 2.84$ (M_w is the weight-average molecular mass). A more active catalyst was formed from amidinate complex **34** ($R^1 = Pr^i$, $R^2 = Bu^t$) using $[Ph_3C][B(C_6F_5)_4]$ as the demethylation reagent. Complex **55** {An = $[B(C_6F_5)_4]$} is more active in the reaction of ethylene polymerisation: its activity in toluene at 60 °C is 2480 (M_n = 272 200, M_w/M_n = 3.30) and at 85 °C, 3050 g mol^{-1} h^{-1} atm^{-1} (M_n = 184 700, M_w/M_n = 2.23).

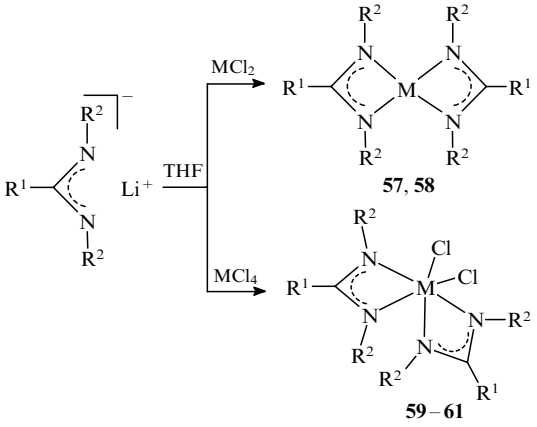
Polymerisation of ethylene in the presence of aluminium amidinate complexes **54** and **55** became the subject of detailed theoretical studies.[67–70] This process was simulated by different quantum-chemical methods: *ab initio*,[67, 70] semi-empirical (AM1)[69] and DFT.[67, 68, 70] According to these calculations, the transfer of the polymeric chain occurs by a β-hydride shift mechanism. Low catalytic activity of dinuclear complexes of type **54** is due to a high activation barrier for the rate-determining stage of ethylene insertion. Mononuclear complexes **55** are more active polymerisation catalysts. The activity depends on their concentration in the solution. It was shown that the presence of bulky substituents (for example, Bu^t and Pr^i) in the amidinate ligand favours the formation of mononuclear complexes and decreases the energy barrier to ethylene insertion during polymerisation. An increase in temperature has a similar effect.

Gallium amidinate complexes **56** are also used as catalysts of olefin polymerisation. Besides, they are used for the preparation of gallium nitride-based materials.[71–73]

e. Group 14 elements (Si, Ge, Sn and Pb)

The recently increased interest in amidinate complexes of Group 14 elements is due to their potential application as starting materials in the manufacture of semiconductors based on germanium and tin nitrides.[74] The major method of the synthesis of amidinate derivatives of divalent (**57**, **58**) and tetravalent (**59**–**61**) elements is the reaction of element chlorides with 2 equiv. of lithium amidinate.[75–80]

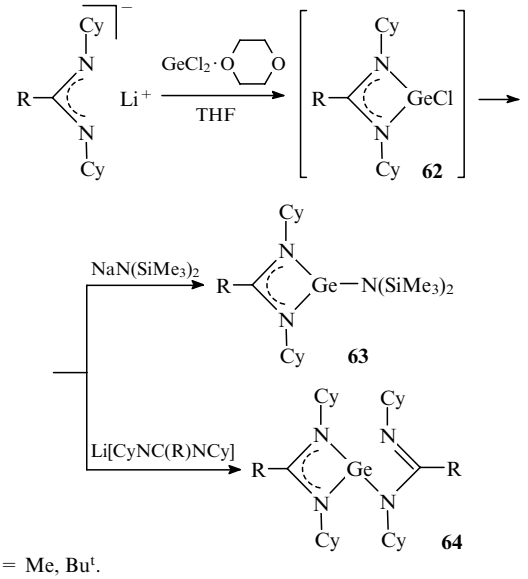
‡ The activity of a catalyst is defined as the mass of a polymer per mol of the catalyst per hour at 1 atm.



57, **60**: M = Ge, R^1 = Me, R^2 = Pr^i;
58: M = Sn; R^1 = Me, Bu^t, Ph; R^2 = Cy, $SiMe_3$, $SiMe_2Ph$;
59: M = Si, R^1 = Me, R^2 = Pr^i;
61: M = Sn; R^1 = H, Me, Bu^t; R^2 = Cy, $SiMe^3$.

These reactions proceed under mild conditions and for the tetravalent elements result in the corresponding bis(amidinate) complexes **57**–**61** in satisfactory yields (> 50%).

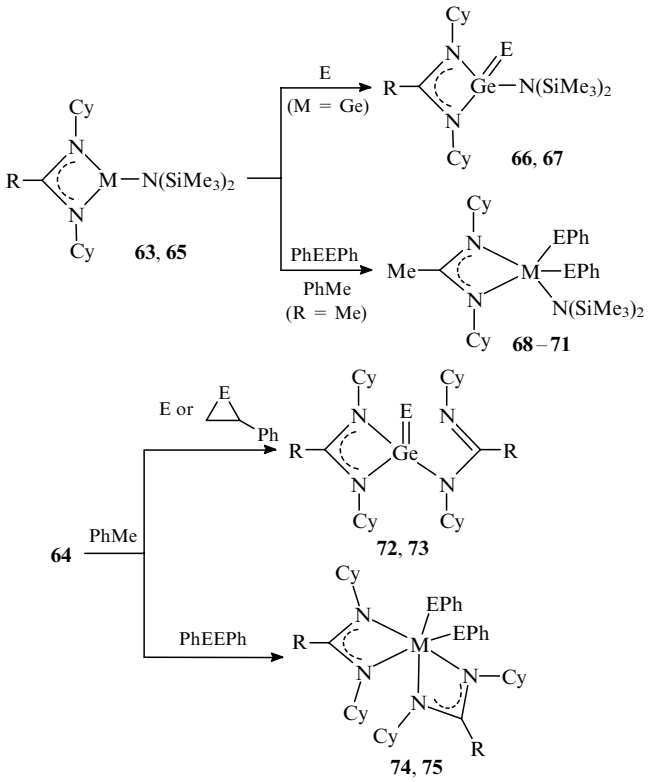
The process can be selectively stopped at the stage of monoderivative **62** if one equivalent of the lithium salt is used in the reaction.[78] Further addition of $NaN(SiMe_3)_2$ results in the corresponding silylamidoamidinate derivative **63**. If the divalent germanium derivative **62** contains bulky substituents (*e.g.*, cyclohexyl), the second amidinate ligand coordinates the central atom in a σ-mode to form complex **64**.



R = Me, Bu^t.

Divalent germanium (**63**, **64**) and tin (**65**) amidinate derivatives undergo oxidative addition of chalcogens (sulfur and selenium).[78, 79, 81] Elementary sulfur and selenium,[78] 2-phenylthiirane(selenerane) as well as organic disulfides(diselenides) were used as reagents in these processes.[79, 81]

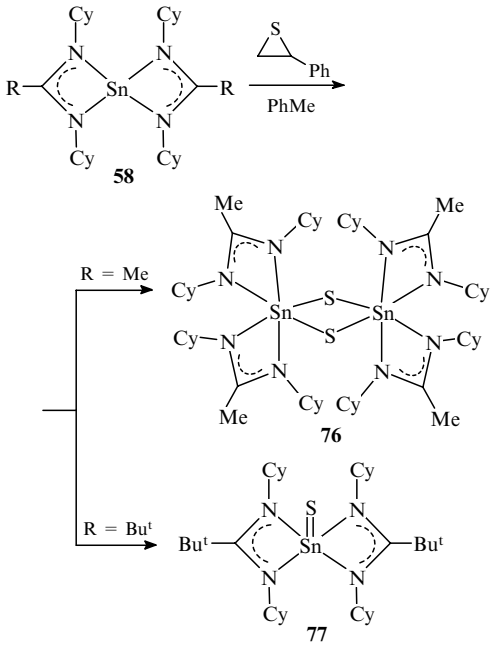
The reaction products are formed in high yields (> 80%). The structures of complexes **66**–**75** were determined by X-ray diffraction analysis. The Ge—N bond lengths in η^1-coordinated amidinate ligands are in the range of 1.8–2.0 Å, *i.e.*, they are shorter than the corresponding Ge—N bonds in chelated amidinate ligands (2.0–2.05 Å). Interestingly, the coordination of the second amidinate ligand is changed upon formation of germanium bissulfide (or bisselenide) amidinate complexes **74** and **75**. Such transformations are not observed in Sn-analogues due to the smaller atomic radius of germanium in comparison with that of tin.



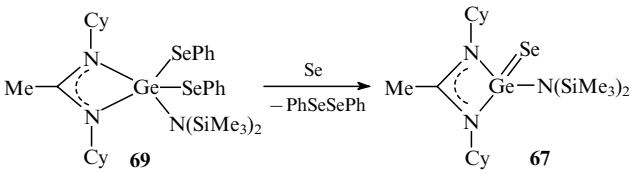
R = Me, Bu^t; M = Ge (**63**, **68**, **69**), Sn (**65**, **70**, **71**);
E = S (**66**, **68**, **70**, **72**, **74**), Se (**67**, **69**, **71**, **73**, **75**).

One of the amidinate ligands in complexes **72** and **73** (as well as in the starting compound **64**) is linked to the metal atom through only one nitrogen atom.

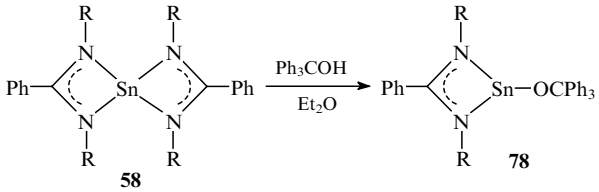
The steric strain in amidinate ligands also affects the structures of the complexes obtained in the oxidative addition reactions. Thus the structure of the reaction product of compound **58** with phenylthiirane depends on the bulk of the substituent at the amidinate carbon atom.[79] If this substituent is a methyl group, then bridged bissulfide dimer **76** is formed. In the case of a bulky *tert*-butyl substituent in the amidinate ligand, the tin atom is sterically overcrowded and only monomeric complex **77** containing a double bond Sn = S is formed in this reaction.



The reaction of germanium bisselenide complex **69** with elementary selenium yields compound **67** and diphenyl diselenide is eliminated.[81]



Tin(II) mixed amidinate-alkoxide complexes **78** were obtained in the reaction of the corresponding silylamide derivatives **58** with triphenylmethanol.[80] The coordination number 3 relatively rare for tin compounds is found for the tin atoms of both complexes by X-ray diffraction analysis.



R = $SiMe_3$, $SiMe_2Ph$.

Compounds **78** turned out to be active catalysts of lactide polymerisation in toluene at 80 °C. The activity of complex **78** with a trimethylsilyl substituent is 63.5 kg mol^{-1} (polydispersity of the polymer obtained was 1.48), which is more than twice that of the compound with dimethylphenylsilyl group (28.9 kg mol^{-1}). However, the polydispersity of the polymer obtained using the latter catalyst was 1.18.

It can be noted at the end of this Section that not a single paper was published on lead amidinate derivatives during the last decade. Earlier papers dealing with lead amidinate complexes are cited in the review.[9]

f. Group 15 elements (Sb and Bi)

So far no practical application has been found for antimony and bismuth amidinate complexes due to their lability and difficulties of preparation. Data on the chemistry of these derivatives published before 1994 has been summarised in reviews.[6,9] Phosphorus and arsenic amidinate derivatives, being purely organic compounds, are beyond the scope of the present review on organometallic complexes.

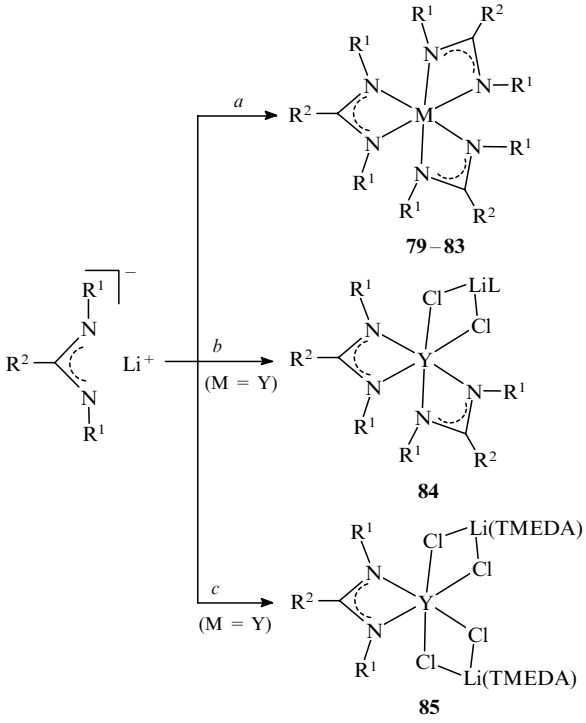
2. Amidinate complexes of transition metals

a. Group 3 elements (Sc, Y, lanthanides and actinides)

The chemistry of lanthanide amidinate complexes has been significantly developed over the last decade. Most of the data are documented in the review[82] published in 2002. Here we discuss only those papers that have not been surveyed previously.

The reaction of the corresponding alkali metal (usually, lithium) amidinates with commercially available lanthanide chlorides is the major method of synthesis of tris(amidinate) derivatives of lanthanum group metals **79**–**83** as well as of the most similar complexes of transition metals.[23,82–85] These reactions proceed under mild conditions and result in high yields of the target products.

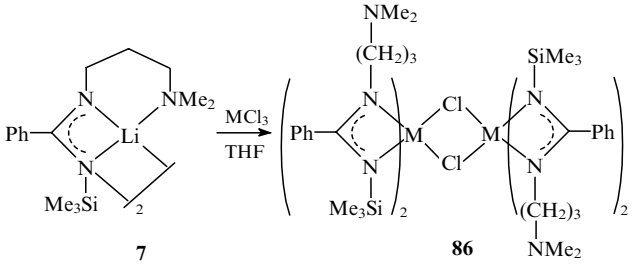
In some cases (like for yttrium), stable adducts **84** and **85** containing one or two lithium atoms coordinated to chloride ligands are obtained.



(*a*) MCl_3 (1/3 equiv.), Et_2O; (*b*) YCl_3 (1/2 equiv.), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or THF; (*c*) YCl_3 (1 equiv.), TMEDA, THF;

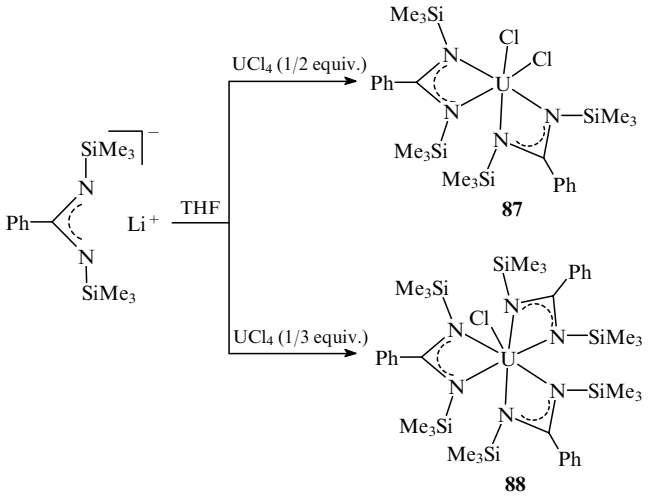
79: M = La; R^1 = Pr^i; R^2 = Me, Bu^t;
80: M = Nd; R^1 = Cy; R^2 = Me, Ph;
81: M = Gd, R^1 = Cy, R^2 = Me;
82: M = Yb; R^1 = Cy; R^2 = Me, Ph;
83: M = Y, R^1 = Cy, R^2 = Ph;
84: R^1 = $SiMe_3$, 2,6-$Et_2C_6H_3$; R^2 = Ph, *p*-Tol; L = TMEDA, THF;
85: R^1 = Pr^i, R^2 = 2,6-$Mes_2C_6H_3$.

It should be noticed, that, due to their larger atomic radii, the lanthanum group metals are more prone to form bis- and tris(amidinate) complexes, than the Group 13 elements (B, Al, Ga, In). Thus the reaction of lithium derivative **7** with lanthanum and cerium trichlorides yields bis(amidinate) dinuclear complexes **86** containing pentacoordinated dimethylamino groups. At the same time, aluminium and gallium trichlorides form monoamidinate complexes **8** and **9** with 'constrained' geometry under similar conditions.[23] The yields of complexes **86** are ~70%.

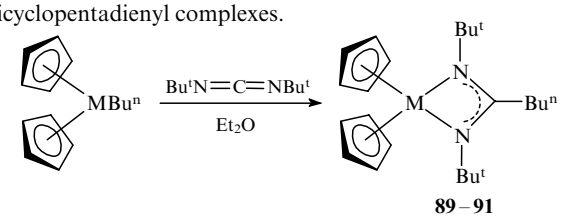


M = La (67%), Ce (78%).

Uranium bis- (**87**) and tris(benzamidinate) (**88**) complexes are formed in the reaction of uranium tetrachloride with two or three equivalents of lithium amidinate, respectively (yields are 60%–70%).[86] No corresponding mono- or tetrasubstituted amidinate derivatives were obtained.

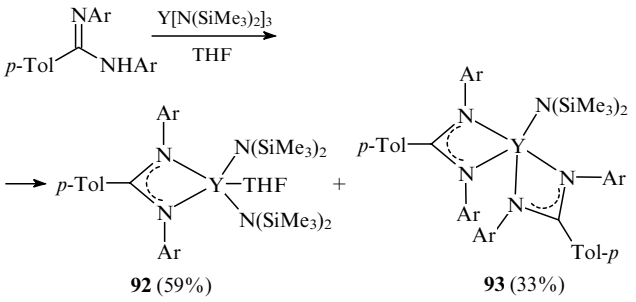


An alternative method of synthesis of lanthanide amidinate complexes is the addition of carbodiimide to the metal–carbon bond of alkylmetal derivatives. This method was applied for the synthesis of europium, ytterbium and gadolinium compounds.[87] For instance, amidinate complexes **89**–**91** were obtained by reaction of di(*tert*-butyl)carbodiimide with n-butyllanthanide dicyclopentadienyl complexes.



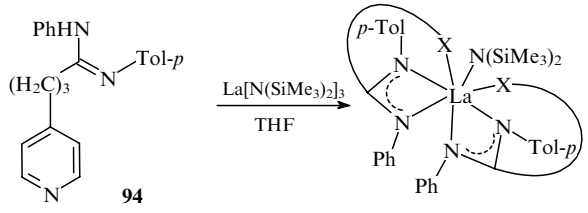
M = Er (**89**), Y (**90**), Gd (**91**).

Deprotonation of arylamidines by silylated lanthanide tris(amides) results in the corresponding amidinates. Thus a mixture of yttrium mono- (**92**) and bis(amidinate) (**93**) complexes was obtained by this method.[88]



Ar = 2,6-$Et_2C_6H_3$.

A lanthanum bis(amidinate) complex with tridentate ligands was synthesised similarly from amidine **94**.[88]



X = $(CH_2)_3$Py-4.

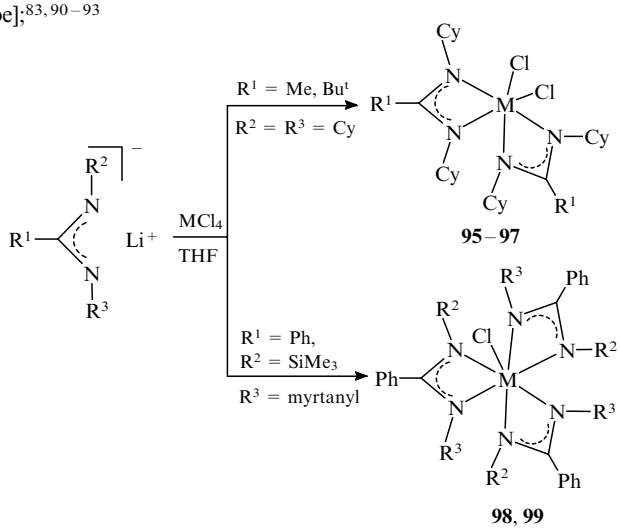
Little is known about the properties of amidinate complexes of lanthanides. Dynamic behaviour of some of them in solution and reactions with alkenes and terminal alkynes have been discussed.[82] Practical interest in these compounds is caused by their high catalytic activities in polymerisation reactions of ethylene (compound **86**),[89] ε-caprolactone (complexes **79**–**83**),[84] D,L-lactide (compounds **84** and their phenoxide analogues obtained by substitution of the $OC_6H_3R_2$-2,6 group, where R = Me, Bu^t, for the chlorine) [85] as well as in the reaction of cyclotrimerisation of phenyl isocyanide (complex **90**).[87] The polymers formed have high molecular mass (> 10^4) and low polydispersity (< 2). Moreover, volatile lanthanum amidinate derivatives were used in membrane manufacturing by CVD.[83]

b. Group 4 elements (Ti, Zr and Hf)

Most of the papers on amidinate derivatives published over the last decade deal with the Group 4 metal complexes. This is due to several reasons: cheap and commercially available starting materials, simplicity of the synthesis of complexes, their thermal stabilities and, first of all, potential application in such an important area as catalytic polymerisation of olefins.

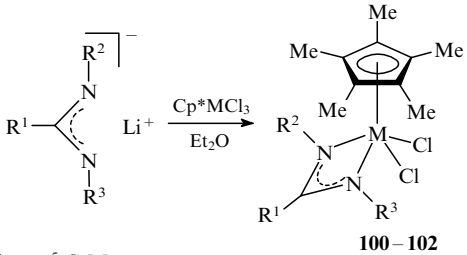
As for most known amidinate derivatives, the main method of synthesis of amidinate complexes of the Group 4 metals is the reaction of lithium amidinate with the corresponding metal halide (usually, chloride). Reactions with these commercially available reagents proceed under mild conditions and result in acceptable yields of the target products (> 60%). Lithium salts of different amidinate ligands are usually synthesised *in situ* from carbodiimides and alkyllithium derivatives. Below, there are examples of three types of reaction of lithium amidinate with the Group 4 metal derivatives:

— reactions with chlorides [either bis- (**95**–**97**) or tris(amidinate) (**98**, **99**) derivatives are formed depending on the ligand type];[83,90–93]



M = Ti (**95**, **98**), Zr (**96**, **99**), Hf (**97**); myrtanyl is 6,6-dimethylbicyclo[3.1.1]hept-2-ylmethyl.

— reactions with monocyclopentadienyl derivatives to give monoamidinate monocyclopentadienyl compounds **100**–**102**;[94–97]



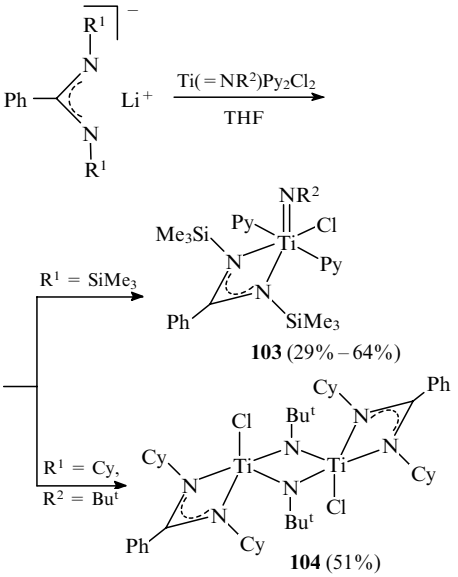
Cp* = η^5-C_5Me_5;

100: M = Ti, R^1 = Me, R^2 = R^3 = $SiMe_3$;

101: M = Zr; R^1 = H, Me, Bu^t, Ph; R^2 = R^3 = Pr^i, $SiMe_3$; R^2 = Et, R^3 = Bu^t;

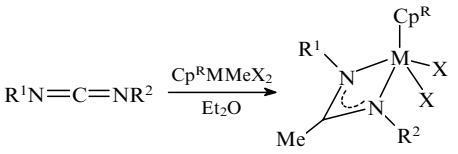
102: M = Hf; R^1 = Me; R^2 = R^3 = $SiMe_3$; R^2 = Et, R^3 = Bu^t.

— reactions with monoimide complexes to give monoamidinate monoimide complexes **103** or their dimers **104**.[98,99]



R^2 = Bu^t, Ar.

Another relatively common method of synthesis of amidinate complexes of the Group 4 metals is an insertion of free carbodiimide into a metal–carbon σ-bond. This approach was successfully used for the synthesis of titanium (**105**), zirconium (**106**) and hafnium (**107**) monocyclopentadienyl monoamidinate complexes.[100–105] An alkyl (mostly, methyl) group is the most common substituent. The insertion reactions proceed under mild conditions and afford target products in good yields.

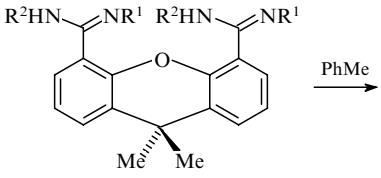


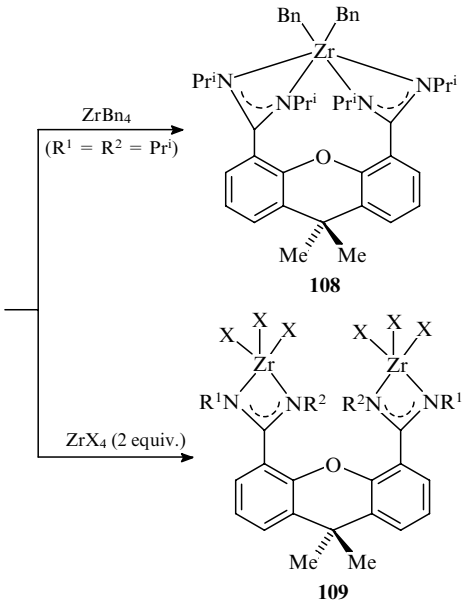
105: M = Ti; R^1 = Bu^t, Cy; R^2 = Et, Pr^i, 2,6-$Me_2C_6H_3$; Cp^R = Cp, Cp*; X = Me;

106: M = Zr; R^1 = Et, Pr^i, Bu^t, Cy, *o*-Tol; R^2 = Et, Pr^i, Bu^i, Bu^t, *neo*-C_5H_{11}, Bn, 3-ClC_6H_4, Mes; Cp^R = Cp, Cp*; X = Me, Cl;

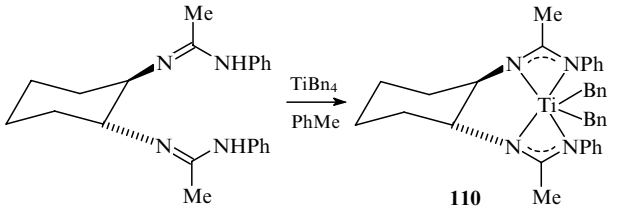
107: M = Hf, R^1 = Et, R^2 = Bu^t, Cp^R = Cp*, X = Me.

The third method of synthesis of titanium and zirconium complexes is the deprotonation of amidines, which has already been discussed earlier. Tetrabenzyl and tetrakis(dimethylamide) metal derivatives can be used as the deprotonating agents. Zirconium complexes **108** and **109** containing sterically hindered amidinate ligands were synthesised by this method.[95,106] Titanium bis(amidinate) complex **110** was also obtained by similar way.[107] However, this method is used less often than the two mentioned above mainly due to longer reaction times. In some cases, it also requires higher temperature, which usually results in lower yields of the target products.

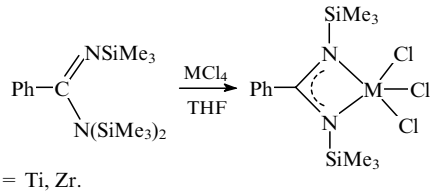




R^1 = R^2 = Pr^i, X = Bn; R^1 = Et, R^2 = Bu^t, X = NMe_2.



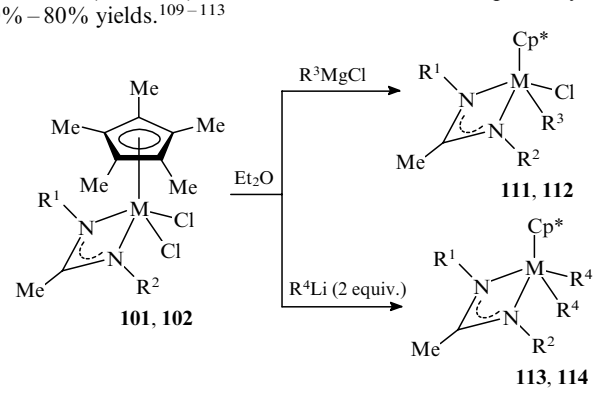
Yet another method of synthesis of amidinate complexes of the Group 4 metals is metathesis of metal tetrachlorides and silylated amidine derivatives.[9,108]



M = Ti, Zr.

At present, this method is almost out of use due to its synthetic limitations and the existence of other more convenient synthetic procedures.

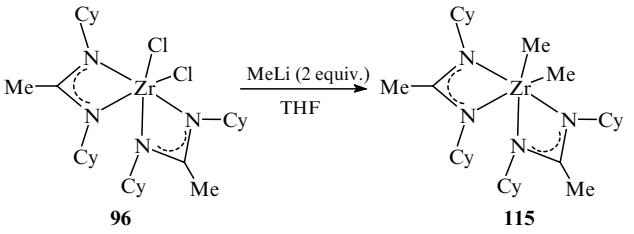
The properties of amidinate complexes of the Group 4 metals are fairly well studied. Thus the reaction of monocyclopentadienyl monoamidinate dichloride complexes **101**, **102** with the Grignard reagents and organolithium compounds (1 or 2 equiv.) has been investigated. In these reactions, mono- (**111**, **112**) and dialkylamidinate (**113**, **114**) derivatives are formed, respectively, in 40%–80% yields.[109–113]



M = Zr (**101**, **111**, **113**); Hf (**102**, **112**, **114**);

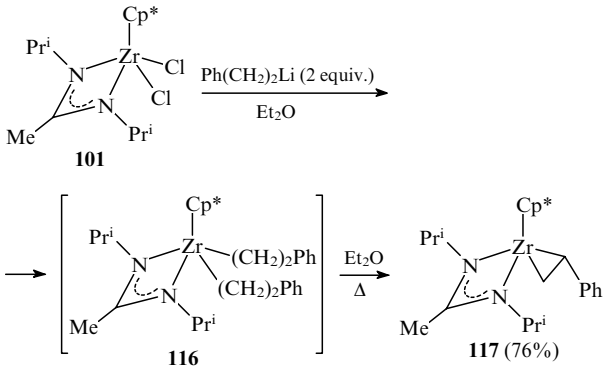
R^1 = Et, R^2 = Bu^t; R^1 = R^2 = Pr^i; R^3 = Me, Bu^i; R^4 = Bu^n, Bu^i.

The reaction of zirconium bis(amidinate) dichloride complex **96** with 2 equiv. of methyllithium proceeds similarly furnishing compound **115**.[92]



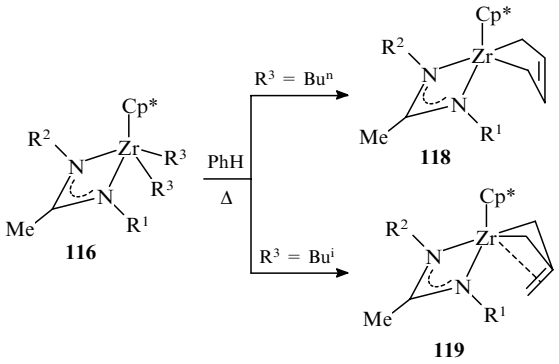
96 **115**

Unlike metallocene dialkyl complexes, their amidinate analogues are less prone to β-hydride elimination reactions. Some amidinate derivatives undergo thermal conversions resulting in metallacycles. Thus the intermediate dialkyl complex **116**, obtained from dichloride **101** ($R^1 = R^2 = Pr^i$) and dialkyllithium, converts into phenylzirconacyclopropane derivative **117** on heating in ether.[110]



101 **116** **117** (76%)

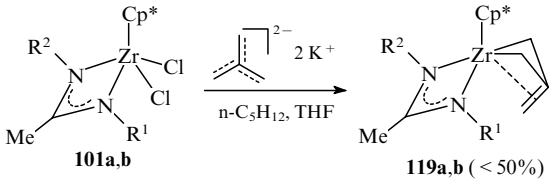
Thermolysis of n-butyl and isobutyl derivatives **116** results in the formation of complexes **118** and **119** as the main products in moderate yields and in elimination of butane and isobutane, respectively (according to data from NMR spectroscopy) and hydrogen.[109, 111] The mechanisms of these thermal conversions are not established yet.



116 **118** **119**

$R^1 = R^2 = Pr^i$; R^1 = Et, $R^2 = Bu^t$; $R^3 = Bu^n$, Bu^i.

Trimethylenemetane (TMM) derivatives **119a**,**b** were obtained by another method, *viz*., by the reaction of corresponding dichlorides **101a**,**b** with dipotassium isobutylenediide.[114]



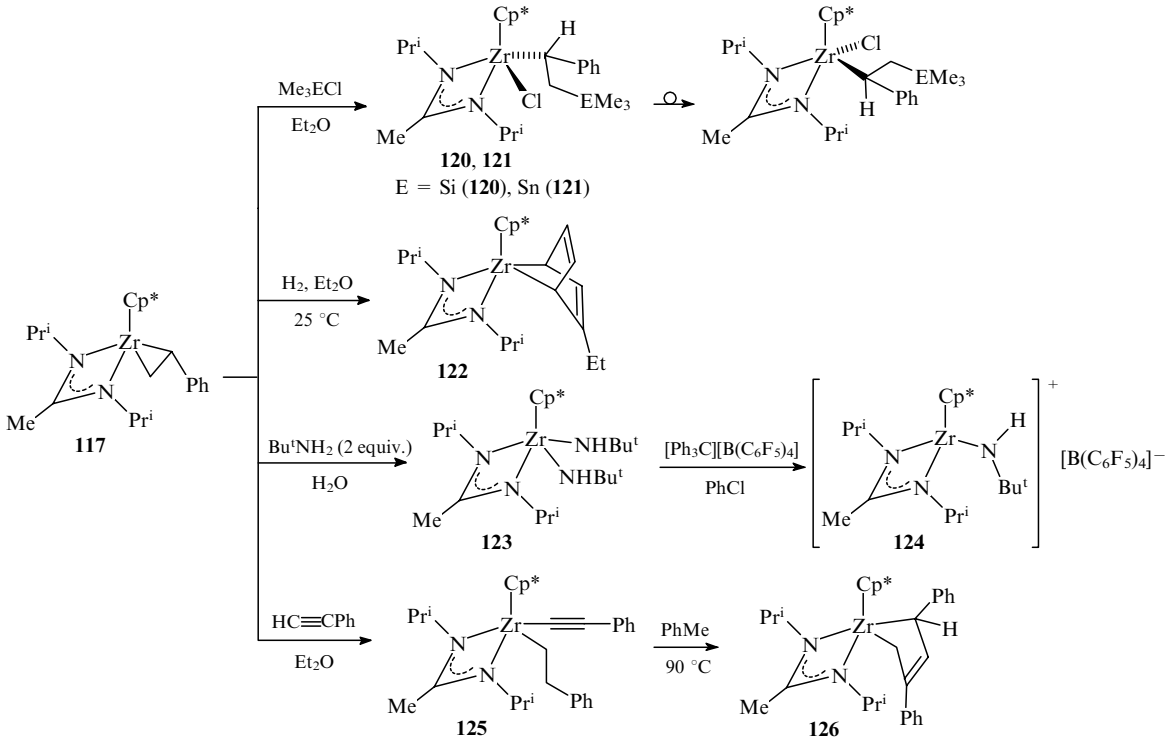
101a,**b** **119a**,**b** (< 50%)

$R^1 = R^2 = Pr^i$ (**a**); R^1 = Et, $R^2 = Bu^t$ (**b**).

The chemical properties of zirconacyclopropane complex **117** and TMM derivatives **119** were studied in detail.[111, 114, 115] A remarkable feature of these compounds is their high reactivities with respect to weak electrophilic reagents, such as Me_3SiCl, Me_3SnCl, *etc*.,[111, 115] which does not occur for simple σ-alkyl zirconium complexes. Most of the reactions for compounds **117** and **119** proceed with quantitative yields. DFT quantum-chemical calculations of the complex **119a** reveal high polarisation of the molecule in the ground state,[113] which was confirmed by relatively high experimental value of the dipole moment of this compound (3.5 D). Hence, the organic ligand (TMM) in such complexes carries significant negative charge and can react even with weak organic electrophiles.

Reactions of the phenylzirconacyclopropane derivative **117** with chlorotrimethylsilane and -stannane accompanied by three-

Scheme 2



117 **120**, **121** E = Si (**120**), Sn (**121**) **122** **123** **124** **125** **126**

membered ring opening have been described.[111] Chiral organometallic complexes **120** and **121** thus formed epimerise in benzene at room temperature (Scheme 2).

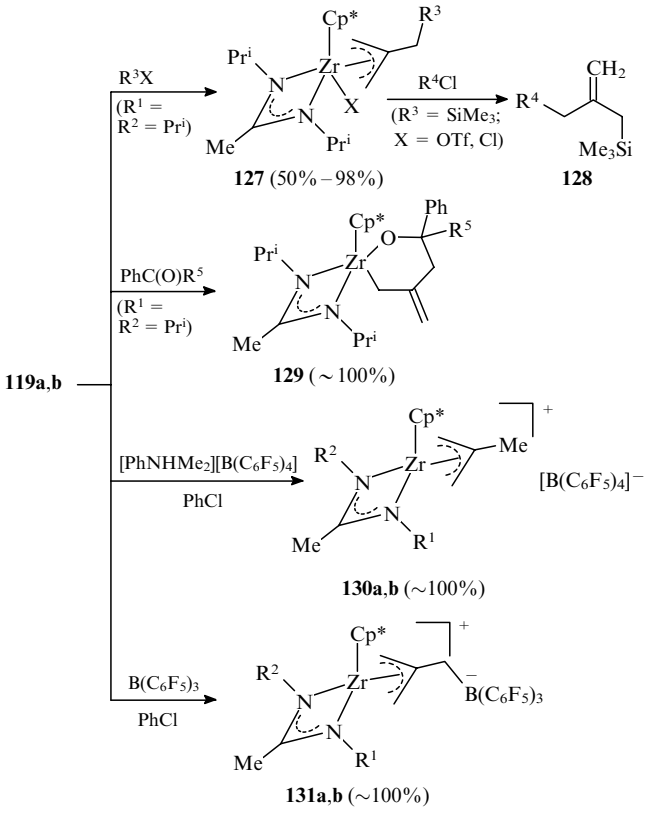
Compound **117** reacts with hydrogen at room temperature yielding an unusual zirconanorbornadiene complex **122** (see Ref. 111). The latter is of particular interest as a thermodynamically stable homoaromatic structure. In complex **122**, the lengths of two Zr–C σ-bonds are 2.313(2) and 2.3501(19) Å. Relatively short contacts between the metal atom and carbon atoms of the alkene (~2.51 Å) suggest the presence of non-valent interactions between the electron-deficient zirconium atom and C=C double bonds of the norbornadiene moiety. These interactions provide additional stability to the structure.

Metathesis of σ-alkyl bond in compound **117** in the presence of an excess of *tert*-butylamine results in the formation of corresponding bis(amidinate) derivative **123**. It should be noted that dimethyl derivative **105** (R^1 = Et, R^2 = Bu^t, Cp^R = Cp*) is completely inactive in similar reaction even at elevated temperatures.[111] Bis(amidinate) complex **123** undergoes unique deamination in the presence of $[Ph_3C][B(C_6F_5)_4]$ yielding a cationic complex **124**.

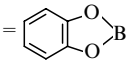
Protolysis of compound **117** with phenylacetylene results in σ-alkynyl derivative **125**. Thermolysis of the latter furnishes zirconacyclopentenyl complex **126**.

Trimethylmethane complex **119a** also reacts with weak organic electrophiles. On treatment of trimethylsilyl derivatives **127** (R^3 = $SiMe_3$; X = Cl, OTf) with strong electrophiles (*e.g.*, B-catecholchloroborane or chlorotrimethylstannane) non-symmetrically substituted isobutylenes **128** are formed.[115]

The reaction of TMM complex **119** with carbonyl compounds yields C=O insertion derivatives **129**.

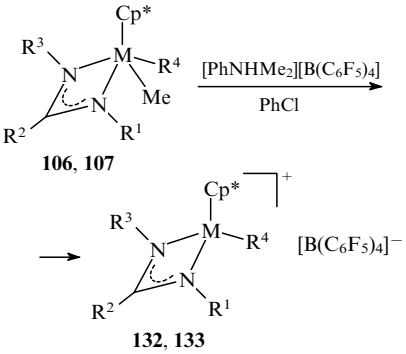


R^1 = R^2 = Pr^i (**a**); R^1 = Et, R^2 = Bu^t (**b**); R^3 = Me, Et, Bn, $SiMe_3$;

R^4 =  ; $SnMe_3$; R^5 = H, Ph; X = OTf, Cl, Br.

Complexes **119a**,**b** also react with Brønsted (*e.g.*, $[PhNHMe_2]$.$[B(C_6F_5)_4]$) and Lewis [*e.g.*, $B(C_6F_5)_3$] acids to give the corresponding allylic cationic (**130a**,**b**) and zwitter-ionic (**131a**,**b**) derivatives as the reaction products.[115] The transition from neutral covalent complex **119b** to the metallyl derivative **130b** is accompanied by a significant shortening of the Zr–N bonds from 2.2306(12) to 2.149(3) Å. Such shortening of the metal–nitrogen bonds compared with those in neutral complexes is also typical of the majority of cationic amidinate derivatives of other elements, for example, aluminium, gallium [56] and ruthenium.[10]

In spite of diverse reactivity of Group 4 metal amidinate complexes, the primary attention is paid to their application as olefin polymerisation catalysts.[110] Monoalkyl cationic complexes of zirconium **132** (see Refs 102–104 and 116–120) and hafnium **133** (see Ref. 121) were obtained from dialkyl complexes **106**, **107** in the reaction with $[Me_2NHPh][B(C_6F_5)_4]$ as a protonating reagent in quantitative yields.



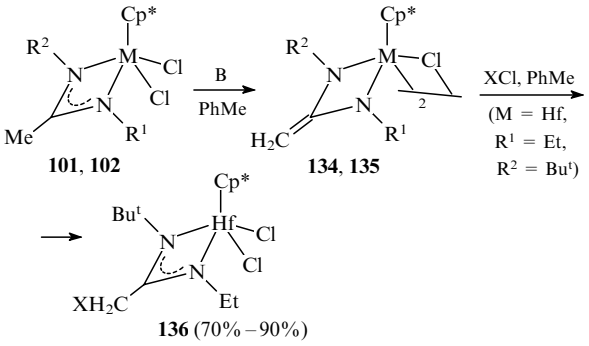
106, **132**: M = Zr; R^1 = Et, Pr^i, Bu^i, Bu^t, *neo*-C_5H_{11}, Cy, Bn, *o*-Tol, 3-ClC_6H_4, Mes; R^2 = H, Me, Bu^t, Ph; R^3 = Et, Pr^i, Bu^t, Cy; R^4 = Me, Et, Bu^i;

107, **133**: M = Hf; R^1 = Et; R^2 = Me; R^3 = Bu^t; R^4 = Me, Bu^i.

Really unique was the discovery of a high catalytic activity of such monoalkyl complexes in stereoregular living polymerisation of a number of α-alkenes (ethylene, propylene, but-1-ene, hex-1-ene, oct-1-ene, dec-1-ene, dodec-1-ene) as well as hexa-1,5-diene. Polymerisation of these olefins in chlorobenzene at −10 °C results in isotactic polymers in almost quantitative yields and low (< 1.1) polydispersity, which is characteristic of living polymerisation. β-Hydride abstraction under these conditions is negligible. Cationic complex **132** (R^1 = Et, R^2 = R^4 = Me, R^3 = Bu^t) [102] is the most efficient catalyst, but other complexes, for example, compounds **132** with R^1 = Bn, *neo*-C_5H_{11}, also show similar activity.[104] Such catalysts can be used for the preparation of different block co-polymers [103] and isotactic–atactic block co-polymers by degenerated alkyl group transfer mechanism (for details, see Ref. 120). The structure of catalytically active species has been studied.[120]

A series of titanium and zirconium monoamidinate complexes (**105** and **106**) were tested as catalysts for ethylene polymerisation in the presence of methylalumoxane (MAO).[92, 101, 121–123] Quantum-chemical calculations were performed for this reaction.[15] A detailed analysis of the polymerisation results is published in a recent review.[5]

A study of the reactions of zirconium and hafnium dichloride derivatives (**101** and **102**) [124] has to be noted among the latest papers on the properties of Group 4 metal amidinate complexes. Thus these compounds react with strong non-nucleophilic bases producing dimeric derivatives **134** and **135**, respectively.

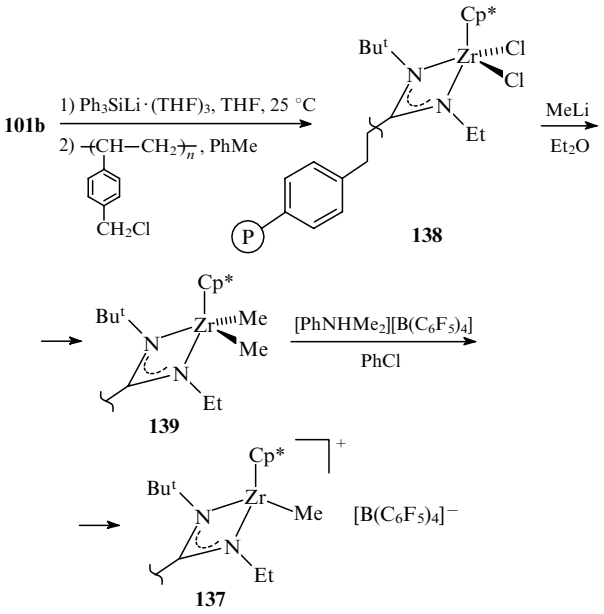


101, **102** **134**, **135** **136** (70% – 90%)

B = Ph_3SiLi, $KN(SiMe_3)_2$; M = Zr (**101**, **134**), Hf (**102**, **135**);
X = CH_2Cl, Bn, $SiMe_2Cl$.

The deprotonated carbon atom of the amidinate ligand in dimers **134** and **135** is nucleophilic. For instance, hafnium complex **135** (R^1 = Et, R^2 = Bu^t) reacts with such organic electrophiles as CH_2Cl_2, BnCl and $SiMe_2Cl_2$ to give CH_2-substituted amidinate derivatives **136**.[124]

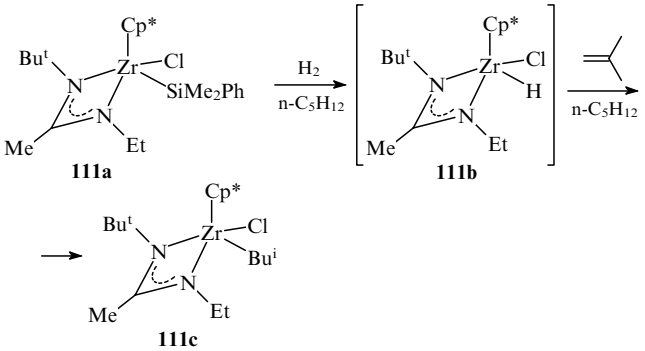
Similar reaction has been used for the synthesis of a polymer-bound amidinate catalyst **137**. The commercially available polystyrene polymer Bio-Beads^{tm} S-X1 has been used as a support; the transformations involved immobilised zirconium complexes **138** and **139**.[125]



(P) is a polymer.

Cationic complex **137** is quite resistant toward oxidation and at the same time is highly active as a polymerisation catalyst.

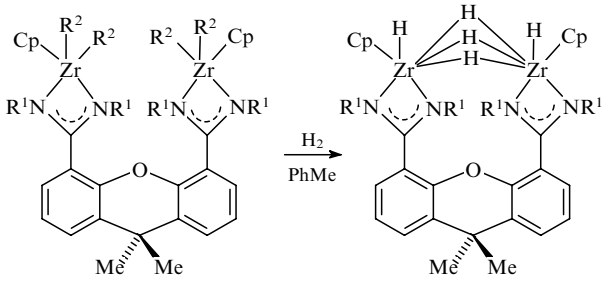
A possibility of synthesis of a hydride chloride monoamidinate analogue of Schwarz catalyst, Cp_2ZrHCl, starting from zirconium monocyclopentadienyl amidinate complexes was studied. Hydride chloride intermediate **111b** was obtained by hydrogenation of the corresponding silyl chloride complex **111a**.[126]



111a **111b** **111c**

Intermediate **111b** is unstable and rapidly decomposes. However, it may be quenched as α-alkene hydrozirconation products, for example, as complex **111c** upon hydrozirconation of isobutylene.

Recently a stable zirconium hydride amidinate complex **140** has been obtained.



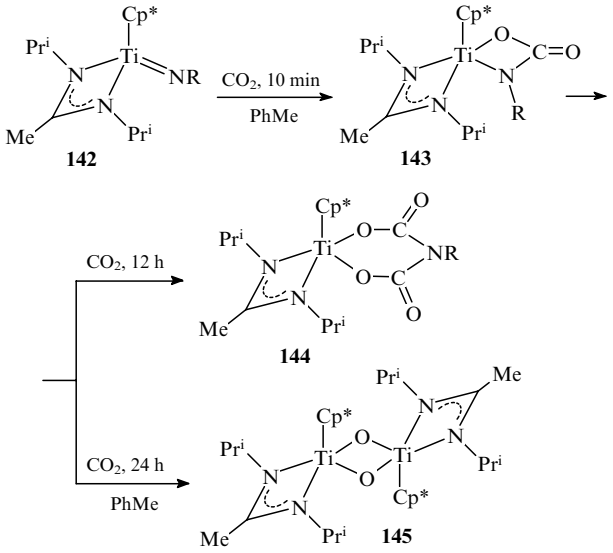
109 **140** (69%)

R^1 = Pr^i, R^2 = CH_2SiMe_3.

It was formed upon hydrogenation of the corresponding zirconium tetrakis(trimethylsilylmethyl) dinuclear derivative **109**.[95] Complex **140** exhibit dynamic behaviour, which results in exchange between bridged and terminal hydrogen atoms.

At the end of this Section, two recent publications [127, 128] have to be noted. They describe the reactivities of titanium amidinate complexes **141** and **142**. The chloride ligand in monochloro derivatives **141** may be nucleophilically substituted by such groups as Cp, OAr, $N(SiMe_3)_2$, $CHRSiMe_3$ or by second amidinate ligand (Scheme 3).[127]

Titanium pentamethylcyclopentadienyl amidinate complex **142** rapidly reacts with CO_2 giving rise to the insertion product **143**.[128] Depending on the duration of the reaction with carbon dioxide, different products, *viz*., complexes **144** or **145**, are formed.



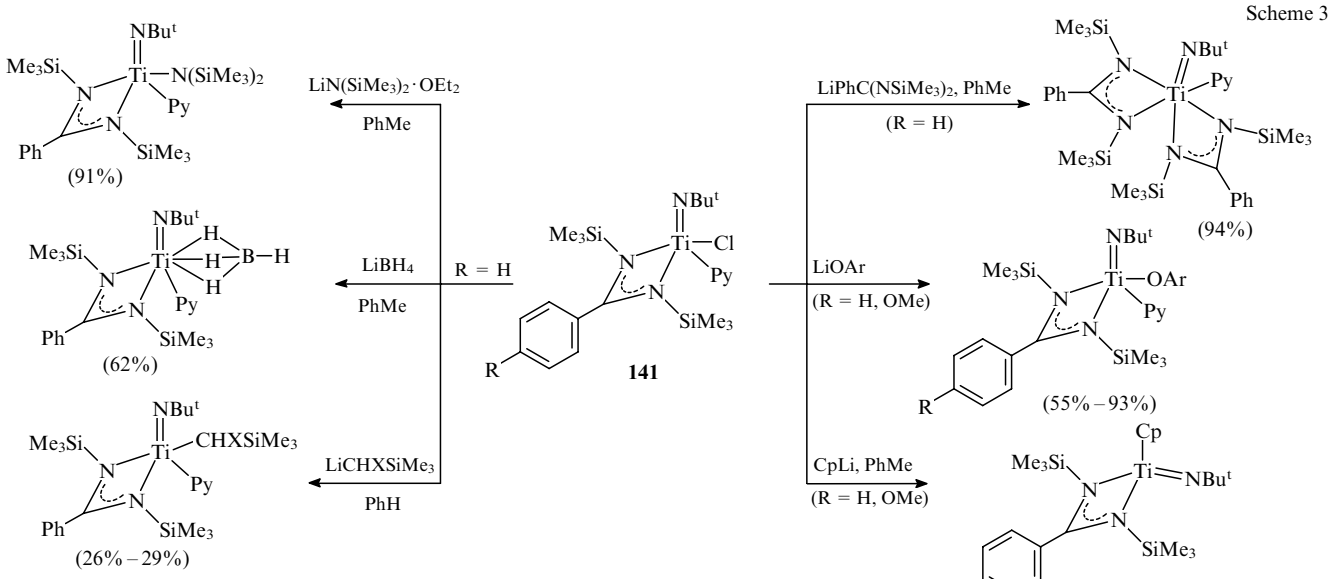
142 **143** **144** **145**

R = Bu^t, 2,6-$Me_2C_6H_3$.

c. Group 5 elements (V, Nb and Ta)

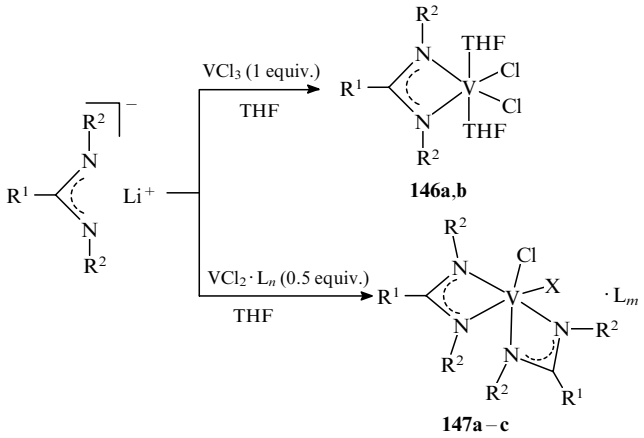
Very few papers were published on Group 5 metal amidinate complexes over the last decade. The primary attention was given to vanadium and tantalum derivatives, while no niobium amidinate complexes have been synthesised during this period. Earlier work in this area has been summarised in reviews.[8, 9]

Scheme 3



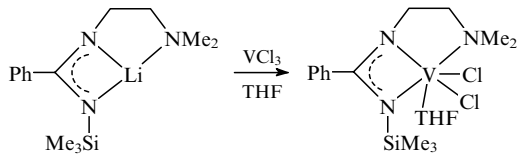
X = H, $SiMe_3$; Ar = 2,6-$Me_2C_6H_3$; 2,6-$Bu^t_2C_6H_3$.

At present, the only method of synthesis of such derivatives is the reaction of lithium amidinates with Group 5 metal chlorides or organometallic chlorine-containing complexes.[129–132] These reactions proceed under mild conditions in yields not less than 50%. For example, vanadium mono- (**146a**,**b**) and bis(amidinate) (**147a–c**) derivatives were synthesised by this method.

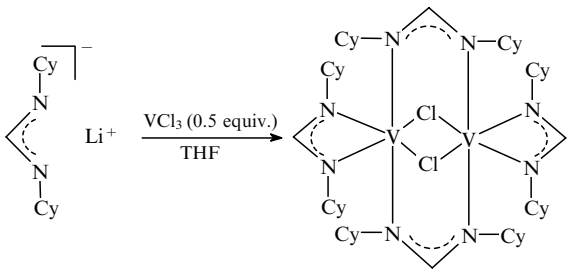


146: R^1 = Ph, R^2 = $SiMe_3$ (**a**); R^1 = Bu^t, R^2 = Pr^i (**b**);
147: R^1 = Ph, R^2 = $SiMe_3$ (**a**); R^2 = Cy: R^1 = H (**b**), Me (**c**);
L_n = Cl, X = THF, L_m is absent;
L_n = TMEDA, THF: X = Cl, L_m = L_n.

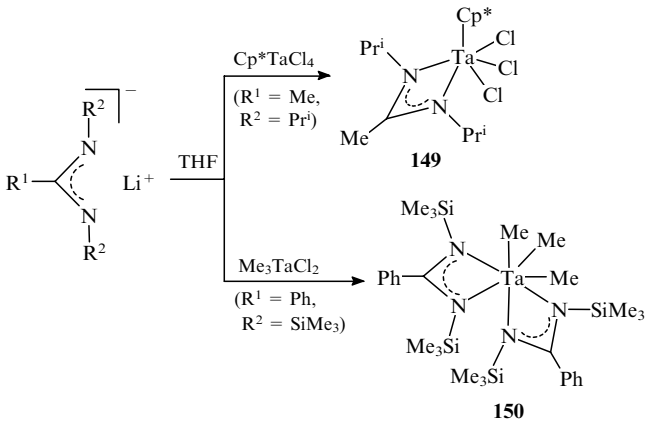
Vanadium complex **148** with a tridentate amidinate ligand was obtained similarly.[129]



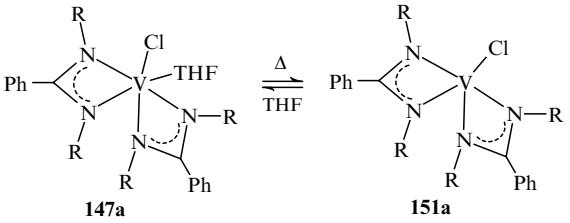
When bulky substituents, such as cyclohexyl ring, were present at the nitrogen atoms of the amidinate fragment, the bridged dinuclear complexes **14** were obtained in the reaction of vanadium chloride with 2 equiv. of lithium amidinate.[130]



Tantalum mono- (**149**)[133] and bis(amidinate) (**150**)[132] complexes were synthesised from lithium amidinates using the organotantalum chlorides as the reagents.



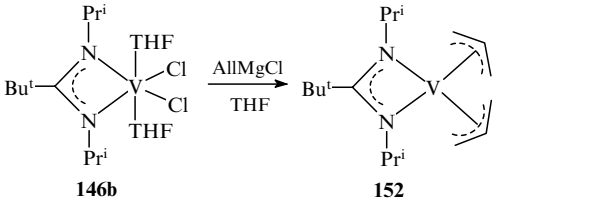
A characteristic feature of vanadium amidinate complexes is the formation of adducts with donor molecules, for example, with THF, which is a common solvent.[131] Thus, either a solvent molecule or a ligand from the reagent (organometallic complex) can be inserted into the coordination sphere of the metal. It becomes possible, because the coordination of vanadium atom in such complexes is incomplete. Sometimes, especially in the cases of sterically hindered complexes like **147a**, such insertion is reversible: heating of the product results in formation of pentacoordinated vanadium compound **151a**.



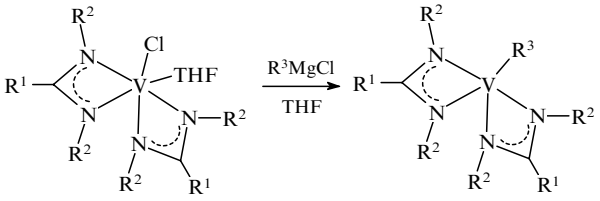
147a **151a**

R = $SiMe_3$.

The mechanism of formation of amidinate derivatives of Group 5 metals discussed above may be regarded as nucleophilic substitution of the amidinate group for the chloride ligand. Chloride ligands in complexes **147b** and **147a**,**d** undergo further substitution in reactions with alkyl and allyl (All) Grignard reagents resulting in acceptable yields of the corresponding derivatives **152** and **153a**,**d** (see Refs 131 and 134).



146b **152**

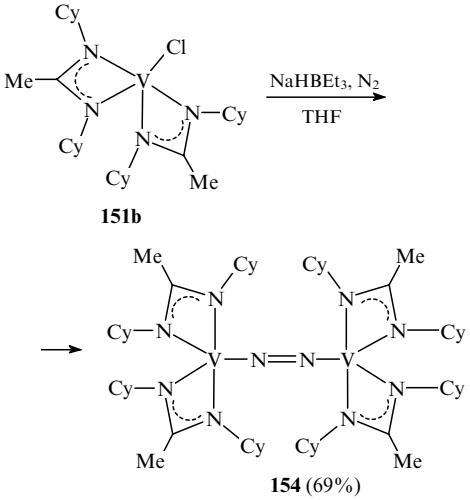


147a,**d** **153a**,**d**

R^1 = Ph, R^2 = $SiMe_3$ (**a**); R^1 = Bu^t, R^2 = Pr^i (**d**); R^3 = Et, All.

Different types of coordination of allylic ligands in vanadium mono- (**153**) and bis(allyl)- (**152**) complexes are worth mentioning. In the former, the allyl group is η^1-bound to the metal, while in the latter, both allyl ligands are η^3-coordinated.

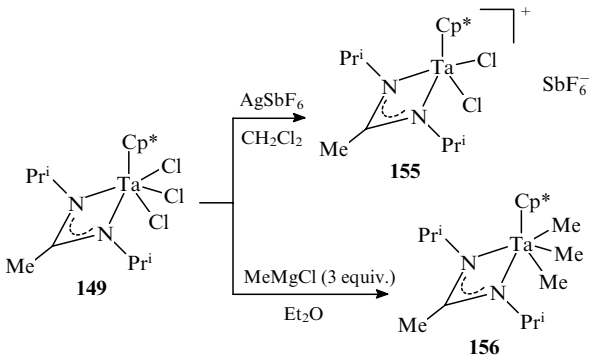
An unusual reaction has been found in the reduction of compound **151b** with sodium triethylborohydride in THF.[130] The reaction product is a dimeric complex **154** containing a diazo-bridge, which is formed upon insertion of a molecule of the atmospheric nitrogen.



151b

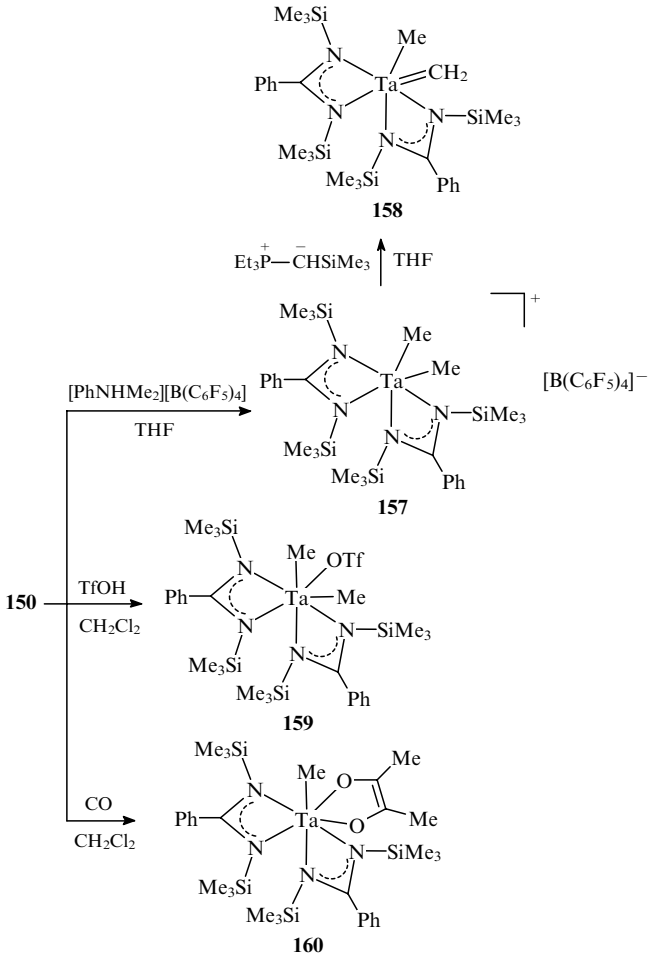
154 (69%)

Cationic compound **155** is formed in reaction of silver hexafluoroantimonate with tantalum monocyclopentadienyl amidinate complex **149**.[133] The reaction of the latter with 3 equiv. of methylmagnesium chloride yields compound **156** in which all three chloride ligands are substituted by alkyl groups.



149 **155** **156**

Chemical properties of tantalum trialkyl bis(amidinate) derivatives **150** are described in detail.[132] The structure of the protonation product of complex **150** depends on the protonating reagent. Ionic derivative **157** is formed when $[PhNHMe_2][B(C_6F_5)_4]$ is used. The reaction of compound **157** with phosphorus ylide yields the carbene complex **158**. If the trifluoromethanesulfonic acid (TfOH) is used as a protonating reagent, the dialkyl monotrifluoromethanesulfonate derivative **159** is obtained. In the presence of an excess of CO, the starting complex **150** undergoes double insertion of carbon dioxide into the Ta–C bond furnishing compound **160**.



158 **157** **159** **160**

And finally, it has to be noted that vanadium and tantalum amidinate complexes were studied as catalysts of olefin polymerisation. Thus compounds **147** (X = THF), **148** and **149** are highly reactive as catalysts of ethylene polymerisation in the presence of MAO.[133, 134] The activity of tantalum complex **149** containing three chloride ligands is equal to 470 g mol^{-1} h^{-1} (see Ref. 133),

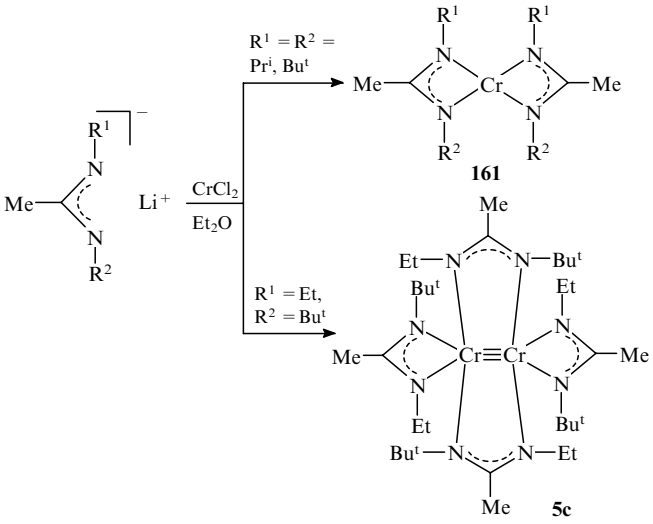
while its trimethyl analogue is inactive under similar conditions. Vanadium complexes **147** (X = THF) are significantly less reactive, ~10 g mol^{-1} h^{-1} (see Ref. 134), the molecular mass of the obtained polyethylene is 80 kDa. At the same time, the activity of vanadium complex **148** with tridentate amidinate ligand is nearly the same (447 g mol^{-1} h^{-1}) as the activity of tantalum derivative **149**.

d. Group 6 elements (Cr, Mo and W)

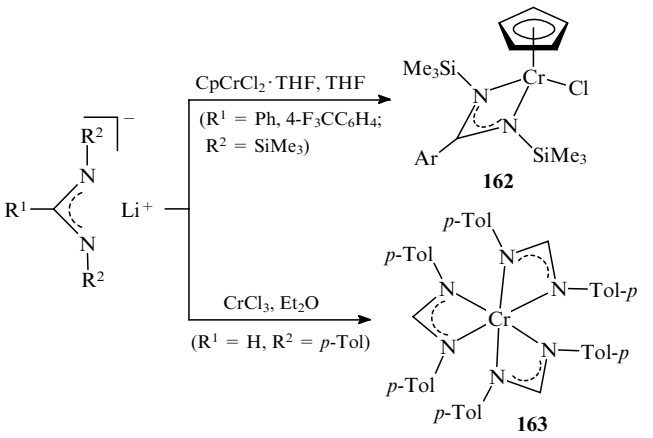
Seven papers on the amidinate complexes of Group 6 metals have been published since 1994. The unusual structures of chromium derivatives with very short Cr–Cr distances (1.84–1.96 Å)[135, 136] are of special interest.

Most of the described chromium and molybdenum amidinate complexes were obtained by standard method, *viz*., by the reaction of lithium amidinate salts with the corresponding metal halides or with organometallic halogen-containing complexes.[24, 135, 137–139]

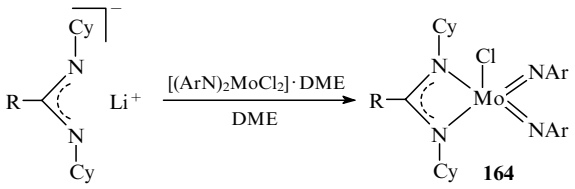
Mononuclear bis(amidinate) derivatives **161** are obtained by the reaction of chromium(II) compounds with amidinates containing bulky substituents (Pr^i, Bu^t) at the both nitrogen atoms. In the case of less sterically hindered amidinate salts, dinuclear complexes **5c** with multiple Cr≡Cr bonds are obtained.[135] The yields of compounds **161** and **5c** are 50%–60%.



The same method was used for the synthesis of chromium mono- (**162**) and tris(amidinate) (**163**) complexes [137]

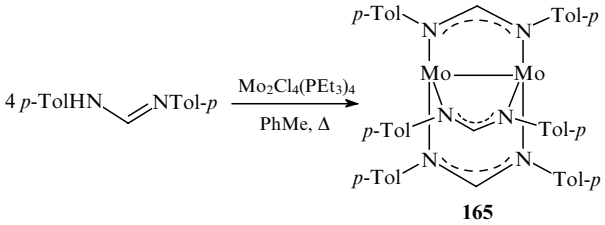


as well as molybdenum derivatives **164**.[138]



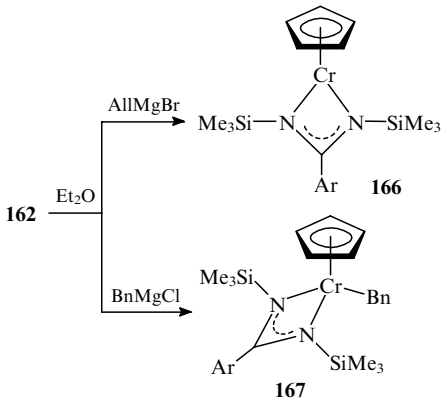
R = Me, Ph; Ar = 2,6-Pr$^i_2$C$_6$H$_3$; DME is dimethoxyethane.

Refluxing of molybdenum tetrakis(phosphine chloride) derivative in toluene with 4 equiv. of amidine yields molybdenum dinuclear tris(amidinate) complexes **165**.[139] According to the X-ray diffraction data, the Mo–Mo bond in the complex **165** is single.

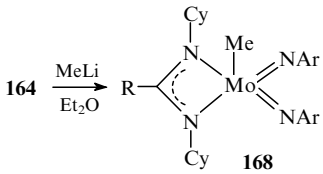


The chemical properties of the amidinate complexes of Group 6 metals are scarcely studied. Only the reactions of chromium complexes **162** and molybdenum complexes **164** with the Grignard reagents or alkyllithium resulting in substitution of the chloride ligands have been described.[137, 138]

Allylmagnesium bromide reduces compound **162** into Cr(II) derivative **166**, while benzylmagnesium chloride replaces the chloride ligand yielding complex **167** (see Ref. 137).



Methyl-substituted amidinate complex **168** was obtained in the reaction of molybdenum complexes **164** with methyllithium.



R = Me, Ph; Ar = 2,6-Pr$^i_2$C$_6$H$_3$.

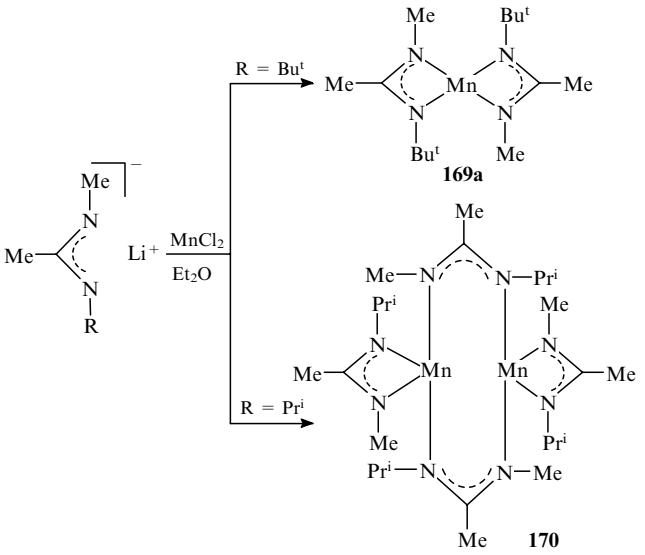
No new tungsten amidinate derivatives have been synthesised during the last decade. Earlier results are summarised in the reviews.[8, 9]

e. Group 7 elements (Mn, Re and Tc)

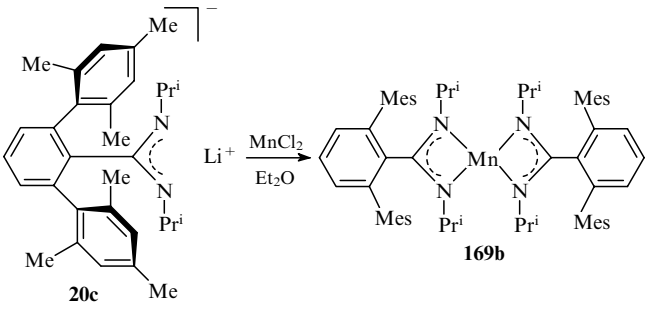
There are very few studies of amidinate complexes of Group 7 metals. Earlier papers mainly discussed the results of X-ray structural studies (see, for example, a review [8]). However, the

application of manganese bis(amidinate) complexes as starting compounds for CVD has been mentioned recently.[83]

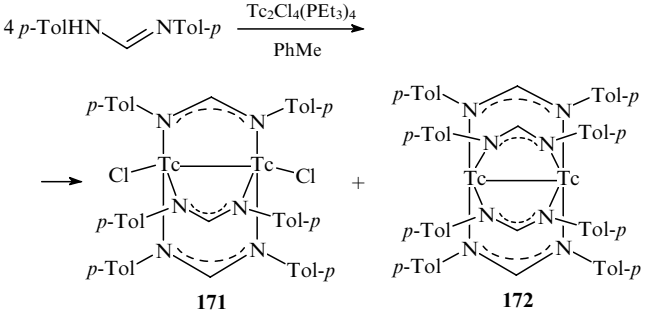
All known Mn(II) bis(amidinate) complexes were synthesised by reaction of lithium amidinates with $MnCl_2$.[83, 140] Mononuclear bis(amidinate) derivative **169a** was obtained in the reaction where the amidinate ligand carried bulky *tert*-butyl substituent at the nitrogen atom. In the case of less bulky isopropyl group, the dinuclear compound **170** was formed.



However, if the starting salt contains sterically hindered substituent at the carbon atom of the amidinate fragment (for example, 2,6-dimesitylphenyl in complex **20c**), the bis-derivative **169b** is also formed. The yields of compounds **169a**,**b** and **170** vary from low to moderate.



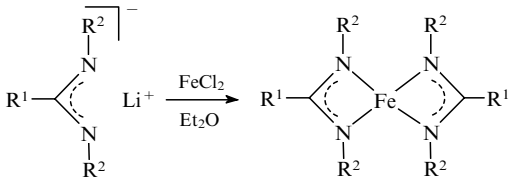
Technetium dinuclear tris- (**171**) and tetrakis(amidinate) (**172**) derivatives were obtained by heating ditechnetium tetrakis(phosphine chloride) with 4 equiv. of amidine.[139]



f. Group 8 elements (Fe, Ru and Os)

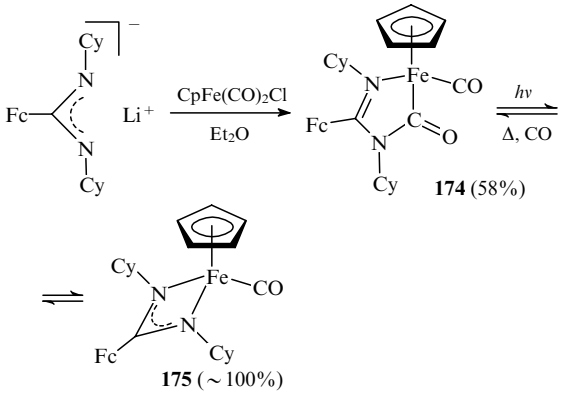
The chemistry of the amidinate complexes of Group 8 metals was successfully developed during the last decade. First of all, it concerns ruthenium amidinate derivatives, which are widely used as the catalysts of the Harash and Tsuji–Trost reactions.[10] The methods of synthesis and chemical properties of these compounds are summarised in a recent review[10] and therefore will not be discussed here.

The studies of iron amidinate complexes were focused mainly on the synthesis of Fe(II) bis(amidinate) derivatives containing bulky chiral amidinate ligands and ferrocenyl substituents.[43, 83, 140–142] Complexes **173** were obtained in satisfactory yields from lithium amidinates and iron dichloride as the starting compounds.

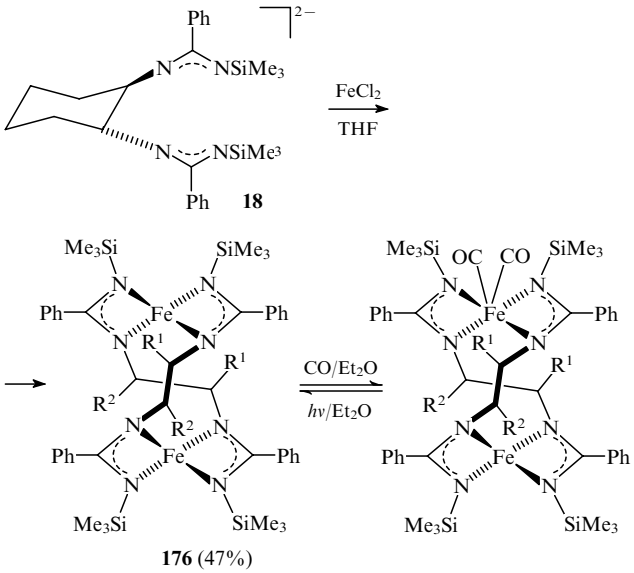


R^1 = Me, R^2 = Bu^t; R^1 = (η^5-C_5H_5)Fe(η^5-C_5H_5) (Fc), R^2 = Cy; R^1 = 2,6-$Mes_2C_6H_3$, R^2 = Pr^i.

However, in the reaction with $CpFe(CO)_2Cl$, ferrocenyl-substituted lithium amidinate forms compound **174**, which is an insertion product of one of the carbonyl groups into the Fe–N bond.[142] UV irradiation of derivative **174** yields the amidinate complex **175**, which is converted to the starting complex **174** on heating in a CO atmosphere.



The synthesis of iron chiral dinuclear complex **176** is described.[43] It appeared that this complex can also add the CO ligands reversibly.



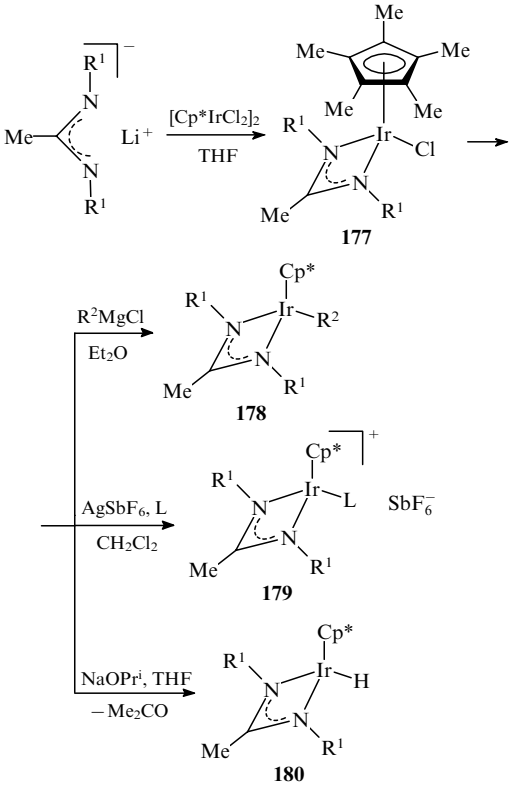
R^1–R^2 = $(CH_2)_4$.

However, in this case the carbonyl group coordinates the iron atom rather than inserts into the Fe–N bond.

No new osmium amidinate derivatives have been synthesised during the last decade. Data on the chemistry of iron and osmium amidinate complexes can be found in reviews.[8,9]

g. Group 9 elements (Co, Rh and Ir)

Only one systematic study[144] on the chemistry of amidinate complexes of Group 9 metals has emerged since the publication of a series of papers[8,9,18,143] on the synthesis and reactivity of rhodium amidinate complexes. The authors synthesised iridium derivatives **177** starting from lithium acetamidinates and a chlorine-containing iridium complex and studied their properties.



177

178

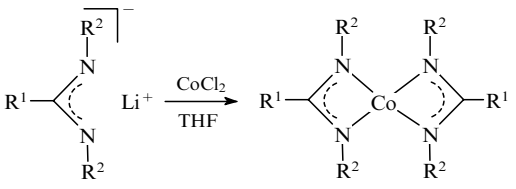
179

180

R^1 = Pr^i, Cy; R^2 = Me, Et, Bn; L = Py, CO.

The corresponding monoalkyl derivatives **178** were obtained from compounds **177** in good yields (>70%) by reaction with equimolar amounts of the Grignard reagents. In the presence of compounds that easily coordinate to metals, such as pyridine or CO, compound **177** reacts with $AgSbF_6$ yielding cationic complexes **179**. In the absence of such ligands, the iridium intermediate decomposes. The reaction of compound **177** with sodium isopropoxide proceeds in an unusual way: hydride complexes **180** are formed instead of the expected isopropoxide derivatives. Apparently, the β-hydride shift accompanied by elimination of acetone occurs in the isopropoxide intermediate.

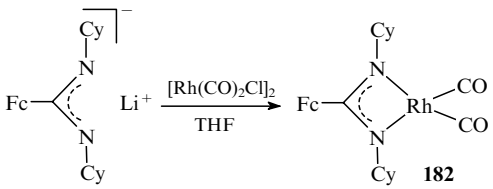
Both conventional cobalt bis(amidinate) derivatives **181a**,**b** and their analogue **181c** with sterically hindered 2,6-dimesitylphenyl substituent in the amidinate ligand have been synthesised recently.[83,140,142]



181a–c (40%–70%)

R^1 = Me, R^2 = Pr^i (**a**); Bu^t (**b**); R^1 = 2,6-$Mes_2C_6H_3$, R^2 = Pr^i (**c**).

Compound **182**[142] is the only ruthenium amidinate complex described so far.

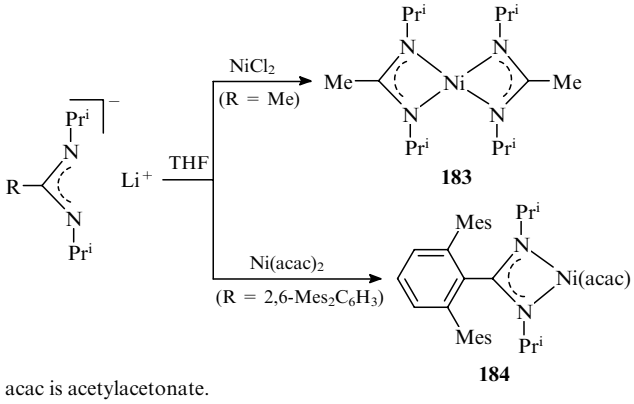


182

Complexes **181a**,**b** and **182** are used as starting compounds in the manufacture of metal oxide thin films.[83]

h. Group 10 elements (Ni, Pd and Pt)

There was no new significant breakthrough in the chemistry of amidinate complexes of Group 10 metals during the last decade. A small number of new complexes have been synthesised from the corresponding lithium amidinates.[83,140,145] Thus nickel bis(amidinate) derivative **183** was obtained by the reaction of lithium salt with nickel chloride. Similar reaction with nickel bis(acetylacetonate) furnishes monoamidinate complex **184**. The yields of the products in these cases are moderate (40%–60%).

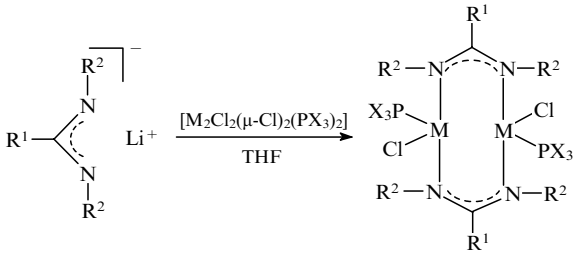


183

184

acac is acetylacetonate.

A series of dinuclear palladium (**185**) and platinum (**186**) complexes containing two bridging amidinate ligands were synthesised by similar method.[145] Chlorine-containing phosphine complexes of these metals were used as the reagents.



185, **186**

185: M = Pd; X_3 = Et_3, Bu^n_3, Me_2Ph; R^1 = H, Me; R^2 = Ph, *p*-Tol, 4-$MeOC_6H_4$;

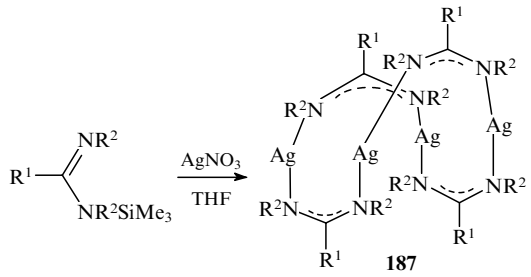
186: M = Pt; X_3 = Bu^n_3, Me_2Ph; R^1 = H; R^2 = Ph.

Chemical properties of amidinate derivatives **183**–**186** are almost unknown. The use of compounds **183** and **184** as the starting components in the manufacture of oxide thin films is an example of practical application of amidinate complexes of Group 10 elements.[83]

i. Group 11 elements (Cu, Ag and Au)

Homoleptic complexes with the composition $[M(R^2NC(R^1)NR^2)]_n$ (n = 1–4) are at present the best known amidinate derivatives of Group 11 metals. The metathesis reaction of trimethylsilyl derivatives of amidinates with inorganic metal salts is the main method of synthesis of such complexes.[146,147]

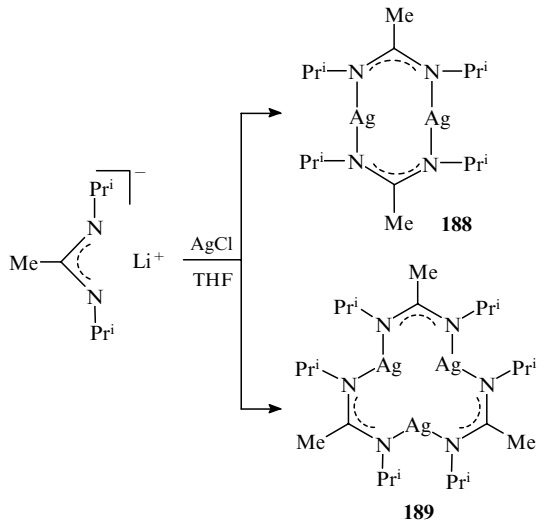
Typically, silver complexes **187** obtained by this method have tetranuclear structures.[8, 147]



187

R^1 = Me, Pr^n, Bu^n, n-C_5H_{11}, n-C_8H_{17};
R^2 = Ph, 4-$Bu^nC_6H_4$, 4-$MeOC_6H_4$.

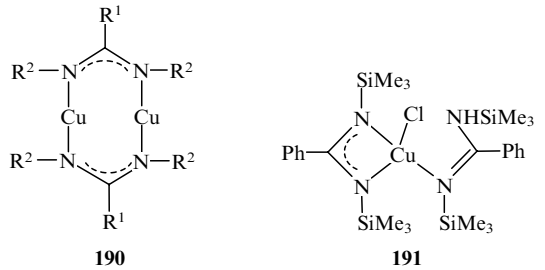
Silver dinuclear (**188**) and trinuclear (**189**) complexes are also known.[83] They were synthesised by the reaction of AgCl with lithium amidinate salts.



188

189

Dinuclear structure is also typical of copper amidinate complexes. The synthesis of bis(amidinate) derivatives **190** containing bridging ligands is described.[146] An exception from this structural type is the mononuclear complex **191** obtained by the reaction of lithium amidinate salt with copper dichloride.[146] Wet acetonitrile has to be used as a solvent in the synthesis of this compound.

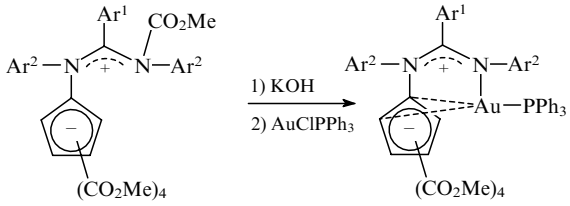


190 **191**

R^1 = H, R^2 = 4-$Bu^nC_6H_4$; R^1 = Me, R^2 = Pr^i; R^1 = Ph, R^2 = $SiMe_3$.

Copper amidinate complexes **190** and **191** were tested as catalysts in polymerisation of carbodiimides [146] and methyl methacrylate.[148] In the presence of these complexes, the polymerisation of carbodiimides proceeds without chain transfer, *i.e.*, living polymerisation occurs, and the activity of the catalysts in an inert atmosphere is almost the same as that in the presence of oxygen. The yields of polymers are 70% – 90%.

Unusual gold amidinate complexes with chiral cyclopentadienyl ligands with *N*-donor side chain have recently been obtained by Minkin and co-workers.[149 – 151] Treatment of zwitter-ionic cyclopentadienyl ligands with alkaline solution followed by addition of Ph_3PAuCl results in the formation of complexes **192** in high yields.



192

Ar^1 = Ph, Ar^2 = *p*-Tol; Ar^1 = 1-naphthyl: Ar^2 = *m*-Tol, *o*-Tol.

According to X-ray diffraction analysis, the metal in these compounds is σ-coordinated by a nitrogen atom of the amidinate ligand and, therefore, complexes **192** belong to the structural type **B** (see Section II). Moreover, the η^2-type coordination of metal by the π-system of cyclopentadienyl ligand is observed, which is highly unusual for gold cyclopentadienyl derivatives.

Copper and silver amidinate complexes are used as starting components in the production of oxide thin films.[83]

The earlier references to the chemistry of amidinate complexes of Group 11 metals can be found in the review.[8]

IV. Conclusion

In conclusion to the review, the large number of publications into the chemistry of main Group and transition metal amidinate complexes unambiguously suggests that this field of research is still under rapid development and growth. It is evident that this trend will continue for at least a near future. Furthermore, despite the fact that there has been no single unique method for the synthesis of amidinate complexes developed since 1994, the existing synthetic methods allow for almost any amidinate derivatives. Most of the metal amidinate complexes known to date are mononuclear. However, di- and polynuclear structures are more common for the late transition metal amidinates (nickel and copper groups) as well as for cationic aluminium amidinate complexes. Metal amidinate complexes have found significant application as catalysis for olefin polymerisation (including stereocontrolled synthesis of block-copolymers) and for a number of organic transformations, as demonstrated for ruthenium amidinate derivatives.

Several potential areas of further studies may be outlined. Thus amidinate complexes of Group 4 and 5 metals may find use as catalysts for nitrogen fixation. Amongst all, Group 4, 8 and 13 metal amidinate complexes are most promising for further studies. Dinuclear amidinate complexes and organometallic clusters with amidinate ligands, which are barely studied yet, may demonstrate unusual reactivity as chemical reagents as well as catalysts of various chemical transformations. Moreover, amidinate ligands are promising precursors for synthesis of volatile organometallic compounds used for the production of metal coatings and membranes. Successful development in this area is related to several factors, namely, availability of starting materials, existence of convenient methods for the synthesis of amidinate complexes, and also thermal stability of amidinate derivatives even when similar metallocene compounds are labile.

Thus, this paper has demonstrated a significant potential of main Group and transition metal amidinate complexes for both fundamental and applied research studies.

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