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N-silylated benzamidines: versatile building blocks in main group and coordination chemistry

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CONTENTS

ABSTRACT

The main group and coordination chemistry of N-silylated benzamidines, $RC_6H_4C(=NSiMe_3)[N(SiMe_3)_2]$, and the corresponding anions, $[RC_6H_4C(NSiMe_3)_2]^-$, is reviewed. Lithium and sodium salts of the type $M[RC_6H_4C(NSiMe_3)_2]$ (M = Li, Na) are easily accessible via addition of $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$ to various substituted benzonitriles. Subsequent reactions with Me_3SiCl lead to the fully silylated benzamidine derivatives. Both the neutral species and the anions are highly useful precursors in main group chemistry, for example, for the preparation of various inorganic heterocycles. They also react with transition metal halides to give in most cases benzamidinato chelate complexes containing planar, four-membered MNCN rings. Other reaction pathways include the formation of transition metal amido, imido, nitrido, and hydrazido complexes. In some cases hydrolytic cleavage of one or more Si—N bonds is observed. The silylated benzamidinate anions $[RC_6H_4C(NSiMe_3)_2]$ are especially useful as novel observer ligands for f-elements. They form low-coordinate, hydrocarbon-soluble complexes with lanthanide and actinide elements.

1. INTRODUCTION

Amidines are difunctional nitrogen compounds of the general formula $RC(=NH)NH_2$. Their use as reagents in synthetic organic chemistry is well established

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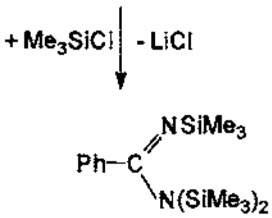
[1]. In recent years the synthetic potential of amidines, especially that of benzamidines, has increased significantly through the use of N-silylated benzamidine derivates. *N,N,N′*-Tris(trimethylsilyl)benzamidine, $PhC(=NSiMe_3)[N(SiMe_3)_2]$ (**1a**), was discovered by Sanger as early as 1973 [2]. It was first obtained via treatment of benzonitrile with lithium bis(trimethylsilyl)amide. The resulting lithiated benzamidine **2a** was reacted with Me_3SiCl to give the fully silylated derivative **1a** (reaction 1).

$$PhCN + LiN(SiMe_3)_2 \rightarrow Li[PhC(NSiMe_3)_2] \quad (\mathbf{2a}) \qquad (1)$$



1a

Interestingly, the formation of **2a** was only observed when the reaction was carried out in diethylether solution. In petroleum ether no lithiated benzamidine **2a** was formed. Instead, the benzonitrile trimerized in the presence of $LiN(SiMe_3)_2$ to give the symmetrical triazine derivative 2,4,6-triphenyl-*s*-triazine [2]. A more elaborate preparation of **1a** and several substituted derivatives was reported by Oakley and co-workers in 1987 (vide infra) [3]. This paper marked the beginning of vigorous research activities dealing with the chemistry of N-silylated benzamidines. Within a few years it was discovered that these materials are equally useful as precursors for inorganic heterocycles as well as benzamidinate complexes of various elements, including the lanthanides and actinides. Only three years after the initial report by Oakley and co-workers the multifaceted chemistry of trimethylsilyl-substituted benzamidines was compiled in a review article by Dehnicke [4]. Since then the number of new results in this area has increased so rapidly and to such a degree that another review on this topic seems timely and appropriate. This article is intended to highlight the recent results and to cover all aspects of the chemistry of N-silylated benzamidines including main group and coordination chemistry.

2. THE STARTING MATERIALS

2.1. *N,N,N′-Tris(trimethylsilyl)benzamidines*

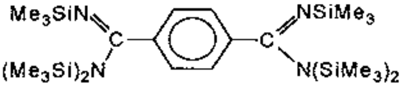
As mentioned above, the parent compounds $PhC(=NSiMe_3)[N(SiMe_3)_2]$ (**1a**) was first made by Sanger in 1973 [2]. The preparation involves addition of $LiN(SiMe_3)_2$ to benzonitrile followed by treatment of the intermediate lithium salt with Me_3SiCl (reaction 2). In 1987 Oakley and co-workers demonstrated that a number of *p*-substituted derivatives of **1a** can also be prepared following this general route [3].

$$RC_6H_4CN \xrightarrow[2.\ Me_3SiCl]{1.\ LiN(SiMe_3)_2} RC_6H_4C(=NSiMe_3)[N(SiMe_3)_2] \qquad (2)$$

1: R = H (**a**), Me (**b**), Cl (**c**), MeO (**d**), Me_2N (**e**), CF_3 (**f**), Ph (**g**), CN (**h**), NO_2 (**i**)

The *N,N,N'*-tris(trimethylsilyl)benzamidines **1a–g** form oily liquids or low-melting solids which are easily purified by vacuum distillation. Typical product yields range from 50% to 72%. For R = CN (**1h**) and NO_2 (**1i**) the formation of the lithiated intermediates was quantitiative by ^1H NMR. However, reaction with Me_3SiCl did not take place. The failure to obtain **1h** and **1i** was attributed to a low nucleophilicity of the intermediates resulting from extensive delocalization over the ring in the case of R = CN and NO_2. Owing to the presence of N–Si bonds the compounds **1** are readily susceptible to hydrolysis and thus quite moisture sensitive. Controlled hydrolysis leads to the corresponding amidines $RC_6H_4C(=NH)NH_2$ in high yields. Thus the overall reaction represents a simple and straightforward preparation of benzamidines from the corresponding benzonitrile precursors [3].

Starting with NCC_6H_4CN Oakley and co-workers [3] also succeeded in the preparation of the fully silylated bis(benzamidine) derivative **3**. More recently the tris(benzamidine) derivative **4** was synthesized by treatment of 1,3,5-$C_6H_3(CN)_3$ with three equivalents of $LiN(SiMe_3)_2$ followed by silylation using Me_3SiCl (colorless needles, 35% yield). Compound **4** served as a starting material for the unusual trifunctional radical 1,3,5-benzene-tris(1,2,3,5-dithiadiazolyl) [5].



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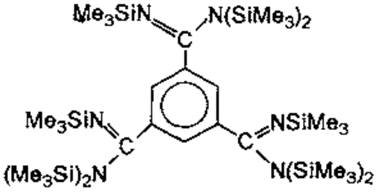


4

An unsuccessful attempt to prepare a lithium *N,N'*-bis(trimethylsilyl)benzamidinate was observed in our laboratory [6]. Two different attempts were made to synthesize the silylated benzamidinate anion containing a ferrocene unit attached to the central carbon atom. Both methods failed to give any isolable product. In the first try cyanoferrocene was reacted in the usual manner with

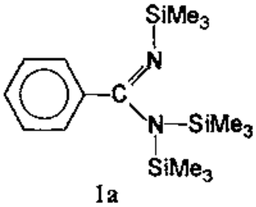
$LiN(SiMe_3)_2$ (reaction 3), but even under reflux conditions no reaction took place. In a different approach lithioferrocene was treated with *N,N'*-bis(trimethylsilyl)-carbodiimide (reaction 4), yet again the starting materials were recovered unchanged even after prolonged heating.

$$FcCN + LiN(SiMe_3)_2 \nrightarrow Li[FcC(NSiMe_3)_2] \qquad (3)$$

$$FcLi + Me_3SiN{=}C{=}NSiMe_3 \nrightarrow Li[FcC(NSiMe_3)_2] \qquad (4)$$

(Fc = Ferrocenyl)

The molecular structures of **1a** and **3** have been determined by X-ray diffraction (Fig. 1) [7,8]. The most notable structural feature of **1a** is the deviation from a planar geometry which normally is typical for so many other carboxylic acid derivatives [7]. Owing to the bulky trimethylsilyl substituents at the nitrogen atoms the dihedral angle between the phenyl ring and the NCN unit is 56.1°. This angle does



1a

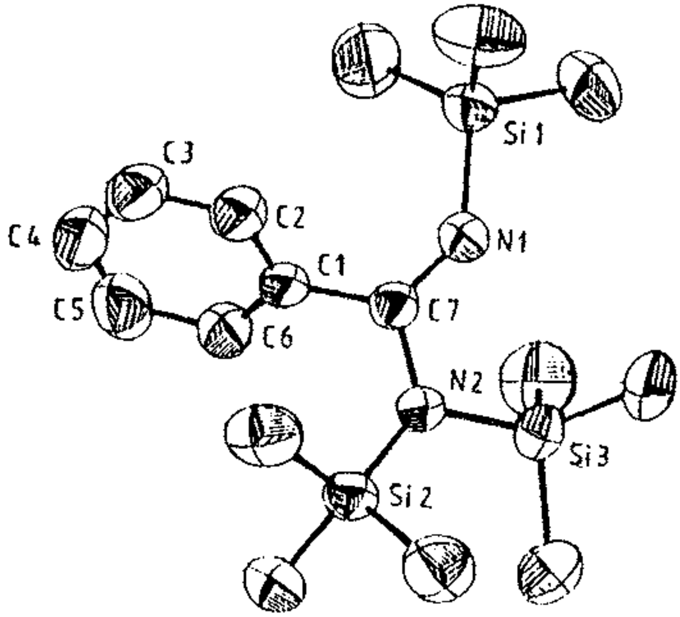


Fig. 1.

not allow a significant conjugation between the two π-systems. The central carbon atom of the NCN unit and the nitrogen atom N2 both exhibit a trigonal planar geometry. In both cases the angle sum is close to 360°. A slight shortening of the bond between C7 and N2 (1.41 Å) compared with a normal C−N single bond (1.46 Å) [9] indicates a low degree of π-bonding between these two atoms. This is in agreement with a significant torsion around the N2−C7 bond (dihedral angle 32.9°). With 1.266 Å, the distance between C7 and N1 is that of a typical C=N double bond [9]. Owing to the different coordination numbers at nitrogen, the N−Si distances in the $N(SiMe_3)_2$ group are slightly larger (ca. 0.05 Å) than the N1−Si1 bond.

Most distances and angles in the centrosymmetric molecule **3** are very similar to those reported for **1a** [8]. The most interesting difference is found for the dihedral angles between the disubstituted phenyl ring and the NCN units of the benzamidinate substituents. With 49.3°, the torsion between these planes is significantly smaller than in **1a**. In fact, this is the smallest dihedral angle found in any derivative of the N-silylated benzamidines. It is still much too large though to allow significant conjugation between the two π-systems.

In marked contrast to the straightforward preparation of several N-silylated amidines derived from aromatic nitriles, the synthesis of analogs containing aliphatic substituents at the central carbon atom proved to be quite difficult. Acetonitrile failed to react with $LiN(SiMe_3)_2$ in the same manner as described for benzonitrile derivatives [3,10]. This difference can be explained by the preferred deprotonation of the methyl group in CH_3CN in the presence of a strong base. It was reported earlier by Krüger that acetonitrile reacts with sodium bis(trimethylsilyl)amide (reaction 5) to give exclusively cyanomethylsodium of unknown structure [11]. CF_3CN was found by Oakley and co-workers to undergo an addition reaction with $LiN(SiMe_3)_2$. The intermediate was not isolated but treated with Me_3SiCl to give stable $CF_3C(=NSiMe_3)[N(SiMe_3)_2]$ (**5**) in 46% yield (reaction 6).

$$CH_3CN + NaN(SiMe_3)_2 \rightarrow NaCH_2CN + HN(SiMe_3)_2 \qquad (5)$$

$$CF_3CN \xrightarrow[\text{2. } Me_3SiCl]{\text{1. } LiN(SiMe_3)_2} \underset{\mathbf{5}}{CF_3C(=NSiMe_3)[N(SiMe_3)_2]} \qquad (6)$$

Compound **5** is a colorless liquid with a boiling point of 40°C at 0.02 Torr. The most recent achievement in this area was the successful preparation of the parent formamidine derivative $HC(=NSiMe_3)[N(SiMe_3)_2]$ (**6**) [12]. It was synthesized in 80% yield together with the persilylated imidoylamidine $Me_3SiN{=}CH{-}N{=}CH{-}N(SiMe_3)_2$ using the reaction sequence 7. $HC(=NSiMe_3)$-$[N(SiMe_3)_2]$ was isolated as a hydrolytically unstable, colorless liquid. The elegant procedure utilizes the ability of *s*-triazine to react as a hydrogen cyanide equivalent. This reflects the formation of *s*-triazine via catalytic trimerization of HCN [13]. So far no other *N,N,N'*-tris(trimethylsilyl)amidines derived from aliphatic nitriles have been described. *t*-Butylcyanide was reported to react with $LiN(SiMe_3)_2$, but the NMR data of the product differed significantly from those of the lithiated intermediates obtained from other nitriles. Vacuum distillation gave a reactive lithium-containing material, which could not be fully characterized. Treatment of this material with Me_3SiCl did not lead to the formation of $^tBuC(=NSiMe_3)[N(SiMe_3)_2]$ [3].

$$\begin{tikzcd} 1/3(HCN)_3 + LiN(SiMe_3)_2 \arrow[r] & Li[HC(NSiMe_3)_2] \arrow[d, "+Me_3SiCl"', "-LiCl"] \\ & HC(=NSiMe_3)[N(SiMe_3)_2] \end{tikzcd} \tag{7}$$

6

2.2. *Alkali metal N,N'-bis(trimethylsilyl)benzamidinates*

In the original work by Oakley and co-workers [3] the lithiated intermediates obtained by addition of $LiN(SiMe_3)_2$ to benzonitrile derivatives were not isolated but reacted in situ with Me_3SiCl to give the fully silylated benzamidine derivatives **1**. A crystalline intermediate, formulated as $LiN{=}C(C_6H_5)N(SiMe_3)_2$, was first described in 1973 by Sanger, who also reported mass spectroscopic and IR data of this material [2]. Pure, crystalline lithium and sodium salts of the N-silylated benzamidinate anions were first described in 1990 [14]. Their synthesis (reaction 8) was made possible through the use of very pure starting materials (e.g. distilled $LiN(SiMe_3)_2$! [15]).

$$RC_6H_4CN + LiN(SiMe_3)_2 \xrightarrow{Et_2O} Li[RC_6H_4C(NSiMe_3)_2] \cdot L \tag{8}$$

2a R = H

2b R = Me, L = $0.5Et_2O$

2c R = MeO

2d R = CF_3

2e R = Me_2N

2f R = NO_2

With the exception of the less soluble *p*-methoxy derivative **2c**, the lithium salts **2** can be recrystallized from hexane. Their high solubility even in aliphatic hydrocarbons can be attributed to the presence of two bulky $SiMe_3$ substituents. Thus the solubility of the silylated benzamidinates differs greatly from that of the corresponding carboxylates. The facile formation of **2b** is remarkable as *p*-tolunitrile is deprotonated at the methyl group on treatment with strong bases such as $LiNMe_2$ or

$LiN(^iPr)_2$ [16]. In this sense the formation of **2b** from *p*-tolunitrile and $LiN(SiMe_3)_2$ appears to be an exception from the "normal" reactivity pattern.

For synthetic purposes a number of sodium *N,N'*-bis(trimethylsilyl)-benzamidinates **7** have been synthesized analogously by addition of $NaN(SiMe_3)_2$ to *p*-substituted benzonitrile derivatives (reaction 9) [14,17]. Generally the yields are high (71%–98%) and the sodium salts **7** are readily isolated as white, crystalline solids. Their solubility in hydrocarbon solvents decreases in the order $R = CF_3 > H > Ph > MeO$. The *p*-trifluoromethyl derivatives **7d** can be recrystallized from hexane. In contrast to the lithium *p*-tolyl derivative **2b**, the corresponding sodium salt **7b** cannot be isolated. At room temperature *p*-tolunitrile does not react with $NaN(SiMe_3)_2$. In THF solution at reflux temperature a deep red coloration quickly develops, indicating deprotonation at the methyl substituent and formation of *p*-cyanobenzylsodium, $NaCH_2C_6H_4CN$ (**8**). When the same reaction is carried out in boiling toluene, **8** precipitates as a dark red crystalline solid (reaction 10) and can be isolated in the form of a pyrophoric material [14].

$$RC_6H_4CN + NaN(SiMe_3)_2 \xrightarrow[\text{or THF}]{Et_2O} Na[RC_6H_4C(NSiMe_3)_2]\cdot L \qquad (9)$$

7a $R = H$, $L = 0.5Et_2O$

7b $R = Me$

7c $R = MeO$

7d $R = CF_3$, $L = Et_2O$

7e $R = Ph$, $L = 1.5THF$

$$MeC_6H_4CN + NaN(SiMe_3)_2 \rightarrow \underset{\mathbf{8}}{NaCH_2C_6H_4CN} + HN(SiMe_3)_2 \qquad (10)$$

Very little is known about *N,N'*-bis(trimethylsilyl)benzamidinate derivatives of the heavier alkali metals, although the salts **9–11** have been prepared by treatment of benzonitrile with the corresponding alkali metal bis(trimethylsilyl)amidines (reaction 11) [4,18]. The derivative chemistry of **9–11** has not been further investigated, although the potassium salt may have some advantages in reactions with transition metal halides because of the low solubility of the potassium halide byproducts which could facilitate their separation.

$$PhCN + MN(SiMe_3)_2 \rightarrow M[PhC(NSiMe_3)_2] \qquad (11)$$

M = K (**9**), Rb (**10**), Cs (**11**)

The molecular structures of two representative examples of alkali metal *N,N'*-bis(trimethylsilyl)benzamidinates have been determined by X-ray diffraction [18]. In an earlier study hints were obtained from spectroscopic data that these salts might exist as dimeric molecules in the solid state. For example, the mass spectrum of **2a** showed the molecular ion of a dimeric unit with high relative intensity [14]. The assumption of dimeric structures was later confirmed through X-ray analyses of $[MeC_6H_4C(NSiMe_3)_2Li(THF)]_2$ (**2b′**) and $[PhC(NSiMe_3)_2Na(Et_2O)]_2$ (**7a′**) [18]. These two well defined solvates were obtained by recrystallization of **2b** and **7a** from THF or diethylether respectively at low temperatures. Single crystals of both solvated benzamidinates are thermally labile and decompose below room temperature. Both compounds are dimeric in the solid state but the molecular structures are strongly influenced by the alkali metal used. For **2b′** a "ladder structure" was found (Fig. 2), which is also characteristic for a number of alkali metal alkoxysilylamides [19,20] and alkali metal diiminosulfinates [21,22]. A folded array of three four-membered ring systems forms the central part of the molecule. The dihedral angles between the outer CN_2Li rings and the inner Li_2N_2 ring are 130.4° and 145.3° respectively. The central Li_2N_2 ring is not planar but folded by 26.3° around the Li(1)···Li(2) vector. An important structural detail is the orientation of the phenyl rings. Compared with the neutral silylated benzamidines (Fig. 1) the steric influence of the Me_3Si groups is even greater in the anionic derivatives, as the phenyl rings are now in a perpendicular arrangement with respect to the NCN heteroallylic units. This orientation does not allow any significant conjugation between the two π-systems.

In **7a′** two chelating benzamidinate anions are centered around a nearly linear O–Na–Na–O unit (Fig. 3) [18]. With 2.741(4) Å the Na(1)···Na(2) distance is the shortest Na···Na contact found in any organometallic compound containing sodium. The coordination sphere of the sodium atoms is completed by diethylether

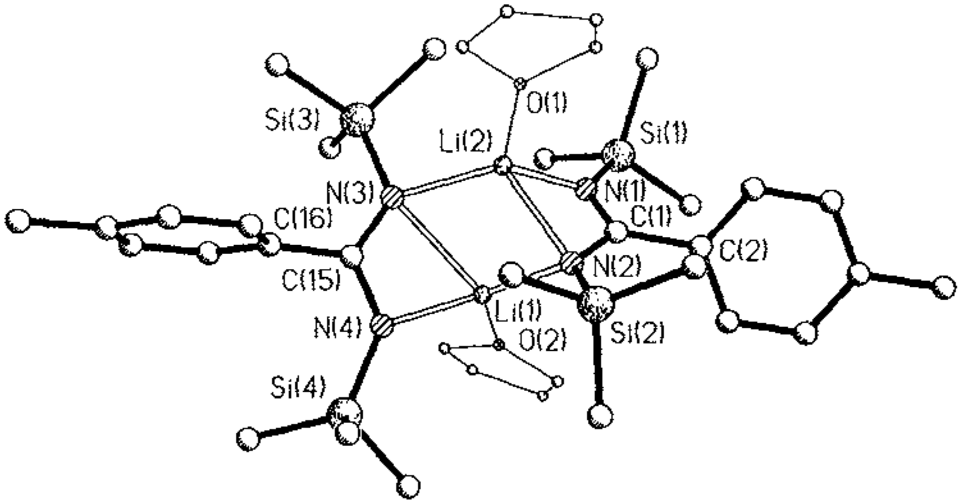


Fig. 2.

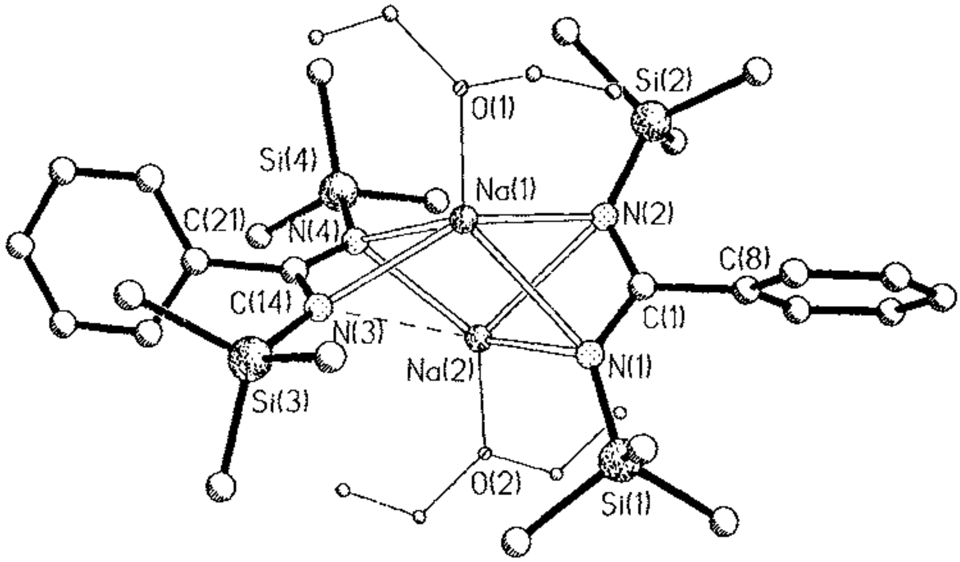


Fig. 3.

molecules. Once again the orientation of the phenyl substituents is perpendicular with respect to the heteroallylic NCN system.

The use of differently substituted *p*-benzonitriles in the preparation of N-silylated benzamidine derivatives allows a variation of the electronic properties. However, substituents at the para position of the phenyl ring do not significantly influence the steric demand of the resulting anions. For the design of versatile new ligand systems it is important to have the possibility of fine-tuning the steric bulk by introduction of substituents. Sterically highly demanding N-silylated benzamidinate anions were prepared using a different synthetic approach [14]. This method uses bis(trimethylsilyl)carbodiimide as a reagent to introduce the $C(NSiMe_3)_2$ unit. The reagent is easily accessible in larger quantities via silylation of cyanamide [23]. Nucleophilic addition of mesityllithium [24] or 2,4,6-tris(trifluoromethyl)-phenyllithium [25] to $Me_3SiN{=}C{=}NSiMe_3$ directly yields the lithium salts **12** in one step (reaction 12).

$$2,4,6\text{-}R_3C_6H_2Li + Me_3SiN{=}C{=}NSiMe_3 \rightarrow Li[2,4,6\text{-}R_3C_6H_2C(NSiMe_3)_2] \qquad (12)$$

12a $R = Me$

12b $R = CF_3$

The lithium benzamidinates **12a** and **12b** can be obtained analytically pure by recrystallization from hexane. Unsolvated **12b** is especially remarkable in that it sublimes readily at room temperature and dissolves freely in non-polar solvents such as toluene or even hexane. Although the molecular structure of **12a** has not been determined by X-ray diffraction, it is highly likely that the 2,4,6-tris(trifluoromethyl)phenyl substituent is responsible for the remarkable properties of this particular lithium benzamidinate. It has been demonstrated that the stabilizing influence of the 2,4,6-tris(trifluoromethyl)phenyl substituent is due to a combination of steric and electronic effects [26]. In addition, this ligand allows the characterization of its derivates by ^{19}F NMR spectroscopy.

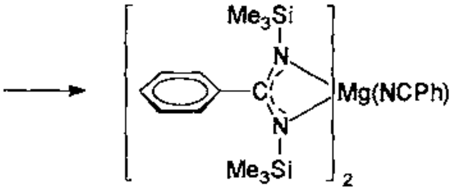
Both the lithium and sodium benzamidinates, as well as the fully silylated neutral benzamidines, have been used extensively as starting materials [4]. All these compounds may serve as highly versatile precursors for the introduction of $RC(NSiMe_3)_2^-$ ligands. However, the two classes of compounds are not equally well suited for all synthetic purposes. In general, the neutral species $RC(=NSiMe_3)[N(SiMe_3)_2]$ are the reagents of choice in main group chemistry. They react with numerous halides of main group elements under elimination of trimethylsilyl halide. Benzamidinate complexes of transition metals have been prepared successfully using either the neutral benzamidine reagents or the anionic derivatives. In some cases different results have been obtained depending on the type of reagent used. Generally the advantage of the fully silylated neutral benzamidines is that the trimethylsilyl halides formed as byproducts in these reactions are easily separated. The alkali metal benzamidinates are the preferred reagents when the reactivity (or solubility) of the transition metal halide is too low to promote elimination of trimethylsilyl halide. This is the case especially with the lanthanides and actinides. Benzamidinates of the f-elements are best prepared by reacting the anhydrous metal halides with lithium or sodium bis(trimethylsilyl)benzamidinates. Anhydrous lanthanide trichlorides are usually unreactive towards the neutral N-silylated benzamidines. Thus in many cases the two types of starting materials supplement each other. With the proper choice of precursors it is now possible to prepare N-silylated benzamidinate complexes of vitually any metallic element in the Periodic Table.

3. MAIN GROUP CHEMISTRY WITH *N,N'*-BIS(TRIMETHYLSILYL)BENZAMIDINATE LIGANDS

Main group chemistry with the N-silylated benzamidinate anions is remarkably diverse. A number of main group elements form simple coordination compounds containing the $[RC_6H_4C(NSiMe_3)_2]^-$ anions as chelating ligands. In many cases further reactions can occur which successively lead to the formation of various inorganic heterocycles. These two possibilities are discussed separately.

Alkali metal derivatives of the N-silylated benzamidinate anions have already been discussed in Section 2.2. More recently, Westerhausen and Hausen have reported the preparation of several alkaline earth metal derivatives. Unsolvated $Mg[N(SiMe_3)_2]_2$ reacts with benzonitrile (reaction 13) in toluene solution to give the benzonitrile adduct **13** [27]. Compound **13** is the only isolable product even if a 50% excess of the magnesium reagent is used. Repeated recrystallization of **13** from toluene did not lead to the unsolvated magnesium benzamidinate $[PhC(NSiMe_3)_2]_2Mg$. When the reaction of $Mg[N(SiMe_3)_2]_2$ with benzonitrile was carried out in THF (reaction 14) solution the bis(THF) solvate **14** was obtained in good yield. The same material is formed on addition of THF to a solution of **13** in toluene [27].

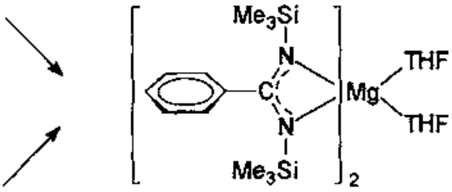
$Mg[N(SiMe_3)_2]_2 + 3PhCN$ (13)



13

$[PhC(NSiMe_3)_2]_2Mg(NCPh)$ (14)

$+ 2THF$



14

$Mg[N(SiMe_3)_2]_2(THF)_2$

$+ 2PhCN$

Both magnesium derivatives **13** and **14** form colorless solids which are sensitive to hydrolysis. Owing to the presence of silicon–nitrogen bonds in the ligands, hydrolytic instability is a phenomenon common to all metal derivatives of the N-silylated benzamidinate anions. The molecular and crystal structure of the benzonitrile adduct **13** has been determined by X-ray crystallography [27]. The coordination geometry around the central magnesium atom is approximately trigonal bipyramidal. The nitrogen atoms N1 and N1′ are in the axial positions with an N1—Mg—N1′ angle of 179.5°. Within the NCN heteroallylic units there is an equilibration of the C—N bonds (average 1.32 Å).

Bis(trimethylsilyl)amides of the heavier alkaline earth metals calcium, strontium and barium have only recently become available [28–33]. They also served as starting materials for the corresponding *N,N′*-bis(trimethylsilyl)benzamidinates of these metals. A THF adduct of calcium-*N*,*N*′-bis(trimethylsilyl)benzamidinate (**15**) was obtained in nearly quantitative yield by reacting calcium bis[bis(trimethylsilyl)amide]·2THF with benzonitrile in THF solution (reaction 15) [34].

$$\mathrm{Ca[N(SiMe_3)_2]_2(THF)_2 + 2PhCN \rightarrow [PhC(NSiMe_3)_2]_2Ca(THF)_2} \qquad (15)$$

15

Compound **15** crystallizes in the form of colorless blocks from THF or THF/petroleum ether. The initial step in the formation of metal benzamidinates is believed to be the substitution of a coordinated ether molecule by the nitrile. An intermediate nitrile adduct was isolated when pivalonitrile was used instead of benzonitrile (reaction 16) [34].

$$\mathrm{Ca[N(SiMe_3)_2]_2(DME)_2 + {}^tBuCN \xrightarrow[-DME]{} Ca[N(SiMe_3)_2]_2(DME)({}^tBuCN)} \qquad (16)$$

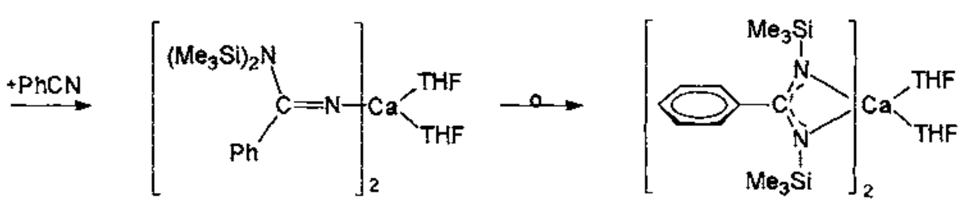
16

The homologous trimethylsilyl cyanide produced insoluble calcium cyanide on reaction with calcium bis[bis(trimethylsilyl)amide] derivatives (reaction 17) [34]. The sterically more demanding 2,4,6-trimethylbenzonitrile did not react with $\mathrm{Ca[N(SiMe_3)_2]_2(DME)_2}$ In DME solution. As a result of these studies a stepwise mechanism (reaction 18) for the formation of the calcium benzamidinate **15** was concluded [34]. The intermediate imido complex could not be detected in the case of calcium. However, a similar imido complex of tantalum was isolated and structurally characterized by Dehnicke and co-workers [35]. The reaction mechanism formulated above should be the same for the other alkaline earth metal benzamidinates.

$$\mathrm{Ca[N(SiMe_3)_2]_2 \cdot 2L + 2Me_3SiCN \rightarrow Ca(CN)_2 \cdot \mathit{n}L + 2(Me_3Si)_3N} \qquad (17)$$

L = THF, DME

$$\mathrm{Ca[N(SiMe_3)_2]_2(THF)_2 + PhCN \xrightarrow[-THF]{} [PhC(NSiMe_3)_2]_2Ca(THF)(PhCN)} \qquad (18)$$



15

The molecular structure of **16** was determined by a single-crystal X-ray analysis [34]. It showed a distorted octahedral coordination geometry around the calcium atom with the two THF ligands in trans positions and Ca—O and Ca—N bond lengths of 2.38 and 2.43 Å respectively. The C—N bond distances of 1.32 Å in the

NCN unit are characteristic of a 1,3-diazaallylic system. Short Si—N bond lengths (ca. 1.705 Å) as well as the high field shift of the ^{29}Si NMR signal (δ – 9.2 ppm) have been taken as evidence for an effective back-donation of the anionic charge from the nitrogen to the silicon atoms. Silylated benzamidinate derivatives are also accessible for strontium and barium using similar synthetic routes [36,37]. Treatment of either the THF adduct or the DME adduct of strontium bis[bis(trimethylsilyl)amide] with benzonitrile in THF solution (reaction 19) always resulted in the formation of $[PhC(NSiMe_3)_2]_2Sr(THF)_2$ (**17**) [36].

$$Sr[N(SiMe_3)_2]_2\cdot 2L + 2PhCN \xrightarrow{THF} [PhC(NSiMe_3)_2]_2Sr(THF)_2 \qquad (19)$$

$L = THF, 1/2DME$ **17**

In contrast, the composition of the barium benzamidinates **18** is determined by the coordinated solvent molecules in the starting material (reaction 20) [36]. The composition of **18a** did not change even after repeated recrystallization from a THF/pentane mixture. All benzamidinate derivatives of the heavier alkaline earth metals are colorless solids which are sensitive to hydrolysis. In the THF adduct **17** the strontium is six-coordinate with the two THF ligands arranged in trans positions. Thus the molecular structure resembles very much that of the corresponding calcium derivative **15** [36].

$$Ba[N(SiMe_3)_2]_2\cdot nL + 3PhCn \xrightarrow{THF} [PhC(NSiMe_3)_2]_2Ba\cdot L\cdot THF\cdot PhCN \qquad (20)$$

$n = 2.5(DME), 2(THF)$ **18a** $L = DME$

18b $L = THF$

The derivative chemistry of **17** was found to be quite limited. No reaction was observed with the stable phosphaalkyne $^tBuC{\equiv}P$. Treatment of **17** with diphenylacetylene in diglyme solution gave an inclusion complex of the composition $[PhC(NSiMe_3)_2]_2Sr(diglyme)\cdot PhC{\equiv}CPh$ (**19**) [36]. No further reaction was observed when **19** was heated to 170°C in diglyme or irradiated with UV light. IR and NMR data indicated the presence of a largely undisturbed diphenylacetylene molecule. Thus unlike in the organocalcium complex $(C_5Me_5)_2Ca(\eta^2\text{-}Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)$ [38] no binding interaction between the metal atom and the acetylene moiety was detected. The coordination polyhedron in the seven-coordinate strontium complex **19** can be described as a distorted antiprism [36]. In **19** the strontium benzamidinate molecules form a three-dimensional network, into which diphenylacetylene molecules are intercalated.

Most recently the molecular structure of $[PhC(NSiMe_3)_2]_2Ba(DME)(THF)$ (**18c**) was also determined by X-ray diffraction (Fig. 4) [37]. As described earlier, $[PhC(NSiMe_3)_2]_2Ba(THF)_2(PhCN)$ (**18b**) was the main product when barium bis[bis(trimethylsilyl)amide] was treated with benzonitrile in THF solution (reac-

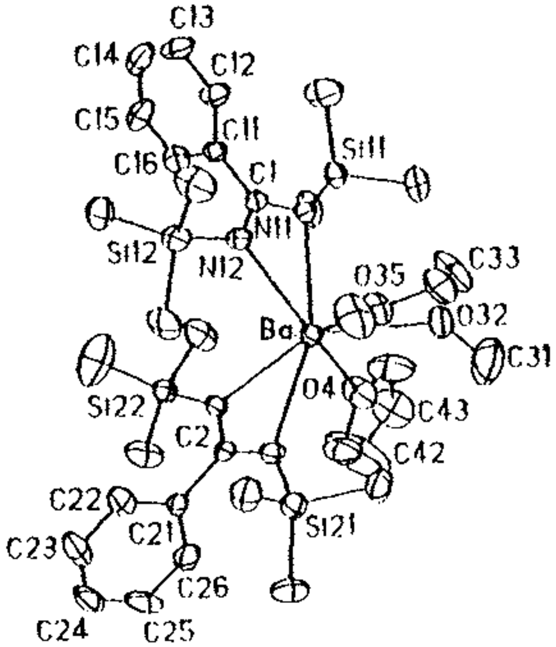


Fig. 4.

tion 21). Recrystallization of this compound from toluene/DME mainly resulted in the formation of the DME adduct **18a**. During this process, however, partial loss of benzonitrile also occurred which produced small amounts of the lesser soluble mixed solvate $[PhC(NSiMe_3)_2]_2Ba(DME)(THF)$ (**18c**) [37].

$$Ba[N(SiMe_3)_2]_2 + PhCN \xrightarrow{THF} \underset{\mathbf{18b}}{[PhC(NSiMe_3)_2]_2Ba(THF)_2(PhCN)}$$

$$\xrightarrow{\text{toluene + DME}} \underset{\mathbf{18c}}{[PhC(NSiMe_3)_2]_2Ba(DME)(THF)} \qquad (21)$$

The X-ray analysis of **18c** showed the barium atom in a distorted monocapped trigonal prismatic coordination geometry (Fig. 4). Similar to the structurally characterized metallocene derivatives of barium [39], the barium bis(benzamidinate) unit is bent with an angle of 120° between the two ligands. For example, in unsolvated $(C_5Me_5)_2Ba$ the corresponding angle is 131° [39–41]. Differences in the Ba—N bond lengths (2.73 and 2.82 Å respectively) originate from interligand repulsion of the trimethylsilyl groups and the DME ligand. Symmetrical bonding was found for the NCN heteroallylic units (C—N 1.32 Å), which indicated delocalization of the anionic charge.

Monomeric *N,N′*-bis(trimethylsilyl)benzamidinate derivatives have been described for all Group 13 elements. The trichlorides of aluminum, gallium, and indium readily react with **1a** in dichloromethane solution (reaction 22) to give the monosubstituted products **20** [42]. Similar treatment of boron trichloride with **1a**

$$\underset{\textbf{1a}}{MCl_3 + PhC(=NSiMe_3)[N(SiMe_3)_2]} \xrightarrow{CH_2Cl_2} [PhC(NSiMe_3)_2]MCl_2 + Me_3SiCl \qquad (22)$$

$$\begin{array}{l} \textbf{20a}\ M = Al \\ \textbf{20b}\ M = Ga \\ \textbf{20c}\ M = In \\ \textbf{20d}\ M = Tl \end{array}$$

produced an oily material which could not be obtained in a crystalline form. In contrast, boron tribromide was found to react with **1a** in CH_2Br_2 to give $[PhC(NSiMe_3)_2]BBr_2$ (**21**) as pale yellow crystals in 93% yield [42]. The product yields of **20a–c** were also reported to exceed 90%. All reactions of **1a** with Group 13 metal trihalides are exothermic. An interesting byproduct was isolated during the preparation of the thallium(III) benzamidinate **20d** in THF solution [43]. This compound was isolated as a white powder in 85% yield. Cooling of the concentrated mother liquid afforded pale yellow crystals of a more soluble byproduct (11% yield) which was shown to be the benzamidinium salt $[PhC(NHSiMe_3)_2]^+[PhC(NSiMe_3)_2TlCl_3]^-$ (**22**) [43]. The formation of **22** was explained according to reaction 23.

$$\underset{\textbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]} + \underset{\textbf{20d}}{[PhC(NSiMe_3)_2]TlCl_2} + 2HCl \qquad (23)$$

$$\rightarrow \underset{\textbf{22}}{[PhC(NHSiMe_3)_2]^+[PhC(NSiMe_3)_2TlCl_3]^-} + Me_3SiCl$$

The benzamidinium cation $[PhC(NHSiMe_3)_2]^+$ is formed by protonation of the fully silylated benzamidine followed by elimination of Me_3SiCl. Hydrogen chloride was believed to result from a reaction of thallium trichloride with the solvent tetrahydrofuran. This hypothesis was subsequently confirmed by carrying out a reaction of anhydrous HCl with a mixture of **1a** and preformed **20d** (molar ratio 1:1) according to reaction 23. This reaction afforded the amidinium salt **22** in 84% isolated yield [43].

Among the Group 13 benzamidinates the compounds **20a** and **22** have been structurally characterized by X-ray analyses. $[PhC(NSiMe_3)_2]AlCl_2$ (**20a**) is monomeric in the solid state [42]. With a dihedral angle of 87.8° between the two planes $AlCl_2/AlN_2C$ the compound displays an almost ideal tetrahedral geometry. The benzamidinate ligand is symmetrically bonded with an average Al—N distance of

1.882 Å. This is a normal value for Al—N single bonds in four-coordinate aluminum compounds (cf. 1.91 Å in $[PhAl(NPh)]_4$ [44]). The dihedral angle between the phenyl ring and the NCN heteroallylic unit is 74.2°, which precludes conjugation between the two π-systems. This is a common structural feature in all *N,N'*-bis(trimethylsilyl)benzamidinate derivatives.

Five-coordinate thallium was found in the salt-like compound **22** [43]. The coordination polyhedron can be described as a distorted trigonal bipyramid with one chlorine and one nitrogen atom in the axial positions. As expected the Tl—Cl(axial) distance (2.56 Å) is longer than the bonds between the thallium and the equatorial chlorine atoms (2.64 Å). All Tl—Cl bonds are longer than those found in neutral thallium chloride species such as $TlCl_3$(4-pyridinecarbonitrile-1-oxide-*O*) (*tbp*, $TlCl_{axial}$ 2.452 Å, $Tl-Cl_{eq}$ 2.403 Å) [45] or $TlCl_3(H_2O)_4$ ($Tl-Cl_{axial}$ 2.837 Å, $Tl-Cl_{eq}$ 2.395 Å) [46]. This is due to the anionic nature of compound **22**. According to the trigonal bipyramidal structure of the anion in **22**, slightly different values are found for the Tl—N bond lengths ($Tl-N_{axial}$ 2.35 Å, $Tl-N_{eq}$ 2.28 Å). It is interesting to note that five-coordinate thallium(III) compounds are exceedingly rare [47]. In the amidinium cation the nitrogen atoms and the central carbon atom all display a planar geometry which accounts for an sp^2-hybridization of the latter. With 1.29 Å and 1.33 Å the C—N bond lengths are very similar to those in the anionic part of the molecule (1.29 Å and 1.53 Å respectively). In addition, the N—C—N angle in the cation is only slightly larger (123°) than the corresponding angle in the anion (120°). Both angles are, however, significantly larger than that in the aluminum derivatives $[PhC(NSiMe_3)_2]AlCl_2$ (**20a**, N—C—N 115°) [42]. As for the anion in **22** the difference is due to the different ionic radii of the metal atoms. All structural parameters in the $[PhC(NHSiMe_3)_2]^+$ cation are very similar to those found in the ionic compound $[PhC(NHSiMe_3)_2][FeCl_4]$ (vide infra).

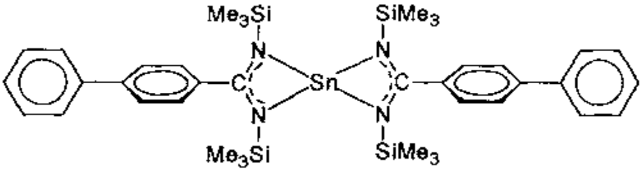
The heavier Group 14 elements have also been demonstrated to form stable complexes with *N,N'*-bis(trimethylsilyl)benzamidinate ligands [4]. Apart from the *N,N,N'*-tris(trimethylsilyl) substituted benzamidines **1** there has been only one other report on a silicon compound derived from these ligands. $[PhC(NSiMe_3)_2]SiCl_3$ (**23**) was prepared in 87% yield by reacting $SiCl_4$ with **2a** in a 1:1 molar ratio (reaction 24). No disubstituted product was observed even when **2a** was used in excess [48].

$$SiCl_4 + \underset{\textbf{2a}}{Li[PhC(NSiMe_3)_2]} \xrightarrow{Et_2O} \underset{\textbf{23}}{[PhC(NSiMe_3)_2]SiCl_3} + LiCl \qquad (24)$$

The heavier homolog tin displays a particular rich coordination chemistry with N-silylated benzamidinate ligands. Various compounds have been described for both the divalent and tetravalent oxidation states. In an early report by Dehnicke et al. it was briefly mentioned that $SnCl_2$ reacts with **1a** to give the dimeric species $[PhC(NSiMe_3)_2SnCl]_2$ (**24**) [49]. A stable, monomeric tin(II) benzamidinate **25** was obtained by reacting $SnCl_2$ with the sodium salt of the *p*-phenyl substituted benzamidinate anion **7e** in a molar ratio of 1:2 (reaction 25) [50]. The colorless

$$SnCl_2 + 2Na[p\text{-}PhC_6H_4C(NSiMe_3)_2]\cdot 1.5THF \xrightarrow[-2NaCl]{THF} \tag{25}$$

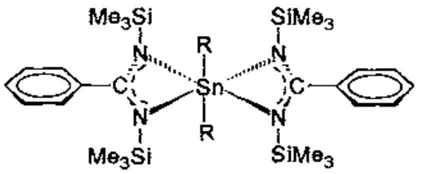
7e



25

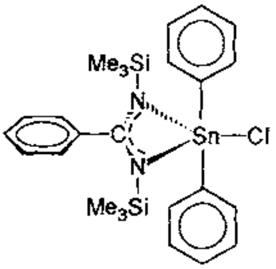
crystalline tin(II) benzamidinate **25** is soluble even in non-polar organic solvents and can be recrystallized from hexane.

Tin(IV) benzamidinates have been prepared by several methods from either $SnCl_4$, Me_2SnCl_2 or Ph_2SnCl_2 and the appropriate benzamidinate reagent. Monosubstitution at tin tetrachloride was achieved by treatment of $SnCl_4$ with one equivalent of **1a** in CH_2Cl_2 [42]. Colorless, crystalline $[PhC(NSiMe_3)_2]SnCl_3$ (**26**) was isolated in 87% yield. The spirocyclic tin(IV) benzamidinates **27** and **28** have been synthesized from the corresponding tin halides and two equivalents of $Li[PhC(NSiMe_3)_2]$ (**2a**) [48]. The sterically more demanding phenyl substituents in Ph_2SnCl_2 inhibit the formation of a similar disubstituted spirocycle. Thus treatment of Ph_2SnCl_2 with **2a** gave the pentacoordinate compound **29** as the sole product in 68% yield [48].



27 R = Cl

28 R = Me



29

An X-ray structure determination of **26** established the monomeric nature of this compound with a pentacoordinate tin atom [42]. The coordination polyhedron can be best described as a distorted tetragonal pyramid with a chlorine atom in apical position. Accordingly the Sn−Cl$_{apical}$ distance (2.321 Å) is slightly shorter than the two equatorial Sn−Cl bonds (2.344 and 2.340 Å respectively). These bond lengths are comparable with those in the trigonal bipyramidal pentachlorostannate anion $SnCl_5^-$ [51], but shorter than the Sn−Cl distances in $SnCl_4$ (average 2.28 Å) [52]. The two Sn−N bond distances to the symmetrically coordinated benzamidinate chelate (Sn−N 2.135 and 2.152 Å) correspond to typical tin–nitrogen single bonds (cf. Sn−N 2.121 and 2.159 Å in $[Sn(N_3)_6]^{2-}$ [53]). The dihedral angle between the phenyl ring and the NCN unit (77.2°) is comparable with that in the aluminum benzamidinate **20a** (74.2°) [42] and is thus sufficiently large to preclude conjugation between the two π-systems.

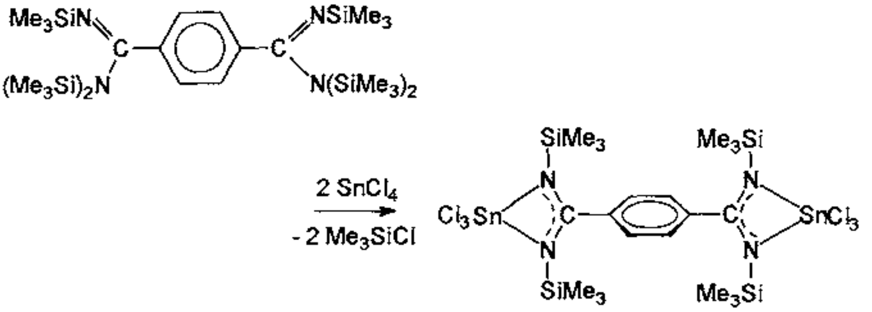
Some interesting derivative chemistry of **26** has been investigated by Dehnicke and co-workers [54,55]. Owing to the pentacoordination around tin the compound was expected to exhibit a certain degree of Lewis acidity. This was confirmed by the reaction of **26** with sodium fluoride in the presence of 15-crown-5 (reaction 26) [54]. The salt-like compound **30** was isolated in 91% yield as a white, moisture-sensitive crystalline solid. Remarkably no Cl/F exchange was observed even when NaF was used in excess. The molecular structure of **30** was determined by X-ray diffraction [54]. An Sn−F−Na bridging unit results in the formation of a tight ion pair. As in the starting material the benzamidinate ligand is symmetrically coordinated but the Sn−N bonds in **30** are slightly longer (2.17 and 2.18 Å respectively). The phenyl/NCN dihedral angle in this compound is 71.0°.

$$\underset{\mathbf{26}}{[PhC(NSiMe_3)_2]SnCl_3} + NaF + 15\text{-crown-5} \xrightarrow{MeCN} \underset{\mathbf{30}}{[Na(15\text{-crown-5})][PhC(NSiMe_3)_2SnCl_3F]} \quad (26)$$

A transformation of the silylated benzamidinate ligand was observed in the exothermic reaction of **26** with hydrogen chloride in dichloromethane solution (reaction 27). The product, benzamidinium hexachlorostannate (**31**), was obtained in nearly quantitative yield [55]. The molecular structure of **31** consists of separated benzamidinium and hexachlorostannate ions. The surrounding of the central carbon atom is exactly planar with bond angles of 120°, thus indicating sp^2-hybridization. All structural parameters of the benzamidinium cation are in good agreement with those reported for the benzamidinium salt $[PhC(NH_2)_2][cis\text{-}Re(CO)_4(CH_3CO)_2]$ [56]. Cations and anions are connected through two different sets of hydrogen bonds to give a three-dimensional network.

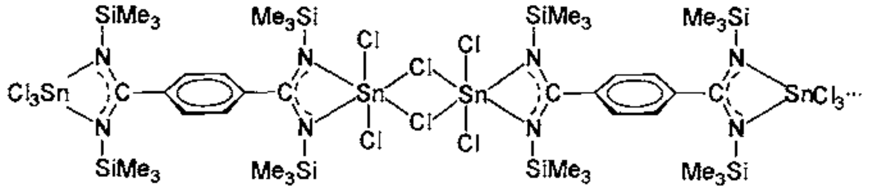
$$2\underset{\mathbf{26}}{[PhC(NSiMe_3)_2]SnCl_3} + 8HCl \xrightarrow{CH_2Cl_2} \underset{\mathbf{31}}{[PhC(NH_2)_2]_2[SnCl_6]} + SnCl_4 + 4Me_3SiCl \quad (27)$$

Perhaps the most interesting tin(IV) benzamidinate species is the dinuclear derivative **32**, which was prepared by reacting the difunctional silylated benzamidine **3** with two equivalents of tin tetrachloride (reaction 28) [57]. Compound **32** is a colorless, moisture-sensitive crystalline powder which is only marginally soluble in dichloromethane. This behavior led to the conclusion that in the solid state **32** consists of chlorine bridged polymers.



(28)

32



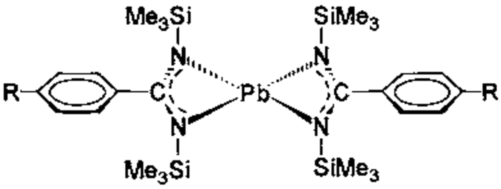
32

The intramolecular chlorine bridges are cleaved by addition of a donor ligand. Unsolvated **32** readily dissolves in acetonitrile. A bis(acetonitrile) adduct **33** can be isolated by concentrating the resulting solutions. The molecular structure of this adduct was determined by X-ray crystallography [57]. Most of the structural parameters are very similar to those of the mononuclear species $[PhC(NSiMe_3)_2]SnCl_3$ (**26**) [42]. The tin atoms are in a distorted octahedral coordination environment. The acetonitrile ligands are only losely coordinated as shown by the long Sn—N distances of 2.44 Å. Significantly shorter Sn—N distances have been reported for the acetonitrile adducts *cis*-$SnCl_4(MeCN)$ (2.33 and 2.34 Å) [58] and $[S_5N_5]^+[SnCl_5(MeCN)]^-$ (2.29 Å) [59]. In good agreement with the weakness of the Sn—N bonds in **33** is the observation that the coordinated acetonitrile is easily given off when the compound is dried under vacuum or in a current of nitrogen. In both cases the unsolvated polymer **32** is formed again. It is interesting to note that the mononuclear tin(IV) benzamidinate **26** shows no tendency to associate and does not add acetonitrile [42]. A remarkable difference between the two compounds **26** and **32** was also found for their reactivity towards sodium fluoride. Treatment of **26** with sodium fluoride in the presence of 15-crown-5 produced the anionic tin(IV) benzamidinate $[Na(15\text{-crown-}5)][PhC(NSiMe_3)_2SnCl_3F]$ (**30**, vide supra). Similar treatment of **32** with excess NaF in acetonitrile solution in the presence of benzo-15-crown-5 resulted in complete displacement of the $SnCl_3$ units from the chelating benzamidinate ligands and formation of $[Na(benzo\text{-}15\text{-crown-}5)]_2[SnCl_6]$ (78% yield) [57].

The first lead(II) derivative with silylated benzamidinate ligands was obtained by Dehnicke during an attempt to prepare a lead(IV) species containing the $[PhC(NSiMe_3)_2]^-$ ligand [4]. Compound **34a** was the only lead-containing product formed in the redox reaction (reaction 29). Recently a more straightforward preparation of silylated benzamidinates of lead(II) was reported. The complexes **34b** and **34c** were isolated by reacting $PbCl_2$ with the corresponding sodium salts (1:2 molar ratio) in THF solution [50].

$$Pb(O_2CMe)_4 + \underset{\textbf{1a}}{2PhC(=NSiMe_3)[N(SiMe_3)_2]}$$

$$\rightarrow \underset{\textbf{34a}}{[PhC(NSiMe_3)_2]_2Pb} + 2MeC(O)OSiMe_3 + (MeCO)_2 + \tfrac{1}{2}O_2 \qquad (29)$$



34a R = H

34b R = Me

34c R = CF_3

All three lead(II) benzamidinates **34** are soluble in non-polar organic solvents such as toluene or hexane. Well formed colorless crystals can be obtained by recrystallization from hexane. It was not possible to isolate a lead(II) analog of compound **25**. $PbCl_2$ did not react with $Na[p\text{-}PhC_6H_4C(NSiMe_3)_2]\cdot 1.5THF$ even under inforced reaction conditions (prolonged reflux in THF solution). The molecular structure of **34c** was determined by X-ray diffraction (Fig. 5) [50].

Most reactions of the N-silylated benzamidines **1** with organophosphorus halides are discussed in the section on inorganic heterocycles (vide infra). Phosphinoamidines of the type **35** have been reported by several groups [60–63]. These compounds have been prepared by reacting lithium *N,N'*-bis(trimethylsilyl)benzamidinates **2** (generated in situ from $LiN(SiMe_3)_2$ and RC_6H_4CN)

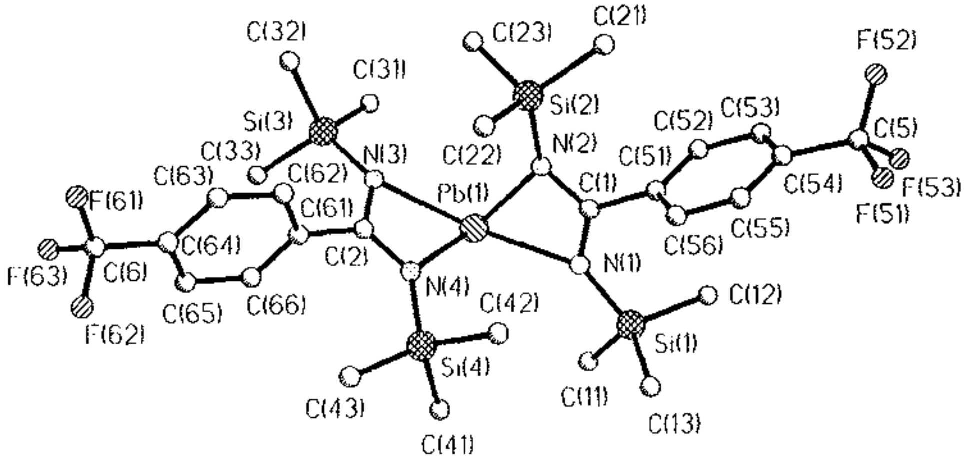


Fig. 5.

with chlorodiphenylphosphine (reaction 30). Two structural isomers (**A** and **B**) are possible for the phosphinoamidines **35** but none of these compounds have been structurally characterized.

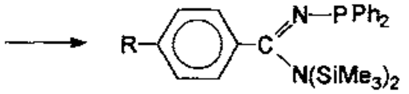
$Li[RC_6H_4C(NSiMe_3)_2] + Ph_2PCl$ (30)

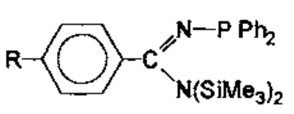
2a $R = H$ **35a** $R = H$

2b $R = Me$ **35b** $R = Me$

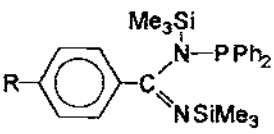
2d $R = CF_3$ **35c** $R = CF_3$

2e $R = Me_2N$ **35d** $R = Me_2N$





A



B

Apparently no arsenic derivatives of N-silylated benzamidinate anions have been mentioned in the literature and information on related antimony and bismuth compounds is scarce. $[PhC(NSiMe_3)_2]SbCl_2$ was obtained on treatment of antimony trichloride with **1a** in dichloromethane at room temperature (reaction 31) [7]. Large colorless crystals were isolated in 92% yield. The X-ray crystal structure analysis of **36** shows a monomeric molecule in which the antimony atom is coordinated by two chlorine atoms and two nitrogens of the chelating benzamidinate ligands [7]. Under the assumption that the lone pair occupies an equatorial position, the coordination geometry can be described as distorted trigonal bipyramidal. This is in agreement with large differences in the Sb—Cl and Sb—N bond lengths. In both cases one ligand atom is in an equatorial position and the other one is in the axial position.

$$\underset{\mathbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]} + SbCl_3 \rightarrow \underset{\mathbf{36}}{[PhC(NSiMe_3)_2]SbCl_2} + Me_3SiCl \qquad (31)$$

A nearly quantitative yield of a disubstitution product was obtained when antimony trichloride was reacted with two equivalents of **1a** in CH_2Cl_2 solution (reaction 32) [64]. Cooling of the saturated solution produced large pale yellow, moisture-sensitive crystals. X-ray crystal structure determinations of **37** were performed at 20°C and at −93°C [64]. In this molecule two chelating $[PhC(NSiMe_3)_2]^-$ ligands are coordinated to the antimony atom. The antimony is bonded to four nitrogens and one chlorine atom. Together with a stereochemically strongly active lone pair of electrons they form an irregular coordination polyhedron around the antimony atom. In both chelating ligands the orientation of the phenyl rings is almost perpendicular with respect to the NCN unit. The compound $[PhC(NSiMe_3)_2]SbCl_4$ (**38**) (from $SbCl_5$ and **1a** in CH_2Cl_2) was briefly mentioned in a preliminary communication, but so far no further details have been published [49].

$$\underset{\mathbf{1a}}{2PhC(=NSiMe_3)[N(SiMe_3)_2]} + SbCl_3 \rightarrow \underset{\mathbf{37}}{[PhC(NSiMe_3)_2]_2SbCl_2} + Me_3SiCl \qquad (32)$$

Among the Group 15 elements only a bismuth(3+) ion is large enough to accomodate three chelating benzamidinate ligands in its coordination sphere. So far only one homoleptic bismuth tris(benzamidinate) was sufficiently stable to be isolated [65]. Treatment of $BiCl_3$ with three equivalents of **7a** led to the formation of a red crystalline compound formulated as $[PhC(NSiMe_3)_2]_3Bi$ (**39a**) in 32% yield (reaction 33). This material was only incompletely characterized (^1H NMR) owing to its pronounced sensitivity to light combined with thermolability. Significantly more stable is the *p*-phenyl substituted derivative **39b**, which is accessible from $BiCl_3$ and **7e** [65]. Compound **39b** crystallizes from hexane as bright red, rod-like crystals, which are stable under inert atmosphere. In solution, this derivative too is somewhat light sensitive. Unfortunately, crystal structure determination was hampered by severe twinning and disorder problems. Bismuth is the only main group element for which a homoleptic tris(benzamidinate) complex has been described. A monosubstituted bismuth derivative, $[PhC(NSiMe_3)_2]BiCl_2$ (**40**) was briefly mentioned in a preliminary communication by Dehnicke et al. [49].

$$\mathrm{BiCl_3 + 3Na[RC_6H_4C(NSiMe_3)_2]\cdot L} \tag{33}$$

7a $R = H, L = 0.5Et_2O$

7e $R = Ph, L = 1.5THF$

$$\longrightarrow \mathrm{[RC_6H_4C(NSiMe_3)_2]_3Bi}$$

39a $R = H$

39b $R = Ph$

Various inorganic heterocycles have been synthesized by reactions of sulfur and selenium halides with the silylated benzamidines **1** or the corresponding lithium salts **2**. Reactions of *N,N,N'*-tris(trimethylsilyl)benzamidines **1** with organosulfur chlorides have been investigated by Chivers and co-workers [66]. The metathetical products $PhC(=NSR)[N(SiMe_3)_2]$ (**41**) are obtained when the reactions are carried out in a 1:1 molar ratio in dichloromethane solution (reaction 34). In two cases stable trisubstituted products have been isolated (reaction 35).

$$\mathrm{PhC(=NSiMe_3)[N(SiMe_3)_2] + RSCl \xrightarrow[-Me_3SiCl]{CH_2Cl_2} PhC(=NSR)[N(SiMe_3)_2]} \tag{34}$$

1a

41a $R = CCl_3$

41b $R = Ph$

41c $R = 2,4\text{-}C_6H_3(NO_2)_2$

$$\mathrm{PhC(=NSiMe_3)[N(SiMe_3)_2] + RSCl \xrightarrow[-Me_3SiCl]{CH_2Cl_2} PhC(=NSR)[N(SR)_2]} \tag{35}$$

1a

42a $R = CCl_3$

42b $R = 2,4\text{-}C_6H_3(NO_2)_2$

The compounds **42** were isolated in excellent yields as air stable, colorless (**42a**) or orange (**42b**) crystals. **42b** was found to decompose explosively at 168°C. The molecular structure of **42a** was determined by X-ray crystallography [66]. In many respects the molecular structure of **42a** resembles that of the N-silylated benzamidine **1a** (cf. Fig. 1) [7]. The only significant difference between the two structures was found for the bond angle at the doubly bonded nitrogen atom, which has a value of $124.1(3)^\circ$ in **42a** compared with $136.6(2)^\circ$ in **1a**. The larger angle in the latter case was attributed to steric hindrance, which is less severe in **42a**. By contrast, the compound $PhC(=NSPh)[N(SPh)_2]$ is thermally unstable and decomposes to give the intensely colored diazene derivative *trans*-PhSN(Ph)CN=NC(Ph)NSPh (**43a**) [66,67]. Similar products were obtained from reactions of **1b** and **1f** with PhSCl in a 1:3 molar ratio (reaction 36). When the reaction of **1a** with PhSCl (molar ratio

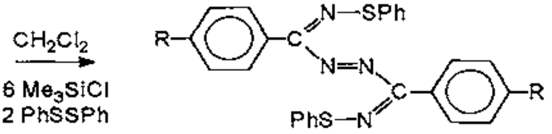
1:3) was carried out in the absence of solvent, the yield of **43a** was reported to exceed 90% [66]. The unusual diazenes **43** were isolated as dark purple solids. EPR spectroscopic investigations of the reaction mixtures have provided evidence for a radical mechanism of the formation of **43**.

$2RC_6H_4C(=NSiMe_3)[N(SiMe_3)_2] + 6PhSCl$ (36)

1a R = H **43a** R = H

1b R = Me **43b** R = Me

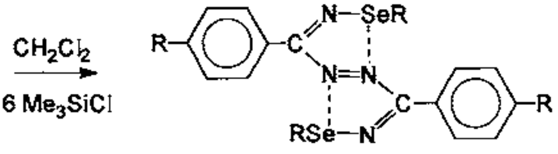
1f R = CF_3 **43c** R = CF_3



Related selenium-containing azo dyes (**44**) have also been prepared by Chivers and co-workers [66,67]. Dark blue *trans*-PhSeN(Ph)CN=NC(Ph)NSePh (**44b**) was prepared in 55% yield by the reaction of **1a** with three equivalents of PhSeCl (cf. reaction 36). An alternative preparation involves treatment of **1a** with organoselenium trichlorides (reaction 37). The molecular structure of dark red **44a** was confirmed by X-ray diffraction [67]. The molecule contains a nearly planar SeNCNNCNSe chain in which the C(Ph)NSeMe substituents are bonded in a trans fashion to the central azo unit. There are short intramolecular contacts (ca. 2.65 Å) between the selenium atom and one of the nitrogen atoms of the N=N group. (The sum of the van der Waals radii for Se and N is 3.5 Å [68].) Such "hypervalence" at the selenium atoms induces a *syn* configuration with respect to the C=N bonds.

$2PhC(=NSiMe_3)[N(SiMe_3)_2] + 2RSeCl_3$ (37)

1a



44a R = Me

44b R = Ph

The compounds $[PhC(NSiMe_3)_2]SeCl_3$ (**45**) and $[PhC(NSiMe_3)_2]SeOCl$ (**46**) have been prepared by Dehnicke et al. from **1a** and $SeCl_4$ or $SeOCl_2$ respectively. These two selenium(IV) derivatives are believed to contain regular chelating benzamidinate ligands [49]. The only structurally characterized Group 16 benzamidinate is $[PhC(NSiMe_3)_2]TeCl_3$ (**47**), which was obtained in a straightforward manner by treatment of $TeCl_4$ with one equivalent of **1a** (reaction 38) [69]. The IR spectrum of **47** shows the typical CN_2 band of the benzamidinate chelate at 1510 cm^{-1}. According to the X-ray crystal structure determination **47** forms monomeric molecules in the solid state [69]. The coordination of three chlorine atoms and the two nitrogen atoms of the benzamidinate ligands result in a Ψ-octahedral coordination geometry at tellurium. The small bite angle of the ligand and the presence of a stereochemically active lone pair cause a severe distortion of the octahedral geometry. The ease of the formation of compound **47** is remarkable in view of the notorious instability of other tellurium–nitrogen derivatives [70].

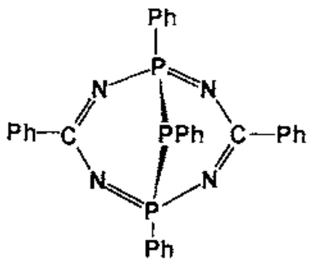
$$\underset{\mathbf{1a}}{\mathrm{PhC({=}NSiMe_3)[N(SiMe_3)_2]}} + \mathrm{TeCl_4} \rightarrow \underset{\mathbf{47}}{\mathrm{[PhC(NSiMe_3)_2]TeCl_3}} + \mathrm{Me_3SiCl} \qquad (38)$$

4. INORGANIC HETEROCYCLES DERIVED FROM *N,N'*-BIS(TRIMETHYLSILYL)BENZAMIDINATES AND RELATED LIGANDS

As mentioned in the previous section, a number of reactions of main group element halides with **1** or **2** result in the formation of novel inorganic heterocycles. Ring formation is dominant especially in the case of phosphorus, sulfur and selenium halides. In addition, several new building blocks for inorganic heterocycles have been prepared from the silylated benzamidinate derivatives **1** and **2** and organophosphorus halides. These starting materials and their derivative chemistry are also discussed in this section.

In 1988 Roesky et al. described the reaction of **1a** with $PhPCl_2$. When carried out in a molar ratio of 2:3 this reaction gave the bicyclic ring system **48** (reaction 39) [71]. According to the X-ray structure analysis, **48** contains an unusual P(V)—P(III)—P(V) bridging unit.

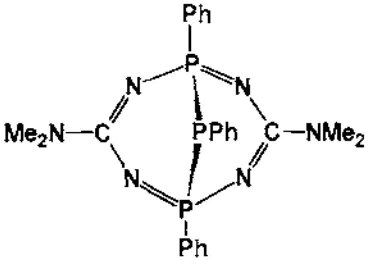
$$2\underset{\mathbf{1a}}{\mathrm{PhC({=}NSiMe_3)[N(SiMe_3)_2]}} + 3\mathrm{PhPCl_2} \xrightarrow[-6\mathrm{Me_3SiCl}]{} \qquad (39)$$



48

Another derivative containing the same bicyclic ring system was obtained when dimethylguanidinium chloride was used instead of **1a** (6% yield) (reaction 40) [71]. As in **48** the $^{31}P\{^1H\}$ NMR spectrum of **49** shows an A_2B spin system with an AB coupling constant of 211.0 Hz. A different product was isolated when Me_2NCN was first treated with $LiN(SiMe_3)_2$ and subsequently reacted with $PhPCl_2$ (1:1.5) in CH_2Cl_2 at −78°C. In this reaction sequence the lithium amidinate $Li[Me_2NC(NSiMe_3)_2]$ can be formulated as an intermediate. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a multitude of signals. Recrystallization of the crude product from CH_2Cl_2/hexane gave colorless crystals of **50** in 10% yield [71]. In **50** two six-membered ring systems are connected through a P(V)−P(III)−P(III)−P(V) chain. In contrast, no clear results have been obtained when **1a** was treated with Me_2NPCl_2 or Et_2NPCl_2.

$$2[Me_2NC(NH_2)_2]Cl + 3PhPCl_2 + 8NEt_3 \xrightarrow[8[Et_3NH]Cl]{} \qquad (40)$$



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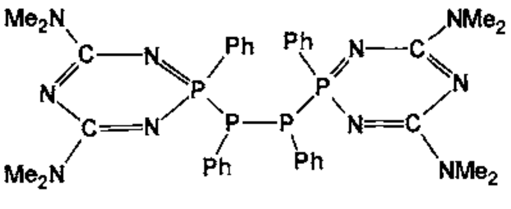
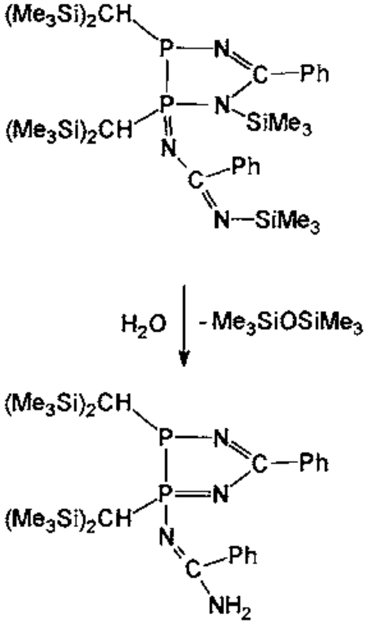


50

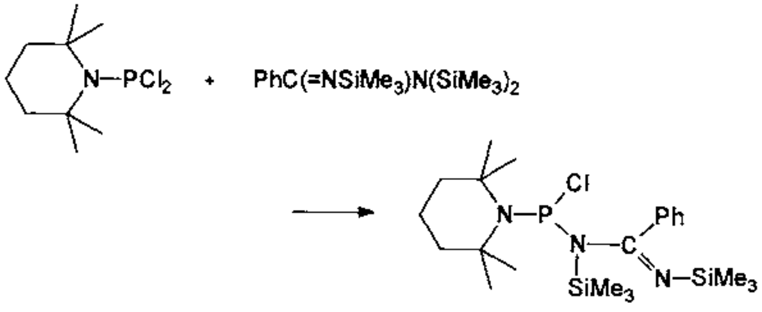
Yet another phosphorus-containing ring system was isolated when **1a** was reacted with $(Me_3Si)_2CHPCl_2$ (reaction 41) [72]. The unexpected formation of a 1,4-diaza-$2\sigma^3\lambda^3$,$3\sigma^4\lambda^5$-diphospholene derivative was clearly established by the X-ray crystal structure determination of **51** [72]. A detailed reaction mechanism has been proposed for the formation of **51** involving several acyclic and cyclic intermediates. However, none of these transient linear or cyclic species have been isolated nor have they been detected by spectroscopic methods. Especially the final step, i.e. the elimination of two silyl groups, and the subsequent rearrangement remain unclear. The addition of tetramethylpiperidino dichlorophosphine to **1a** quantitatively produced the stable phosphinoamidine **52** (reaction 42). A similar compound is believed to be the initial reaction product in the formation of **51** [72]. These results underline the dramatic effect of the substituents at phosphorus on the constitution of the reaction products.

$$2PhC(=NSiMe_3)[N(SiMe_3)_2] + 2(Me_3Si)_2CHPCl_2 \xrightarrow[-2Me_3SiCl]{} \qquad (41)$$

1a



51



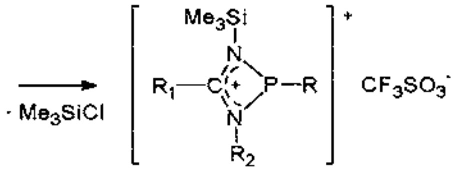
52 (42)

Several four- and five-membered heterocyclic ring systems have also been prepared from silylated benzamidines and organophosphorus halides. The first

1,3-diaza-2-phosphetine cations have been synthesized by Majoral and co-workers using reactions 43 and 44 [61]. In the first step chlorophosphenium ions are generated in situ by adding (trimethylsilyl)trifluoromethanesulfonate to amino-substituted dichlorophosphines. Subsequently the resulting chlorophosphenium ions are treated with N-silylated benzamidines to give the cationic 1,3-diaza-2-phosphetine derivatives as moisture-sensitive yellow crystals. The constitution of the products **53** was substantiated in particular by the position of the signal and the magnitude of the coupling constant for the ring carbon atom in the ^{13}C NMR spectra (δ 173.8–179.5 ppm, $^2J_{CP} = 15–21$ Hz). In addition, the ^{31}P chemical shifts (δ 105.9–112.3 ppm) are in good agreement with a λ^3-phosphorus atom. The IR spectra of **48** showed characteristic C=N and P—N vibrational frequencies at 1640–1665 and 890–910 cm^{-1} respectively. According to an X-ray diffraction study of **53a** the four-membered ring is planar [61]. The two C—N bond lengths within the ring are equal (1.35(1) and 1.33(1) Å) and significantly shorter than a normal C—N single bond (C—N ≈ 1.50 Å, cf. C=N ≈ 1.25 Å). These results indicate that the unsaturation in the cyclic cations is delocalized along the N—C--N fragment. A result of the delocalization is the opening of the N—C—N angle (106.8°). However, the intracyclic N—P—N angle (73.2°) is the smallest one found in a four-membered phosphorus heterocycle.

$$RPCl_2 + CF_3SO_3SiMe_3 \rightarrow [RP(Cl)^+ CF_3SO_3^-] \qquad (43)$$

$$[RP(Cl)^+ CF_3SO_3^-] + R_1\text{-}C(=NSiMe_3)[N(R_2)SiMe_3)] \qquad (44)$$



53a R = ^{i}Pr$_2$N, R$_1$ = Ph, R$_2$ = SiMe$_3$

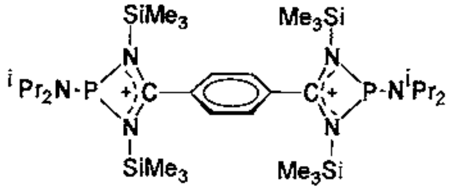
53b R = ^{i}Pr$_2$N, R$_1$ = p-MeC$_6$H$_4$, R$_2$ = Me$_3$Si

53c R = Et$_2$N, R$_1$ = Ph, R$_2$ = SiMe$_3$

53d R = ^{i}Pr$_2$N, R$_1$ = Ph, R$_2$ = ^{t}Bu

53e R = tetramethylpiperidinyl, R$_1$ = p-MeC$_6$H$_4$, R$_2$ = Me$_3$Si

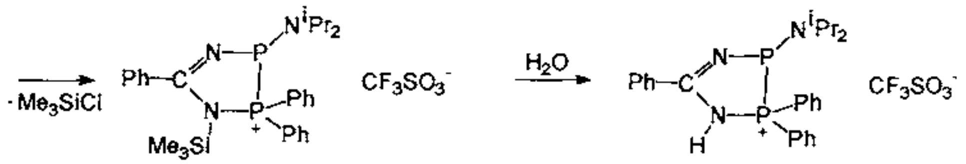
Using the same synthetic approach with the difunctional benzamidine derivative **3** as starting material a dicationic species (**54**) was prepared in 70% yield [61]. The same research group also reported the synthesis of a related cationic five-membered ring system. In this case a phosphinoamidine (**35a**) was used as a precursor (reaction 45). Phosphinoamidine **35a** was prepared by reacting **1a** with chlorodiphenylphosphine (cf. reaction 30) [61]. The cationic five-membered heterocycle **55** was



54

isolated as a mixture of two isomers. Controlled hydrolysis of **55** led to the N−H derivative **56** [61].

$$[{}^{i}\mathrm{Pr_2NP(Cl)^+CF_3SO_3^-}] + \underset{\mathbf{35a}}{\mathrm{PhC({=}NSiMe_3)[N(PPh_2)SiMe_3]}} \qquad (45)$$



55 **56**

The formation of six- and eight-membered carbon–nitrogen–phosphorus heterocycles from silylated benzamidine derivatives (**1** or **2**) has been reported by Chivers and co-workers [62]. Substituted, 1,1,5,5-tetraphenyl-3,7-diaryl-1,5-diphosphatetrazocines (**57**) are formed when the fully silylated benzamidines **1** are treated with Ph_2PCl_3 (reaction 46). The yields of **57** were generally low (less than 30%). An alternative preparation of **57a** involves the reaction of $Li[PhC(NSiMe_3)_2]$ (**2a**) with Ph_2PCl_3 (molar ratio 1:1). In this case a 31% yield of **57a** was obtained, but the six-membered heterocycle $Ph_4P_2N_3CPh$ (**58**) was formed as a byproduct. This six-membered ring was also isolated in low yield when the phosphinoamidine **35a** was treated with two molar equivalents of PhSeCl. The only selenium-containing product from this reaction was PhSeSePh [62]. The molecular structure of **57a** was determined by X-ray methods [62]. The molecule consists of an eight-membered ring in a distorted boat conformation with the phosphorus atoms out of and on the same side of the plane. The carbon atoms are located on the other side of the best plane defined by the nitrogen atoms. One of the nitrogen atoms also deviates significantly from that best plane. The average P−N and C−N bond lengths are ca. 1.60 and 1.41 Å respectively.

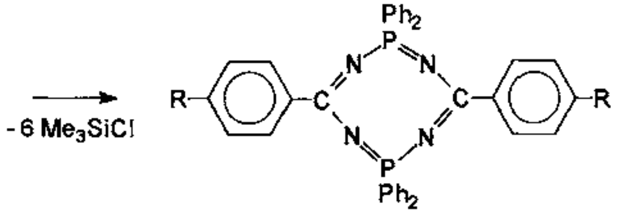
Amidinophosphazenes, an interesting class of precursors for metallacycles, were developed by Roesky and co-workers [60,73–75]. These compounds have been synthesized by reacting lithium benzamidinates **2** with chlorodiphenylphosphine.

$$2RC_6H_4C(=NSiMe_3)[N(SiMe_3)_2] + 2Ph_2PCl_3 \qquad (46)$$

1a R = H

1b R = Me

1f R = CF_3

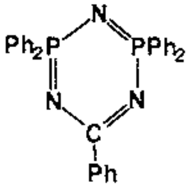


57a R = H

57b R = Me

57c R = CF_3

The resulting phosphinoamidines **35** were treated in situ with trimethylsilyl azide to give the Staudinger-type reaction products **59** (reaction 47). In all four cases the NMR data (^1H, ^{19}F, ^{29}Si, ^{31}P) of **53** showed the presence of two structural isomers **A** and **B** [74]. For **59c** and **59d** it was possible to obtain crystals of pure isomers of type **A**. These two compounds were stucturally characterized by X-ray diffraction [74]. Bond lengths and angles in both derivatives are very similar. The influence of the substituents in the para position of the phenyl rings was found to be negligible. Amidinophosphazenes of the type **59** have been shown to be useful precursors for inorganic ring systems (vide infra).



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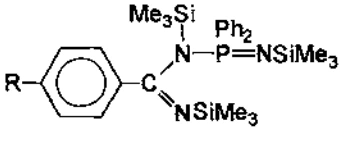
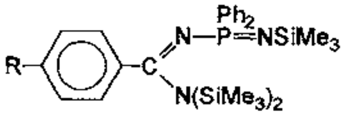
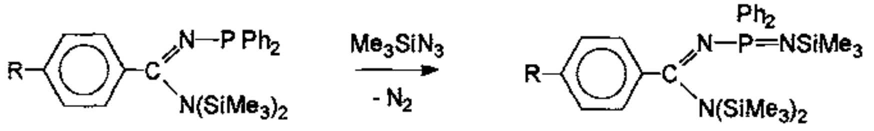


A



B



(47)

35a R = H **59a** R = H

35b R = Me **59b** R = Me

35c R = CF_3 **59c** R = CF_3

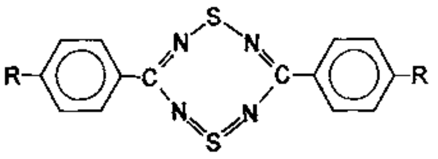
35d R = Me_2N **59d** R = Me_2N

Reactions of N-silylated benzamidine derivatives with sulfur or selenium halides often lead to the formation of various heterocyclic systems. A typical example is the preparation of 1λ^2,5,2,4,6,8-dithiatetrazocines from **1** or **2** and sulfur dichloride [76]. The parent 3,7-diphenyl-dithiatetrazocine (**60a**) has been obtained from SCl_2 and either **1a** or **2a** (reaction 48). Derivatives containing substituents in the para position of the phenyl rings are conveniently prepared from sulfur dichloride and lithium *N,N'*-bis(trimethylsilyl)benzamidinates (**2**) (reaction 49).

$$2RC_6H_4C(NSiMe_3)[N(SiMe_3)_2] + 3SCl_2 \xrightarrow[\substack{-6Me_3SiCl \\ -S}]{} \qquad (48)$$

1a R = H

1b R = Me



60a R = H

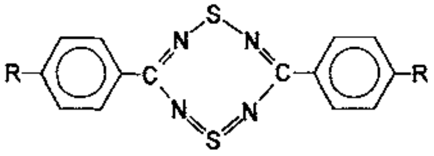
60b R = Me

The eight-membered $C_2S_2N_4$ ring system has been known since 1981. The diphenyl derivative **60a** was first prepared by Woodward and co-workers by reacting benzamidine with sulfur dichloride in the presence of DBU [77]. Several other alkyl and aryl substituted derivatives, with similar properties and structures, were prepared analogously. This method gave low yields (7%) of dithiatetrazocine **60a**, thus the use of silylated benzamidines as precursors represents a significant improvement of the synthetic procedure (reaction 48). The molecular structure of **60a** was also reported by Woodward and co-workers in 1981 [77]. The molecule contains a

$$2Li[RC_6H_4C(NSiMe_3)_2] + 3SCl_2 \xrightarrow[-4Me_3SiCl \atop -S]{-2LiCl} \qquad (49)$$

2d $R = CF_3$

2f $R = NO_2$



60c $R = CF_3$

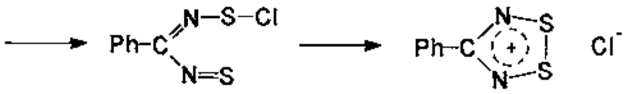
60d $R = NO_2$

planar eight-membered $C_2S_2N_4$ ring. This 10π-electron system is thus comparable with the isoelectronic $S_4N_4^{2+}$ cation. The mass spectra of all four derivatives **60** show the molecular ions. Treatment of **60a** with $AgAsF_6$ in liquid SO_2 leads to $[PhCN_2S_2]^+[AsF_6]^-$ and $3[PhCN_2S_2]^+2[AsF_6]^-Cl^-$ [76].

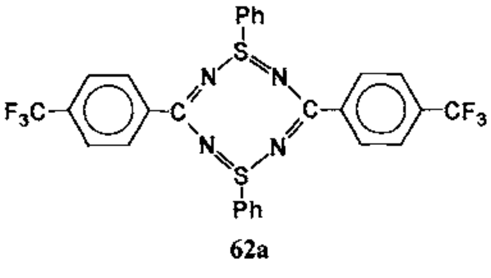
A detailed reinvestigation of the formation of dithiatetrazocines was also published by Amin and Rees [78]. In this study the reaction of **1a** with SCl_2 was shown to give 4-phenyl-1,2,3,5-dithiadiazolium chloride (**61**) as the main product (60%) (reaction 50). In the course of this reaction the silylated benzamidine **1a** is possibly converted into the dithiadiazolium salt via a linear intermediate, which can cyclize and ionize to form the 6π aromatic cation.

$$PhC(=NSiMe_3)[N(SiMe_3)_2] + SCl_2 \qquad (50)$$

A related eight-membered carbon–sulfur–nitrogen ring system was recently described by Chivers and co-workers [66]. Low yields of **62a** were obtained as a by-product in the preparation of **43c** (cf. reaction 36). The other two examples of



61



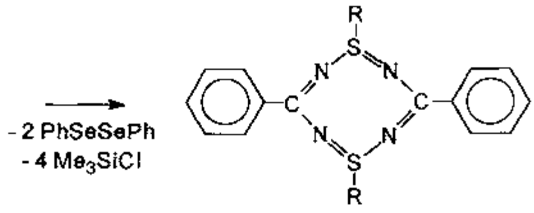
62a

the eight-membered ring system **62** were produced by the reactions of **41a** or **41c** with PhSeCl in a 1:2 molar ratio (reaction 51). The heterocycles **62a–62c** were identified on the basis of their analytical data and molecular weight determinations by vapor-phase osmometry and by mass spectrometry.

$$2PhC(=NSR)[N(SiMe_3)_2] + 4PhSeCl \tag{51}$$

41a $R = CCl_3$

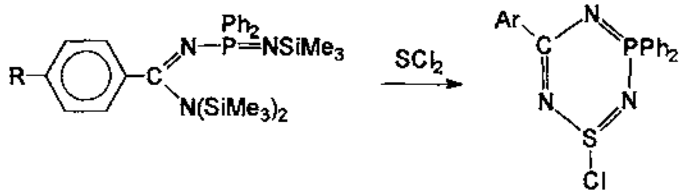
41c $R = 2,4\text{-}C_6H_3(NO_2)_2$



62b $R = CCl_3$

62c $R = 2,4\text{-}C_6H_3(NO_2)_2$

Two substituted derivatives of the 1-chloro-1,3,2,4,6-thiaphosphatriazine ring system **63** have been prepared by Oakley and co-workers [75]. The compounds **63a** and **63b** were synthesized by reacting amidinophosphazenes **59** with sulfur dichloride (reaction 52). Both reactions proceed in high (greater than 80%) yields.



(52)

59a R = H

59b R = Me

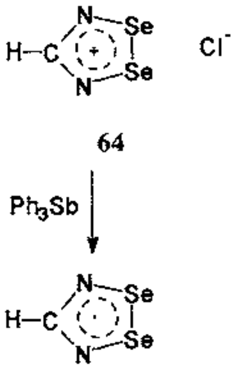
63a Ar = Ph

63b Ar = *p*-Tolyl

A number of interesting selenium–nitrogen heterocycles have been prepared from selenium chlorides and silylated amidines. Interest in the design of molecular conductors based on neutral π-radicals has motivated the investigation of heterocyclic thiazyl and selenazyl radicals, especially derivatives of 1,2,3,5-dithiadiazolyl and 1,2,3,5-diselenadiazolyl [79,80]. These, in turn, are favorably prepared in two steps starting with silylated amidines. Recently the parent 1,2,3,5-diselenadiazolyl,

$[HCN_2Se_2]\cdot$ (**65**) has become available through a novel synthetic route [12]. First, *N,N,N′*-tris(trimethylsilyl)formamidine (**6**) was prepared according to reaction 6. Addition of **6** to selenium dichloride (prepared in situ from Se and $SeCl_4$) afforded the diselenadiazolium cation **64** as a reddish-brown power in virtually quantitative yield (reaction 53). Reduction of the crude salt **64** with triphenyl antimony in acetonitrile gave 1,2,3,5-diselenadiazolyl (**65**), which could be purified through sublimation at 50°C and 10^{-3} Torr as lustrous gray-black needles.

$$\underset{\textbf{6}}{HC(=NSiMe_3)[N(SiMe_3)_2]} + 2SeCl_2 \xrightarrow[-3Me_3SiCl]{} \qquad (53)$$

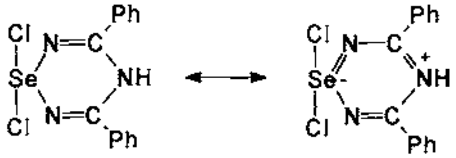


64

65

The molecular structure of **65** consists of antiparallel arrays of cofacial dimers $[HCN_2Se_2]_2$. In the solid state dimeric $[HCN_2Se_2]_2$ is diamagnetic. The single-crystal conductivity of **65** is 7×10^{-6} S cm^{-1}, a value which is at least three orders of magnitude higher than those found in other monofunctional selenium-based radical dimers [81]. In solution (CH_2Cl_2, 22°C) the EPR spectrum of the radical exhibits a featureless singlet at $g = 2.041$ [12].

A six-membered selenium-containing heterocycle was prepared by Dehnicke et al. as a by-product in the reaction of Se_2Cl_2 with **1a** in CH_2Cl_2 solution (reaction 54). This reaction is somewhat complicated and results in the formation of red selenium and several unidentified products. Only a small amount of a crystalline material was isolated, which was subsequently shown to be the selenatriazine derivative **66**. This is a redox reaction in which selenium(II) is oxidized to selenium(IV). The origin of the proton at the nitrogen atom of the heterocycle remains unclear, but it is most probably due to partial hydrolysis. The bonding in **66** can be described by two resonance structures **A** and **B**. According to the X-ray crystal structure determination the molecule consists of a slightly puckered six-membered



A **B**

ring [82].

$$\mathrm{PhC({=}NSiMe_3)[N(SiMe_3)_2]} + \mathrm{Se_2Cl_2}$$

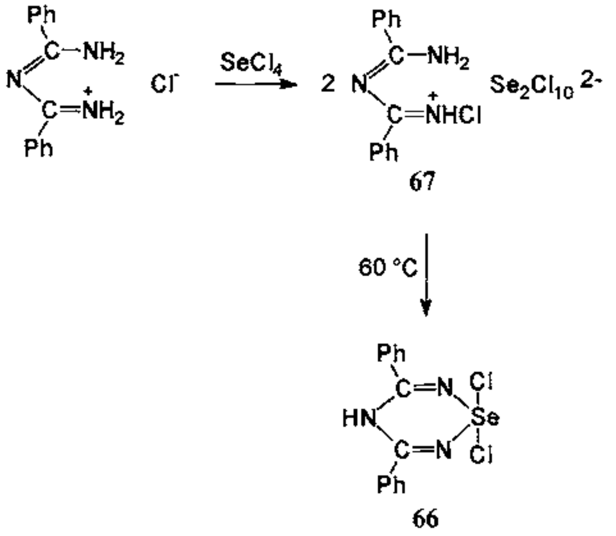
1a

$$\xrightarrow{\mathrm{CH_2Cl_2}} \mathrm{Cl_2Se(HNC_2N_2Ph_2)} + \mathrm{Me_3SiCl} + \mathrm{Se_8} + \ldots \qquad (54)$$

66

The Se—N bond lengths (1.815(2) and 1.822(2) Å) indicate a significant degree of π-bonding. Thus the participation of resonance form **B** in the bonding is not negligible. In the solid state two $\mathrm{Cl_2Se(NHC_2N_2Ph_2)}$ units are associated through weak interactions between chlorine atoms to give centrosymmetric dimers. The same molecular structure was reported earlier by Oakley and co-workers [83,84]. In that study, **66** was prepared by the reaction of $\mathrm{SeCl_4}$ and $\mathrm{H_2NC(Ph)NC(Ph)NH_2^+Cl^-}$ followed by recrystallization from acetonitrile [83]. The structural parameters and the boat-like conformation of the $\mathrm{C_2N_3Se}$ ring are similar to those found in related $\mathrm{C_2N_3S}$ ring systems. The preparation of **66** is in fact a two-step process. In the first step $\mathrm{SeCl_4}$ (prepared in situ from elemental selenium and $\mathrm{Cl_2}$) reacts with *N*-benzimidoylbenzamidine hydrochloride to give $\mathrm{[PhC(NH_2)C(Ph)NHCl]_2^+}$-$\mathrm{[Se_2Cl_{10}]^{2-}}$ (**67**) (reaction 55). When solid **67** was heated at 60°C (0.01 Torr) for 24 h it decomposed to **66** [83].

A novel six-membered selenium-containing heterocycle was prepared independently by Roesky et al. and Oakley and co-workers from amidinophosphazene **59a** and $\mathrm{SeCl_4}$ in $\mathrm{CH_2Cl_2}$ (reaction 56) [73,75]. The resulting red solution yielded a red solid, which was soluble in acetonitrile. Cooling of the acetonitrile solution to -30°C gave yellow crystals of 1-chloro-3,3,5-triphenyl-1λ^4,2,4,6,3λ^5-selenatriazaphosphorine (**68**). Under the conditions in a mass spectrometer, **68** readily loses chlorine to give the fragment ion $\mathrm{M-Cl^+}$ with 85% relative intensity ($\mathrm{M^+}$ 2%). Interestingly the peak with the highest intensity corresponds to the fragment $\mathrm{Ph{-}PN^+}$. The X-ray crystal structure determination shows a planar six-membered ring [73]. The phenyl ring at carbon is nearly coplanar with the heterocycle, whereas the chlorine substituent is in a perpendicular position with respect to the ring (Cl—Se—N(1) 98.3(1)° and Cl—Se—N(2) 104.0(1)°). Comparable angles are found in $\mathrm{Ph_2C_2N_3SeCl}$ (99.8(3)° and 100.3(3)° [83]). The Se—N distances exhibit partial multiple bond character (1.728(2) and 1.755(2) Å) and thus compare well with those in

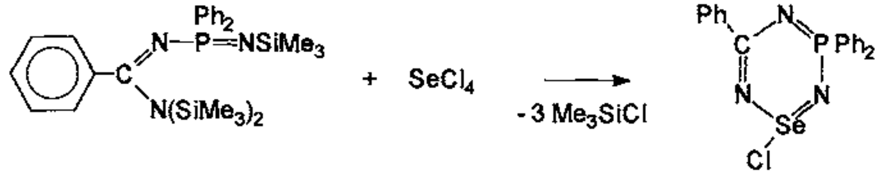


67

66

(55)

$(Ph_3PN)_2SeCl_2$ (1.735(4) Å [85]). Normal Se—N single bond lengths fall in the range 1.824–1.846 Å. The predicted value for an Se=N double bond is 1.64 Å.



68

(56)

The examples reported so far clearly demonstrate that N-silylated benzamidines and related species are highly useful precursors in the chemistry of inorganic heterocycles. The synthetic potential of these materials is far from being exhausted and undoubtedly other interesting inorganic (and organic) ring systems will be prepared in the future through the use of N-silylated benzamidines.

5. TRANSITION METAL CHEMISTRY OF *N,N'*-BIS(TRIMETHYLSILYL)BENZAMIDINATE LIGANDS

By far the largest number of new compounds derived from N-silylated benzamidines are transition metal derivatives. Numerous transition metal halides, acetates, alkoxides, etc. react with the silylated benzamidines **1** or the corresponding anions $[RC_6H_4C(NSiMe_3)_2]^-$ to give preferably complexes with chelating bezamidinate ligands [4]. These chelate complexes contain planar, four-membered MNCN rings. Other reaction pathways include the formation of hydrazido, amido, imido, and nitrido complexes. Occasionally, partial hydrolysis of the benzamidinate reagents leads to the formation of $[PhC(NHSiMe_3)_2]^+$ and $[PhC(NH_2)_2]^+$ cations. Owing to the presence of Si—N bonds all transition metal complexes containing silylated benzamidinate ligands are sensitive to moisture. Under anhydrous conditions, however, the $[RC_6H_4C(NSiMe_3)_2]^-$ ligands appear to be kinetically inert. Today's research activities in this field are stimulated by the possibility of designing new homogeneous catalysts without cyclopentadienyl ligands. In fact, silylated benzamidinate ligands may soon rival the familiar cyclopentadienyl derivatives in their versatility and applicability in synthesis and catalysis.

Especially with the early transition metals many benzamidinate complexes are currently being developed for which catalytic activity is anticipated. Most of these investigations are guided by the positive results obtained in metallocene chemistry. As a typical example, alkyl and hydride derivatives of permethylyttrocene, $(C_5Me_5)_2YR$ ($R = H, CH(SiMe_3)_2$) have been shown to be effective catalysts for a variety of reactions [86–89]. Today there is great interest in the development of similar catalysts containing ligands other than cyclopentadienyl or pentamethylcyclopentadienyl. The first promising steps in that direction have recently been made with the use of silylated benzamidinate ligands. Disubstituted early transition metal benzamidinates have now become available and some of them show promising catalytic activity.

Group 3 chemistry with *N,N'*-bis(trimethylsilyl)benzamidinate ligands has recently been investigated by Teuben and co-workers [90] as well as in our laboratory [91,92]. Precursors analogous to permethyl scandocene and -yttrocene chloride are easily accessible in multigram-quantities by treatment of either $ScCl_3(THF)_3$ or $YCl_3(THF)_{3.5}$ with two equivalents of lithium salts **2** (reaction 57). All complexes **69** and **70** are easily characterized especially by NMR spectroscopy. For example, **69c** contains not less than five NMR-observable nuclei (^1H, ^{13}C, ^{19}F, ^{29}Si, ^{89}Y). Unlike many other metallocene halides of the Group 3 and lanthanide elements the complexes **69** and **70** show no tendency to retain LiCl in the coordination sphere of the metal. In most cases the product yields are low to moderate. An interesting alternative is the use of yttrium triflate, $Y(O_3SCF_3)_3$, as starting material instead of anhydrous yttrium trichloride. The reaction of $Y(O_3SCF_3)_3$ with two equivalents of **2a** gave **71a** in 83% yield (reaction 58). The para-substituted derivatives **71b** and **71c** were prepared analogously [92,93].

$$ScCl_3(THF)_3 + 2Li[RC_6H_4C(NSiMe_3)_2] \xrightarrow[2LiCl]{THF} [RC_6H_4C(NSiMe_3)_2]_2MCl(THF)$$

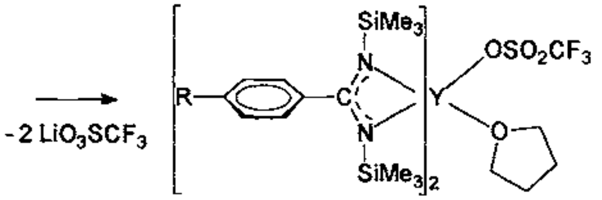
$$\begin{array}{lll}
\text{or } YCl_3(THF)_{3.5} & \mathbf{2a}\ R = H & \mathbf{69a}\ M = Sc,\ R = H \\
 & \mathbf{2c}\ R = MeO & \mathbf{69b}\ M = Sc,\ R = MeO \\
 & \mathbf{2d}\ R = CF_3 & \mathbf{70a}\ M = Y,\ R = H \\
 & & \mathbf{70b}\ M = Y,\ R = MeO \\
 & & \mathbf{70c}\ M = Y,\ R = CF_3
\end{array} \qquad (57)$$

$Y(O_3SCF_3)_3 + 2Li[RC_6H_4C(NSiMe_3)_2]$ (58)

2a R = H

2c R = MeO

2d $R = CF_3$

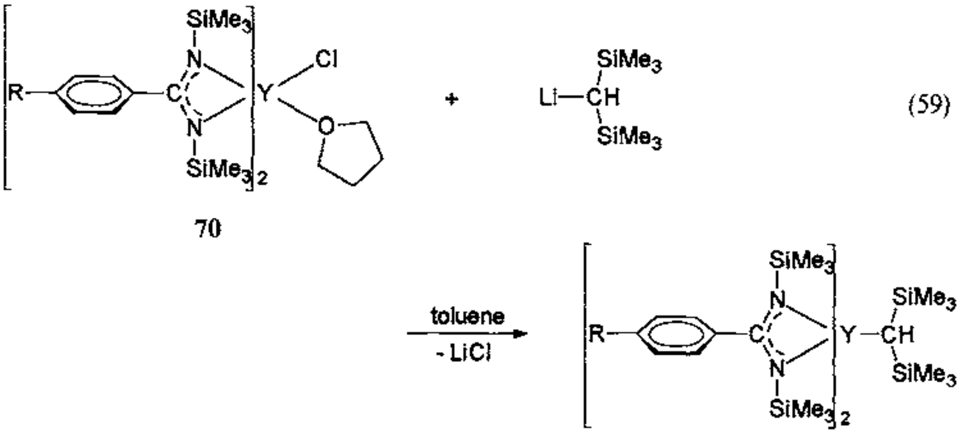


71a R = H

71b R = MeO

71c $R = CF_3$

In organolanthanide chemistry the specific advantages of the use of metal triflates have recently been pointed out by Schumann et al. for cyclopentadienyl complexes [94] and by us for cyclooctatetraenyl complexes [95]. In both cases the product yields are often higher and subsequent reactions are facilitated as LiO_3SCF_3 is more easily separated than LiCl. Complexes of the type **69–71** are excellent precursors for new alkyl complexes, as shown by the successful synthesis of salt-free $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**72**) (reaction 59) [90,91,93].



(59)

70

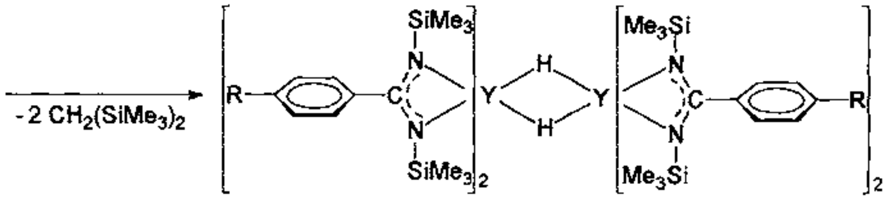
72

Compound **72** represents a novel class of catalytically active early transition metal alkyls completely free of cyclopentadienyl ancillary ligands. As in

$(C_5Me_5)_2YCH(SiMe_3)_2$ ($^1J_{C—H} = 84$ Hz) [96] the small coupling constant for the α-carbon resonance in the proton coupled ^{13}C NMR spectrum of **72** ($^1J_{C—H} = 88$ Hz) indicates an agostic interaction of the alkyl C−H bond with the yttrium atom [90]. This is typical for an electronically very unsaturated yttrium compound. Treatment of **72** with hydrogen resulted in a clean conversion to the dimeric yttrium hydride **73** (reaction 60) [90,91].

$2[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2 + H_2$ (60)

72



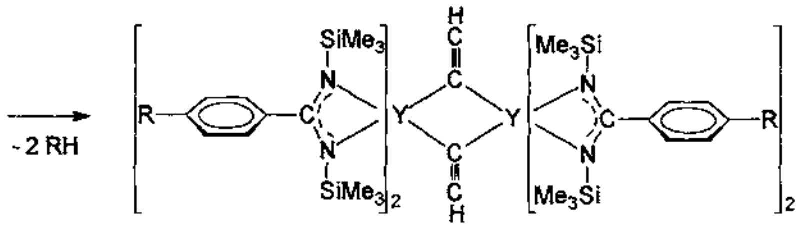
73

The ^1H NMR data of **73** indicate a symmetric dimeric structure in solution. Both complexes **72** and **73** are very air sensitive but show no sign of disproportionation or decomposition when heated at 100°C for 24 h in benzene [90]. Hydride **73** is quite reactive. Although it does not dimerize ethyne, a remarkably selective dimerization of terminal alkynes HC≡CR (R = ^tBu, $SiMe_3$, Ph) was observed. For R = $SiMe_3$ the head-to-head coupled product, *trans*-R(H)C=C(H)C≡CR was obtained, whereas the other two alkynes gave the head-to-tail coupled dimers $H_2C=C(R)C≡CR$ (R = ^tBu, Ph). Treatment of either **72** or **73** with excess ethyne gave **74**, a dimer with bridging ethynyl groups (reaction 61) [90]. The molecular structure of **74** has been determined by X-ray diffraction [90]. In contrast to several $(C_5Me_5)_2Ln$ systems (Ln = La, Ce, Sm) [97,98], no coupling of the acetylide units is observed. In the solid state the bridges are clearly asymmetric with strong interactions of the α-carbon atoms with both yttrium centers. Y−C distances in **74** compare well with those in similar lanthanide alkynyl complexes of the type $[Cp'_2Ln(\mu\text{-}C≡CR)]_2$ (Cp′ = substituted cyclopentadienyl, Ln = Sm, Er), when the differences in ionic radii are taken into account. Additional exploratory experiments have revealed that **74** polymerizes ethylene under mild conditions. These experiments clearly show that effective catalytic systems based on organolanthanides may soon be available without the use of cyclopentadienyl ancillary ligands [90–92].

$2[PhC(NSiMe_3)_2]_2YR + 2HC≡CH$ (61)

72 R = $CH(SiMe_3)_2$

73 R = H



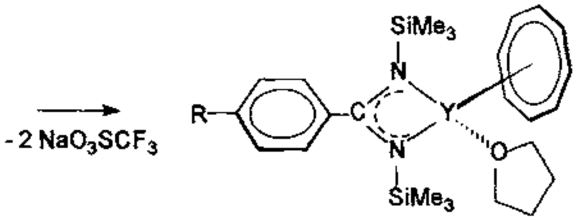
74

Two novel yttrium half-sandwich complexes containing η^8-cyclooctatetraenyl and benzamidinate ligands have recently been prepared in our laboratory [99]. The complexes **75** are obtained by reacting the new starting material $[(COT)Y(\mu\text{-}O_3SCF_3)(THF)_2]_2$ with two molar equivalents of sodium *N,N'*-bis(trimethylsilyl)benzamidinates **7** (reaction 62).

$[(COT)Y(\mu\text{-}O_3SCF_3)(THF)_2]_2 + 2Na[RC_6H_4(NSiMe_3)_2] \cdot L$

7c R = MeO

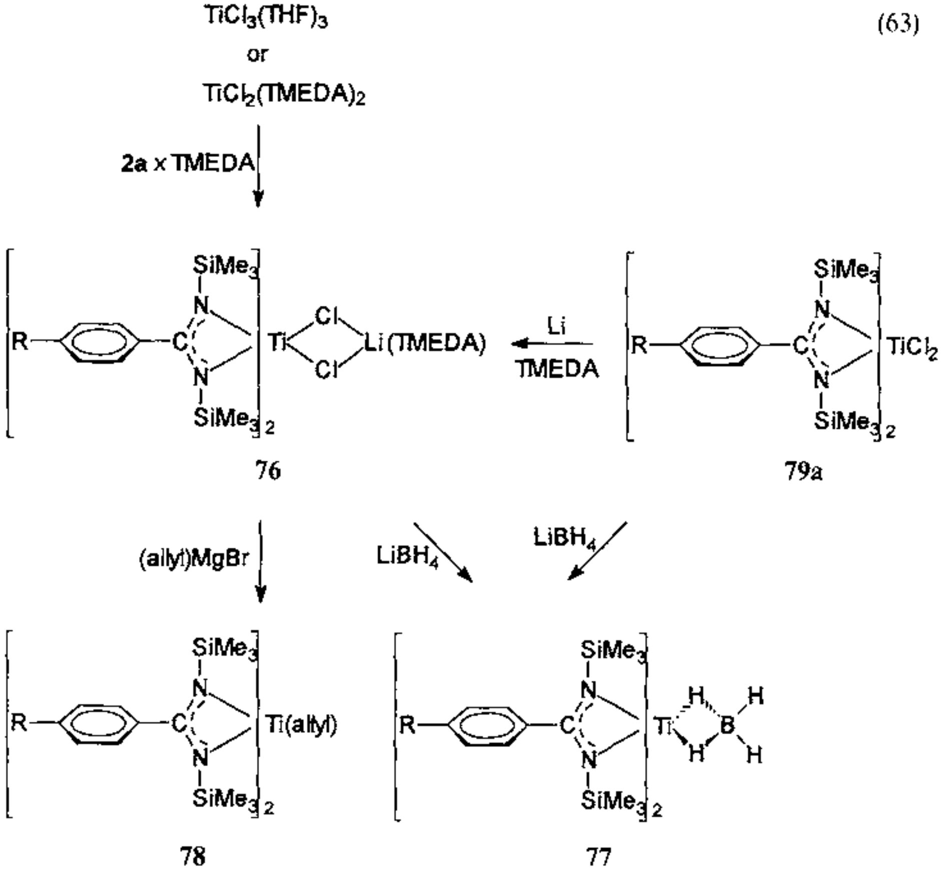
7d $R = CF_3$, $L = Et_2O$



75a R = MeO

75b $R = CF_3$ (62)

In view of designing potential new catalysts, Group IV metal benzamidinate chemistry has been thoroughly investigated. Several titanium(III) benzamidinates have recently been described by Gambarotta and co-workers [100]. The reactions of either $TiCl_2(TMEDA)_2$ or $TiCl_3(THF)_3$ with two equivalents of $[PhC(NSiMe_3)_2]Li(TMEDA)$ (**2a** × TMEDA) gave forest green crystals of $[PhC(NSiMe_3)_2]_2Ti(\mu\text{-}Cl)_2Li(TMEDA)$ (**76**) in good yield (reaction 63). This material was also prepared via reduction of the known titanium(IV) complex **79a** (vide infra) with metallic lithium in the presence of TMEDA. Subsequent treatment of **76** with $LiBH_4$ formed light brown crystals of $[PhC(NSiMe_3)_2]_2Ti(BH_4)_2$ (**77**). The titanium(III) borohydride was also formed in low yield when $[PhC(NSiMe_3)_2]_2TiCl_2$ (**79a**) was reacted with either a stoichiometric amount or an excess of $LiBH_4$. In analogy to the corresponding titanocene derivatives [101] it



(63)

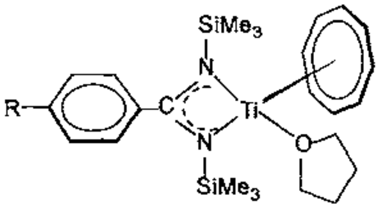
was not possible to prepare a titanium(IV) borohydride complex of the type $[PhC(NSiMe_3)_2]_2Ti(BH_4)_2$ [100].

Reactions of **76** with various organolithium or Grignard reagents in most cases gave oily or intractable materials. Only with (allyl)MgBr was it possible to isolate a thermally stable, yellow-green titanium(III) allyl complex (**78**). The complexes **76–78** are paramagnetic and show magnetic moments as expected for a d^1 electronic configuration. The X-ray crystal structures of all three compounds have been determined [100]. In **76** the titanium atom is octahedrally coordinated by two chlorine atoms which connect the titanium to a Li(TMEDA) unit. The central four-membered $TiCl_2Li$ ring is almost planar ($Ti-Cl-Li-Cl$ $5.6(5)^\circ$). This MCl_2Li core is unprecedented in the chemistry of titanium(III) although very common in organolanthanide chemistry [102].

In complex **77** the coordination geometry around titanium is also slightly distorted octahedral. The two chelating benzamidinate ligands form planar four-membered rings with the titanium atom. The borohydride ligand is coordinated in a bidentate fashion and the TiH_2B ring is slightly folded (Ti—H—B—H 7.0°) with a relatively short Ti—B distance (Ti—B 2.421(4) Å).

The molecular structure of the allyl complex **78** shows a similar arrangement of the two chelating benzamidinate ligands. The η^3-allyl ligand adopts a rather unusual asymmetric conformation which was explained by the considerable steric hindrance provided by the two benzamidinate ligands. The angle at the central carbon atom of the allyl ligand is rather wide and the two C—C bond distances are significantly different (1.333(8) Å and 1.160(7) Å), thus suggesting different bond orders. However, the Ti—C distances are comparable with the shortest Ti—C bond being formed to the central carbon atom (Ti—C 2.263(4) Å).

Two monomeric organotitanium(III) half-sandwich complexes with η^8-cyclooctatetraenyl and benzamidinate ligands have been synthesized in our laboratory by reacting the readily available $[(COT)Ti(\mu\text{-}Cl)(THF)_2]_2$ with equimolar amounts of $Na[RC_6H_4C(NSiMe_3)_2]$. The dark green crystalline complexes **79** can be isolated in high yields (cf. reaction 62) [103]. Titanium (IV) and zirconium(IV) benzamidinate complexes were described several years earlier by Roesky et al. [48] and Dehnicke and co-workers [104]. Treatment of $TiCl_4$ or $ZrCl_4$ with **2a** in diethylether or CH_2Cl_2 gave the disubstituted products **79** (reaction 64) [48].



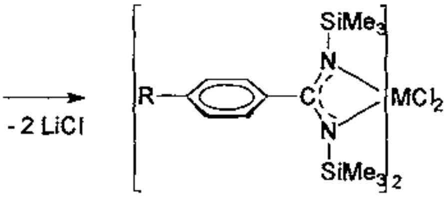
79a R = H

79b R = MeO

The para-substituted derivative $[CF_3C_6H_4C(NSiMe_3)_2]_2TiCl_2$ (**80c**) was prepared similarly [105]. Complex **80a** was also obtained in 53% yield by reacting $TiCl_4(TMEDA)$ with $[PhC(NSiMe_3)_2]Li(TMEDA)$ in THF solution [100]. The molecular structure of **80a** was determined through X-ray crystallography [48]. The central titanium atom is coordinated in a distorted octahedral fashion by two chelating benzamidinate ligands and two chlorine atoms. The $CC(NSi)_2M$ units are planar within 0.07 Å. Owing to the presence of four trimethylsilyl substituents **80a** is quite soluble in various organic solvents and can be easily purified by continuous extraction with hexane. Interestingly the visual appearance of the crystalline material resembles that of titanocene dichloride, Cp_2TiCl_2 [105]. Just like the cyclopentadienyl analogue, **80a** too is currently developing into a highly useful starting material for other titanium benzamidinate complexes. Stable σ-methyl complexes have been isolated from reactions of **80a** and **80b** with methyllithium (reaction 65) [105].

$MCl_4 + 2Li[PhC(NSiMe_3)_2]$ (64)

2a



80a M = Ti, R = H

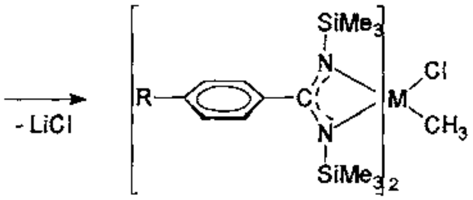
80b M = Zr, R = H

80c M = Ti, R = CF_3

$[PhC(NSiMe_3)_2]_2MCl_2 + CH_3Li$ (65)

80a M = Ti

80b M = Zr



81a M = Ti, R = H

81b M = Zr, R = H

In the case of titanium and zirconium different results are obtained when the metal tetrahalides are reacted with **1a** instead of the lithium benzamidinate **2a** (reaction 66). The synthesis of monosubstitution products was described by Dehnicke and co-workers [104]. The reactions were carried out at room temperature in CH_2Cl_2 solution. The products form moisture-sensitive, dark red (**82a**) or white (**82b,c**) crystals, which were characterized by X-ray crystal structure determination. Both the titanium and zirconium compounds were found to crystallize isotypically. In the solid state two $[PhC(NSiMe_3)_2]MCl_3$ units are associated via chlorine bridges to give centrosymmetric dimers. The metal atoms are octahedrally surrounded by one chelating benzamidinate ligand and four chlorine atoms. The nitrogen atoms of the benzamidinate ligand are in equatorial and axial positions. This accounts for significant differences in the M–N bond lengths (**82a** 2.420 and 2.538 Å, **82b** 2.537 and 2.649 Å) [104]. The dihedral angles between the MN_2C planes and the phenyl rings (**82a** 65.5°, **82b** 64.2°) are relatively small compared with most other bezamidinate complexes (e.g. $[PhC(NSiMe_3)_2]SbCl_2$ 88.9° [7]). They are, however, still large enough to inhibit an effective conjugation between the two π-systems.

$$PhC(=NSiMe_3)[N(SiMe_3)_2] + MCl_4 \rightarrow [PhC(NSiMe_3)_2]MCl_3 + Me_3SiCl \qquad (66)$$

1a

82a M = Ti

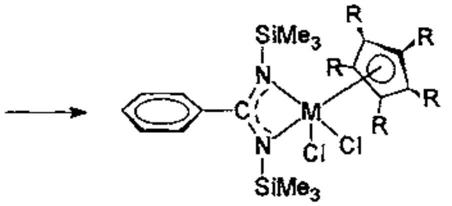
82b M = Zr

82c M = Hf

In contrast to the disubstituted complexes $[PhC(NSiMe_3)_2]_2MCl_2$ (**80**) the derivative chemistry of **82** has not yet been investigated. In view of the easy accessibility of multigram-quantities of these compounds a derivatization study should be worthwhile. They appear to be ideal starting materials for reactions with cyclopentadienyl transfer reagents which would lead to mixed-ligand complexes of the type $[PhC(NSiMe_3)_2]MCl_2(Cp')$ ($Cp' = C_5H_5$, substituted cyclopentadienyl, indenyl, etc.). The first compound of this type, $[PhC(NSiMe_3)_2]TiCl_2(Cp)$ (**83a**) was prepared in our laboratory by reacting $CpTiCl_3$ with one equivalent of **7a** [65]. Recently the corresponding zirconium and hafnium complexes have been obtained by Green and co-workers [106] by the same synthetic procedure using the lithium salt **2a** (reaction 67). The molecular structure of **83c** has been determined. The four-membered chelate ring HfN_2C is slightly puckered with a dihedral angle between N—Hf—N and N—C—N of 11.5° [106].

$$(C_5R_5)MCl_3 + Li[PhC(NSiMe_3)_2] \qquad (67)$$

R = H, Me **2a**



83a M = Ti, R = H

83b M = Zr, R = H

83c M = Hf, R = H

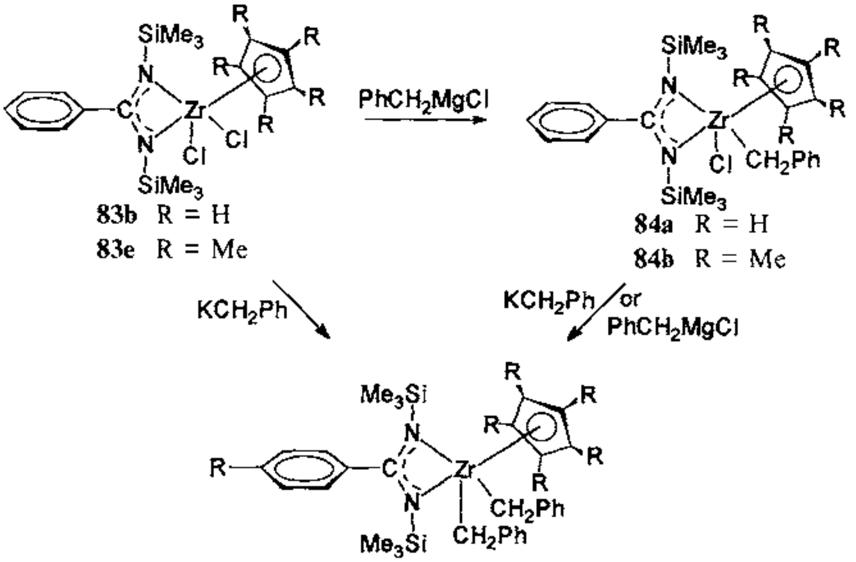
83d M = Ti, R = Me

83e M = Zr, R = Me

Initial studies show that stable alkyl derivatives of **83** can be prepared by treatment with alkyllithium or Grignard reagents (reaction 68). Green et al. reported on the preparation of a series of mono- and dibenzyl substituted derivatives [104]. In general, the *N,N'*-bis(trimethylsilyl)benzamidinate anions appear to be equally well suited for both early and late transition elements. In that respect the ligand system seems to be as versatile as the cyclopentadienyl ligands.

Closely related to the N-silylated benzamidinate ligands are the dianions of bis(organoamino)phenyl boranes, $PhB(NR)_2^{2-}$. These boraamidinates are in fact isoelectronic with the corresponding benzamidinate monoanions. The main difference is that the boraamidinates are dianionic ligands, thus the complexation with tetravalent metal atoms results in the formation of neutral homoleptic species. Five compounds of that type have been prepared according to reaction 69 [107]. The molecular structure of the spirocyclic titanium compound **86d** has been determined by X-ray diffraction. In two cases monosubstituted metal boraamidinates have been isolated (70) [107].

Benzamidinate chemistry of the Group 5 metals vanadium, niobium and tantalum is also currently under active investigation. An interesting class of high-valent vanadium benzamidinates is derived from the nitrido vanadium(V) complexes $(^{t}BuN)VCl_3$ and $(p\text{-TolN})VCl_3$ (reaction 71) [108]. The molecular structure of $[PhC(NSiMe_3)_2]_2VCl(NTol\text{-}p)$ (**90b**) was determined by X-ray diffraction. In a preliminary account the preparation of $[PhC(NSiMe_3)_2]NbCl_4$ (**92a**) and $[PhC(NSiMe_3)_2]TaCl_4$ (**92b**) has been briefly mentioned [49]. So far no Group 5

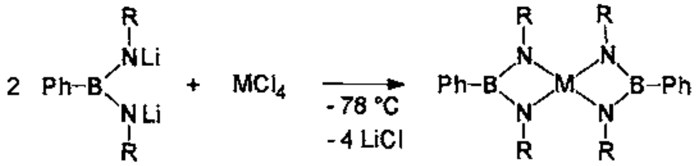


83b R = H
83e R = Me

84a R = H
84b R = Me

85a R = H
85b R = Me

(68)



(69)

86a $M = Ge$, $R = {}^iPr$

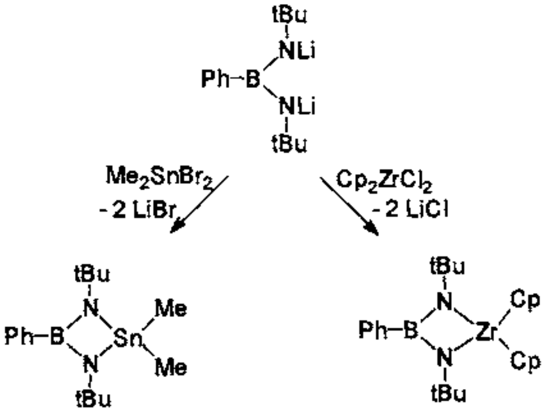
86b $M = Ge$, $R = {}^tBu$

86c $M = Sn$, $R = {}^tBu$

86d $M = Ti$, $R = {}^tBu$

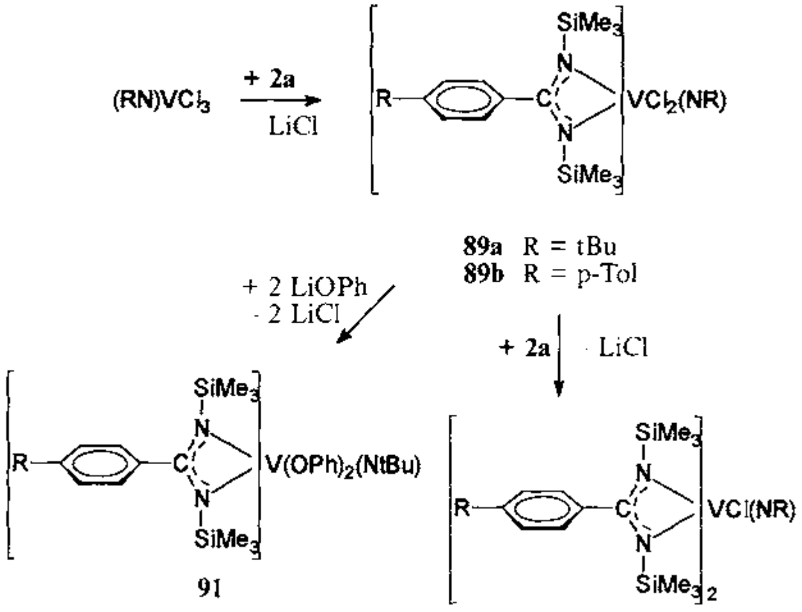
86e $M = Ti$, $R = SiMe_2{}^tBu$

benzamidinates in low oxidation states have been described. A series of tantalum(V) benzamidinates derived from $(C_5Me_5)TaF_4$ (reaction 72) have been reported by Roesky and co-workers [109]. The compounds **93** are isolated as white or pale yellow crystalline solids. Only **93e** forms a yellow-brown oil owing to its very high solubility in organic solvents. An X-ray crystal structure determination has been carried out on **93c**. It shows the typical perpendicular orientation of the aromatic ring with respect to the four-membered TaNCN chelate ring. The Ta–F bond lengths (Ta–F_{eq} 1.906 Å (average), Ta–F_{axial} 1.947(3) Å) are comparable with those in the parent organotantalum fluoride $(C_5Me_5)TaF_4$(Ta–F 1.903 Å (average)) [109].



(70)

87 **88**



(71)

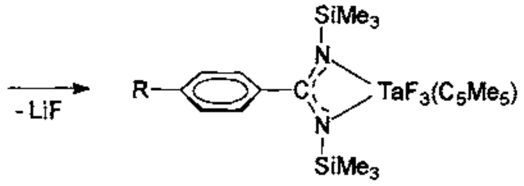
89a R = tBu
89b R = p-Tol

91

90a R = tBu
90b R = p-Tol

$(C_5Me_5)TaF_4 + Li[RC_6H_4C(NSiMe_3)_2]$ (72)

2



93 R = H (**a**), Me (**b**), OMe (**c**), CF_3 (**d**), NMe_2 (**e**), CN (**f**)

A surprising result was reported by Dehnicke and co-workers for the reaction of $[TaCl_5]_2$ with **1a** [35]. When a suspension of $[TaCl_5]_2$ in CH_2Cl_2 was treated with one equivalent of **1a**, the metal halide dissolved completely to give a dark brown solution (reaction 73). Concentration and slow cooling of the reaction mixture gave yellow-brown, moisture-sensitive crystals of the imido complex **94**. Crystals of **94** contain two equivalents of dichloromethane, which is slowly given off on drying under vacuum. According to the X-ray structure determination, **94** forms centrosymmetric molecules dimerized via chloro bridges (Fig. 6). The Ta—Cl bond lengths within the central Ta_2Cl_2 ring are in trans positions to the imido group [35].

$$\underset{\textbf{1a}}{[TaCl_5]_2 + 2PhC(=NSiMe_3)[N(SiMe_3)_2]}$$

$$\xrightarrow{CH_2Cl_2} \underset{\textbf{94}}{[TaCl_4NC(Ph)N(SiMe_3)_2]_2} + 2Me_3SiCl \qquad (73)$$

The most remarkable feature of complex **94** is the presence of $(Me_3Si)_2NC(Ph)N$ imido ligands. These ligands are believed to be the initial products in the addition of nitriles to metal bis(trimethylsilyl)amides. A similar imido derivative has been postulated as an intermediate in the formation of $[PhC(NSiMe_3)_2]_2Ca(THF)_2$ (**15**) from $Ca[N(SiMe_3)_2]_2(THF)_2$ and benzonitrile (vide supra) [34]. The bonding in **94** can be described by means of the two resonance forms **A** and **B**. A participation of resonance form **B** is indicated by the planar surrounding of the tricoordinated carbon and nitrogen atoms (angle sum 360.0(8)° at C(1) and 359.9(5)° at N(2)) and the short C(1)—N(2) distance of 1.34(1) Å,

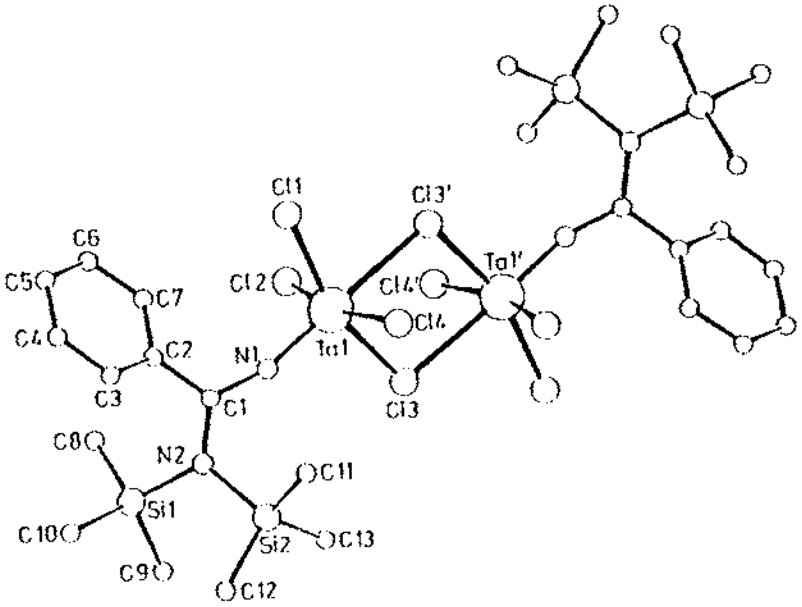
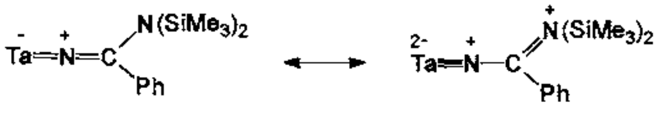


Fig. 6.



A **B**

which is not much different from the distance C(1)–N(1) (1.32(1) Å). The Ta–N bond length of 1.835(8) Å comes close to the expected value for a tantalum–nitrogen double bond [35].

Two homoleptic benzamidinates of chromium(II) have been prepared via normal metathetical reactions between $CrCl_2(THF)_2$ and sodium benzamidinates (reaction 65) [65]. The chromium(II) benzamidinates **95** form black-red, needle-like crystals which are quite air sensitive. They are soluble even in non-polar organic solvents such as toluene or hexane. Unsolvated **95a** has been characterized by X-ray crystallography (Fig. 7) [65].

$$CrCl_2(THF)_2 + Na[RC_6H_4C(NSiMe_3)_2]\cdot L \rightarrow [RC_6H_4C(NSiMe_3)_2]_2Cr \qquad (74)$$

7a $R = H, L = 0.5Et_2O$ **95a** $R = H$

7d $R = CF_3, L = Et_2O$ **95b** $R = CF_3$

The coordination geometry around the four-coordinate chromium atom is close to planar. A significant deviation from planar geometry results from steric hindrance between opposite trimethylsilyl groups. The torsion angle between the two four-membered CrNCN rings is 22.8°. In the closely related ytterbium(II) complex $[PhC(NSiMe_3)_2]_2Yb(THF)_2$ (vide infra) the corresponding interplanar angle is 26.3°. In contrast to the small chromium atom the coordination sphere of ytterbium has enough room to accomodate two additional THF ligands. With

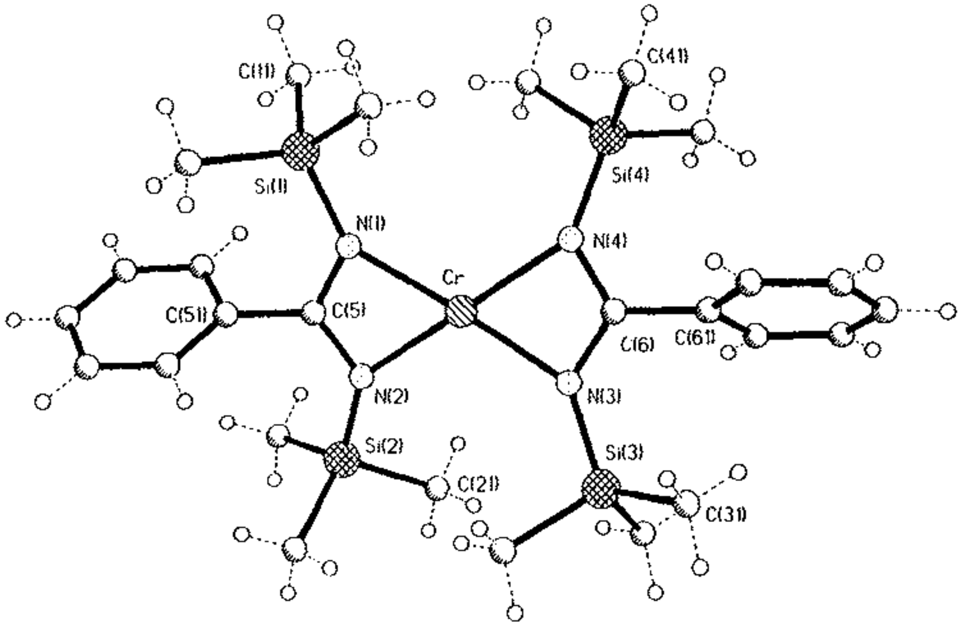


Fig. 7.

2.096(4) Å (average) the Cr—N distances are almost identical with those found in the square planar chromium(II) amide $\mathrm{Cr[N(SiMe_3)_2]_2(THF)_2}$ (2.089(10) Å) [110]. Preliminary experiments indicate that the chromium(II) benzamidinates are very reactive and readily undergo addition reactions with "slim" ligands such as nitriles, isonitriles or carbon monoxide. Thus far no other chromium complexes with silylated benzamidinate ligands have been described. In contrast, benzamidinate chemistry of molybdenum and tungsten is more diverse. In the case of molybdenum such complexes have been prepared with the metal in both low and high oxidation states. An interesting molybdenum(II) derivative was described by Dehnicke and co-workers [111]. A nearly quantitative yield of **96** was obtained when molybdenum(II) benzoate was treated with **1a** in refluxing dichloromethane (reaction 75).

$$\mathrm{Mo_2(O_2CPh)_4} + \underset{\textbf{1a}}{\mathrm{2PhC({=}NSiMe_3)[N(SiMe_3)_2]}}$$

$$\rightarrow \underset{\textbf{96}}{\mathrm{Mo_2(O_2CPh)_2[PhC(NSiMe_3)_2]_2}} + \mathrm{2Me_3SiOC(O)Ph} \tag{75}$$

Even after prolonged heating or by using an excess of **1a** the remaining benzoate ligands cannot be substituted. This result was attributed to steric hindrance of the bulky trimethylsilyl groups. The yellow-orange crystals of **96** are not moisture sensitive and are reasonably soluble in various organic solvents. The X-ray crystal structure determination revealed the presence of a typical dimolybdenum(II) species in which the $\mathrm{Mo_2}$ unit is coordinated by four oxygen and four nitrogen atoms. With 2.083(1) Å the Mo–Mo distance is slightly shorter than that in the starting material $\mathrm{Mo(O_2CPh)_4}$ (2.10 Å) [112]. The average Mo—N bond lengths in **96** are 2.151(6) Å and thus comparable with the Mo–N distances in other molybdenum amidinates (e.g. $\mathrm{Mo_2[PhC(NPh)_2]_4}$ Mo–N 2.125(9)–2.163(19) Å [113]).

Spirocyclic benzamidinates of molybdenum(VI) and tunsten(VI) were described by Roesky et al. [48]. The oxo complexes **97** were obtained by treatment of $\mathrm{MoO_2Cl_2}$ or $\mathrm{WO_2Cl_2}$ with two equivalents of **2a** in THF (reaction 76). The molecular structure of **97a** very much resembles that of the titanium(IV) complex $\mathrm{[PhC(NSiMe_3)_2]_2TiCl_2}$ (**80a**). The oxo ligands are in cis position with an Mo—O angle of 106.2(3)° [48]. Alternatively, compound **97b** can be prepared from $\mathrm{WO_2Cl_2}$ and **1a** in $\mathrm{CH_2Cl_2/MeCN}$. $\mathrm{WOCl_4}$ reacts with **1a** to give $\mathrm{[PhC(NSiMe_3)_2]WOCl_3}$ (**98**) [49].

$$\mathrm{MoO_2Cl_2} + \underset{\textbf{2a}}{\mathrm{2Li[PhC(NSiMe_3)_2]}} \xrightarrow[-2\mathrm{LiCl}]{\mathrm{THF}} \underset{\substack{\textbf{97a}\ \mathrm{M = Mo}\\ \textbf{97b}\ \mathrm{M = W}}}{\mathrm{[PhC(NSiMe_3)_2]_2MoO_2}} \tag{76}$$

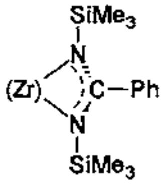
In the case of a molybdenum nitride precursor a *bis*(trimethylsilyl)amido ligand was introduced upon treatment with **1a** [111] (reaction 77). The coordination geometry at molybdenum can be described as a tetragonal pyramid with the nitrido ligand in apical position [114]. The basal positions are occupied by the three chlorine atoms and the nitrogen atom of the amido ligand. The nitridic Mo—N distance of 1.648 Å is typical for an Mo≡N triple bond [115]. The other Mo—N bond length (1.937 Å) is significantly shorter than the expected value for an Mo—N single bond (ca. 2.05 Å). The shortening of the Mo—N bond and the planar geometry at nitrogen have been explained with π-bonding between these two atoms. Owing to the steric demand of the bulky $N(SiMe_3)_2$ ligand the Mo—Cl distances in **99** (average 2.435 Å) are longer than in the $[MoNCl_4]^-$ anion (2.344 Å) [116].

$$[PPh_4][MoNCl_4] + \underset{\mathbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]}$$

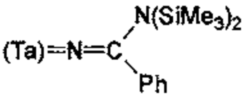
$$\rightarrow \underset{\mathbf{99}}{[PPh_4][MoNCl_3\{N(SiMe_3)_2\}]} + PhCN + Me_3SiCl \qquad (77)$$

Yet again a different reaction pathway was observed when tungsten hexachloride was reacted with **1a**. When the reaction was carried out in CCl_4 red needle-like crystals were isolated which have been shown to be the benzonitrile adduct of tungsten nitride trichloride (reaction 78). In this case the N-silylated benzamidinate reagent serves only to introduce a nitrido function [117]. Red-brown, very moisture-sensitive **100** is only sparingly soluble in CCl_4. However, dark red single crystals of the composition $[WNCl_3(PhCN)]_4 \cdot 3CH_2Cl_2$ have been grown from dichloromethane solution. In the tetrameric molecule the four tungsten atoms are connected via linear W≡N—W nitrido bridges with alternating short and long W—N bonds (average 1.66 and 2.11 Å). The N-atoms of the benzonitrile ligands are found in the positions trans to the W≡N units (W—N(PhCN) 2.37 Å) [117]. An interesting comparison can be made for the reaction products of **1a** with $ZrCl_4$, $TaCl_5$ and WCl_6 [35]. Zirconium tetrachloride yields the regular benzamidinate chelate complex (**A**) with Zr—C single bonds, whereas in the case of $TaCl_5$ the resulting imido complex **B** formally contains a Ta=N double bond. Finally, with WCl_6 a triply bonded tungsten nitride species (**C**) is obtained.

$$WCl_6 + \underset{\mathbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]} \xrightarrow{CCl_4} \underset{\mathbf{100}}{WNCl_3(PhCN)} + 3Me_3SiCl \qquad (78)$$



A

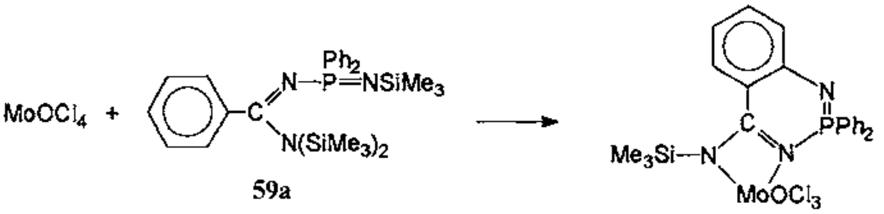


B

$(\mathrm{W})\equiv\mathrm{N}$

C

An unusual molybdenum-containing heterocycle was synthesized by reacting $MoOCl_4$ with the amidinophosphazene derivative **59a** (reaction 79) [60]. Dark green crystals of **101** have been obtained from acetonitrile solution. In the molecule, two nitrogen, three chlorine, and one oxygen atom form a distorted octahedron around the central molybdenum atom [60].

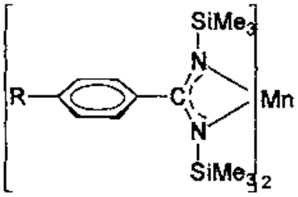


(79)

59a

101

Only a small number of manganese benzamidinates have been described in the literature. The complexes **102** were obtained by reacting $MnCl_2(THF)_2$ with two equivalents of sodium *N,N'*-bis(trimethylsilyl)benzamidinates **7** (cf. reaction 73) [65,118]. A THF adduct of **102c** has been structurally characterized by X-ray diffraction [118]. Apparently no other complexes of Group 7 metals containing silylated benzamidinate ligands have been mentioned in the literature.



102a R = H

102b R = CF_3

102c R = Ph

An interesting series of iron(III) complexes derived from *N,N,N'*-tris(trimethylsilyl)benzamidine **1a** has been described by Dehnicke and co-workers [119–121]. Depending on the reaction conditions, two different products can be isolated from the reaction of **1a** with anhydrous $FeCl_3$ (reaction 80). When carried out in CH_2Cl_2 or CCl_4 the main product is the cyclic hydrazido complex **103**, which can be isolated as dark red, moisture-sensitive crystals in 68% yield [119]. According to the X-ray crystal structure determination, compound **103** forms centrosymmetric molecules in which the two iron atoms are incorporated into two fused planar FeNCNN heterocycles with an NN unit as the common edge. The N−N bond length (1.425(9) Å) is very similar to the N−N distance in free hydrazine [119]. The bonding situation in this unusual metallacycle can be described by the following resonance structures.

$$4FeCl_3 + 2\underset{\mathbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]}$$

$$\rightarrow \underset{\mathbf{103}}{Fe_2N_2Cl_4(PhCNSiMe_3)_2} + FeCl_2 + 4Me_3SiCl \qquad (80)$$

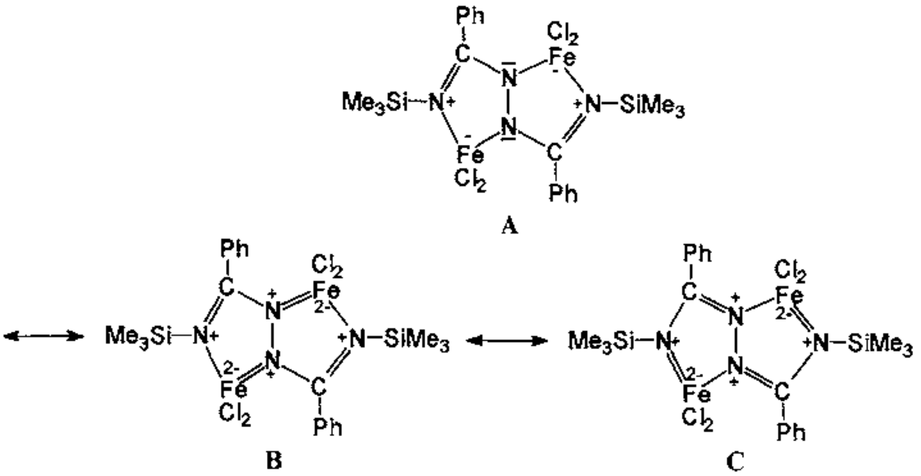
The synthesis of **103** is accompanied by the formation of a side-product which can be isolated in ca. 20% yield if the reaction is carried out in the presence of THF (reaction 81). In this case *N,N′*-bis(trimethylsilyl)benzamidinium tetrachloroferrate(III) (**104**) is obtained in the form of pale yellow crystals [119,120]. The hydrogen chloride originates from a reaction of iron trichloride with the solvent tetrahydrofuran. Treatment of **104** with excess HCl resulted in a complete loss of all trimethylsilyl substituents and formation of benzamidinium tetrachloroferrate(III) (**105**) (reaction 82) [120]. Similar compounds containing the benzamidinium cation have been obtained by treatment of either $[PhC(NSiMe_3)_2]AlCl_2$ (**20a**) or $[PhC(NSiMe_3)_2]SnCl_3$ (**26**) with excess HCl (cf. reaction 82). In the solid state compound **104** forms ion-pairs in which one chlorine atom of the $FeCl_4^-$ anion is chelated by the amidinium cation.

$$FeCl_3 + \underset{\mathbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]} + 2HCl$$

$$\rightarrow \underset{\mathbf{104}}{[PhC(NHSiMe_3)_2]^+[FeCl_4]^-} + Me_3SiCl \qquad (81)$$

$$\underset{\mathbf{104}}{[PhC(NHSiMe_3)_2]^+[FeCl_4]^-} 2HCl \rightarrow \underset{\mathbf{105}}{[PhC(NH_2)_2][FeCl_4]} + 2Me_3SiCl \qquad (82)$$

A regular benzamidinate chelate complex of iron was prepared by the reaction of FeOCl with two equivalents of **1a** in acetonitrile/THF (reaction 83). Independently of the stoichiometry of the starting materials the disubstituted derivative **106** was isolated as the only product of 96% yield. Dark red, very moisture-sensitive single crystals of **106** have been obtained from saturated solutions in acetonitrile or THF. The presence of a disubstituted iron(III) complex with two chelating



$[PhC(NSiMe_3)_2]^-$ ligands was revealed by an X-ray crystal structure determination (Fig. 8) [121]. The central iron atom is surrounded in a distorted trigonal-bipyramidal fashion by the chlorine and four nitrogen atoms. Two nitrogen atoms of different benzamidinate ligands are in equatorial positions while the other two occupy the axial positions. Deviations from an ideal trigonal-bipyramidal geometry result from the small bite angle of the amidinate ligands and from steric hindrance of the trimethylsilyl groups. Compound **106** certainly deserves further investigation as a

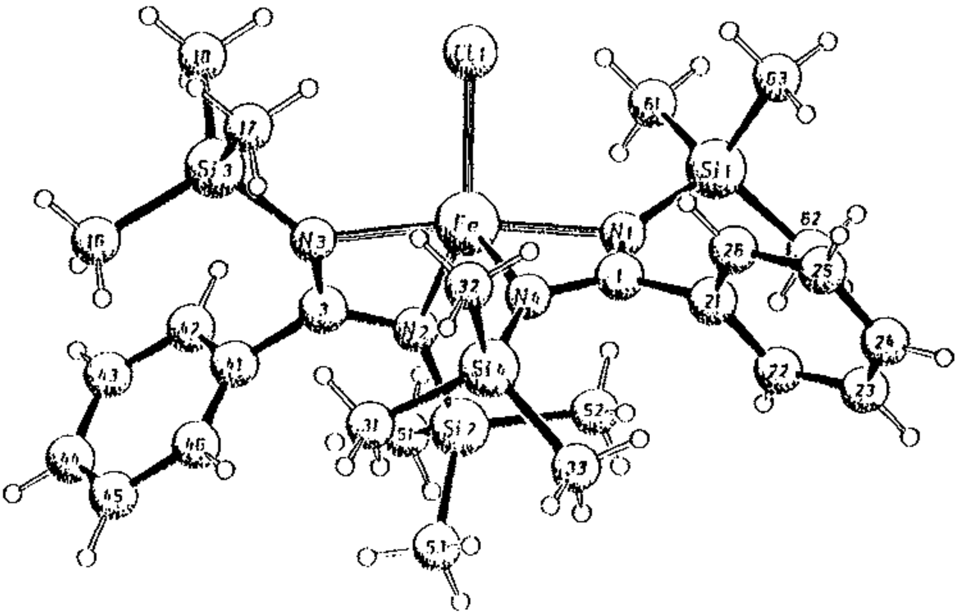
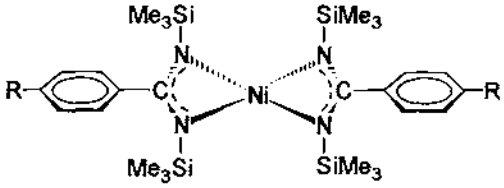


Fig. 8.

precursor for novel iron(III) amides or alkyls which might be accessible through metathetical reactions at the chlorine atom.

$$\underset{}{FeOCl} + \underset{\textbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]} \rightarrow \underset{\textbf{106}}{[PhC(NSiMe_3)_2]_2FeCl} + Me_3SiOSiMe_3 \quad (83)$$

N,N'-Bis(trimethylsilyl)benzamidinate complexes of the elements ruthenium, osmium, cobalt, rhodium and iridium have not been mentioned in the literature. Nickel(II) derivatives of N-silylated benzamidinate ligands **107** have recently been prepared in our laboratory (cf. reaction 73) [122]. These dark brown crystalline materials are very soluble in hydrocarbons and appear to be quite reactive towards small molecules such as acetonitrile, carbon monoxide etc.



107a R = H

107b R = MeO

Hydrolytic transformations characterize the benzamidinate chemistry of palladium. Formation of an amido complex was observed in the reaction of palladium(II) chloride with **1a** in the presence of tetraphenylphosphonium chloride and small amounts of water (reaction 84) [123]. According to the X-ray crystal structure determination of **108**, the resulting dichloro(amido)palladate(II) anion consists of centrosymmetric dimers. Significant differences in the Pd—Cl distances to the bridging chlorine atoms have been attributed to the trans influence of the amido ligands [123].

$$PdCl_2 + \underset{\textbf{1a}}{PhC(=NSiMe_3)[N(SiMe_3)_2]} + [PPh_4]Cl + H_2O$$

$$\rightarrow \underset{\textbf{108}}{[PPh_4][PdCl_2(NH_2)]} + Me_3SiCl + Me_3SiOSiMe_3 \quad (84)$$

Previous cases of hydrolytic cleavage of the N-silylated benzamidinate ligands always resulted in formation of cationic benzamidinium species such as $[PhC(NHSiMe_3)_2]^+$ and $[PhC(NH_2)_2]^+$. Palladium chemistry also offers the first example of a complex containing the unsubstituted benzamidinate anion $[PhC(NH)_2]^-$. $[(\eta^3\text{-allyl})PdCl]_2$ was treated with two equivalents of **2a** in THF solution. Crystallization from hexane afforded bright yellow crystals of the dimeric allyl complex **109** (reaction 85) [124]. Compound **109** is highly soluble in hydrocarbon solvents and very moisture sensitive. Crystals of **109** rapidly disintegrate in contact with moist air. A well defined hydrolysis product was isolated by adding a stoichiometric amount of water to a solution of **109** in diethylether/hexane (reaction 86) [124].

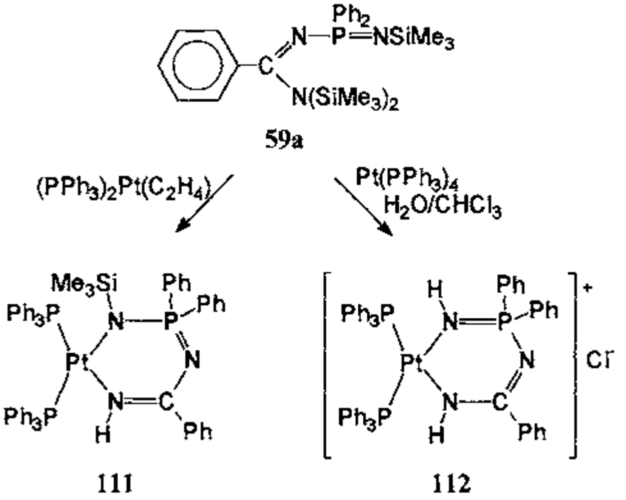
$$[(\eta^3\text{-allyl})\mathrm{PdCl}]_2 + \underset{\mathbf{2a}}{\mathrm{Li[PhC(NSiMe_3)_2]}} \xrightarrow[-\mathrm{LiCl}]{} \underset{\mathbf{109}}{[\mathrm{PhC(NSiMe_3)_2Pd}(\eta^3\text{-allyl})]_2} \tag{85}$$

$$\underset{\mathbf{109}}{[\mathrm{PhC(NSiMe_3)_2Pd}(\eta^3\text{-allyl})]_2} + 2\mathrm{H_2O}$$

$$\rightarrow \underset{\mathbf{110}}{[\mathrm{PhC(NH)_2Pd}(\eta^3\text{-allyl})]_2} + 2\mathrm{Me_3SiOSiMe_3} \tag{86}$$

In the IR spectrum of **110** the presence of a $[\mathrm{PhC(NH)_2}]^-$ ligand is documented by the appearance of ν(NH) bands at 3371 and 3330 cm^{-1}. This is accompanied by the absence of a strong band at ca. 840 cm^{-1} which is generally attributed to the $\mathrm{Me_3Si}$ groups. The X-ray structure determination of **110** shows a dimeric molecule in which the two palladium atoms are bridged by benzamidinate ligands. A similar situation was found by Bear and co-workers in the dinuclear palladium amidinate $(\mu\text{-dpb})_2[\mathrm{Pd(dpb)}]_2$ (dpb = *N,N'*-diphenylbenzamidinate) [125]. In this compound the Pd—Pd distance (2.900(1) Å) is significantly shorter than in **110** (Pd—Pd 3.128(1) Å) [124].

No platinum compound with chelating *N,N'*-bis(trimethylsilyl)benzamidinate ligands has been prepared but two interesting platinum-containing metallacycles have been described by Roesky et al. [73]. Both heterocycles are derived from the



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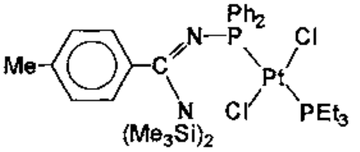

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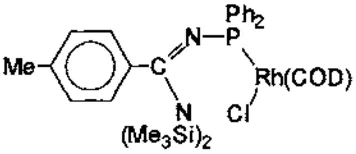
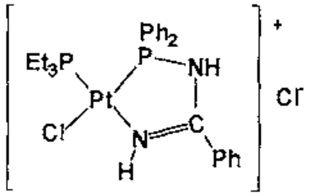


114

amidinophosphazene **59a** (reaction 87). Treatment of **59a** with $(Ph_3P)_2Pt(C_2H_4)$ in THF afforded colorless **111** which was identified by spectroscopy. A similar reaction of **59a** with the platinum(0) complex $Pt(PPh_3)_4$ gave colorless crystals of **112** after recrystallization of the crude product from a mixture of chloroform and wet hexane. Obviously the solvent chloroform must have been the source of the chloride ion in **112**. An X-ray structure analysis showed that compound **112** consists of six-membered rings which are not entirely planar but adopt a half-boat conformation. The two Pt—N bond distances are equal (2.086(10) and 2.062(10) Å). The P—N bond lengths (1.603(11) and 1.620(9) Å) indicate a certain degree of multiple bonding [73].

More recently similar reactions of the phosphinoamidine **35b** with platinum and rhodium complexes have been studied by Chivers et al. [63]. Treatment of 2 molar equivalents of **35b** with $[Pt(PEt_3)Cl_2]_2$ or $[Rh(COD(Cl]_2$ in THF or CH_2Cl_2 at 0°C afforded the monodentate metal-phosphine complexes **113** and **114** as air-stable solids. The salt-like species **115** was obtained when the reaction of **35b** with $[Pt(PEt_3)Cl_2]_2$ was carried out in refluxing THF. Similar treatment of **35b** with $[Rh(CO)_2Cl]_2$ in a 2:1 molar ratio in THF produced the compound **116**, which was identified by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopic data.



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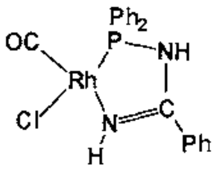
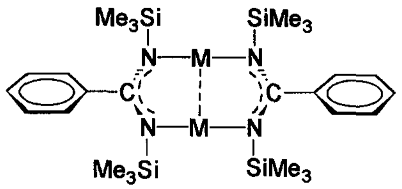


116

Binuclear benzamidinate-bridged complexes have been isolated with copper(I), silver(I), and gold(I). The compounds **117** have been prepared by Dehnicke and co-workers from **1a** and CuCl, AgO_2CCH_3, or (CO)AuCl, respectively [126,127]. X-ray crystal structure determinations have been carried out on all three compounds. The molecules **117** have approximate D_2 symmetry, although the eight-membered rings are not completely planar. All three derivatives have in common short metal–metal distances (M—M **117a** 2.425 Å, **117b** 2.655 Å, **117c** 2.644 Å). In the case of copper and silver these distances can be interpreted by assuming very weak metal–metal interactions. For $d^{10}d^{10}$ interactions in gold compounds, however, the distance



117a M = Cu

117b M = Ag

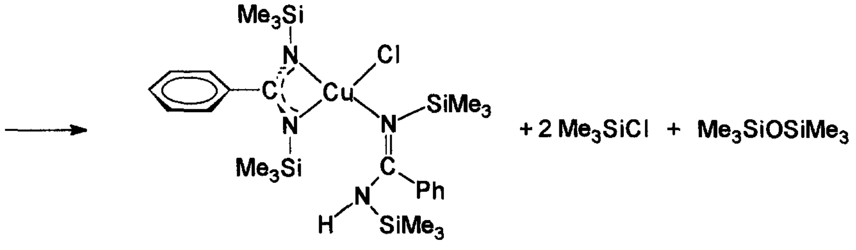
117c M = Au

of 2.644 Å is unusually short. Relativistic effects are thought to be responsible for this type of interaction and normally an Au···Au distance of approximately 3.00 Å or less is regarded a bonding interaction [128,129]. In **117c** the Au—Au distance even comes close to the covalent Au—Au bond length in the gold(II) complex $Et_2P[CH_2{-}Au(Cl){-}CH_2]_2PEt_2$ (Au—Au 2.597 Å [130]).

A copper(II) benzamidinate **118** was prepared by the reaction of copper(II) chloride with **1a** in acetonitrile solution in the presence of traces of water (reaction 88) [131]. Compound **118** was isolated in 54% yield in the form of dark green, moisture-sensitive crystals. In the monomeric molecule, three nitrogens and one chlorine atom form a distorted tetrahedron around the central copper atom [131]. One *N,N′*-bis(trimethylsilyl)benzamidinate ligand is coordinated in the normal chelating fashion, while partial hydrolysis has led to the formation of a neutral *N,N′*-bis(trimethylsilyl)benzamidine donor ligand. As in the chelating ligand the C—N bond lengths are almost equal (1.30 and 1.35 Å). This can be explained by participation of the resonance structure **B** in the bonding.

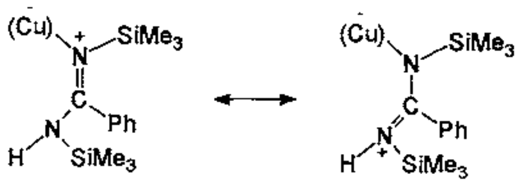
$2CuCl^2 + 4PhC({=}NSiMe_3)[N(SiMe_3)_2] + H_2O$ (88)

1a



118

In addition to the gold(I) derivative **117c** the chelating $[PhC(NSiMe_3)_2]^-$ ligand is also able to stabilize an $AuCl_2^+$ fragment. $[PhC(NSiMe_3)_2]AuCl_2$ (**119**) has been prepared by a reaction analogous to reaction 22 from anhydrous $AuCl_3$



A **B**

and **1a** in CH_2Cl_2 suspension [132]. In the course of this exothermic reaction the insoluble gold trichloride dissolves completely. Cooling of the concentrated solution afforded orange-red, moisture-sensitive crystals of **119** in 90% yield. In the square-planar, monomeric molecule the central gold atom is coordinated by two nitrogen atoms of the chelating benzamidinate ligand (Au—N 2.106(7) and 2.303(6) Å) and two chlorine atoms (Au—Cl 2.279(3) and 2.285(2) Å [132].

Only one fully characterized zinc benzamidinate has so far been described. $[PhC(NSiMe_3)_2]_2Zn$ (**120**) was obtained as a white crystalline solid by reacting anhydrous $ZnCl_2$ with two equivalents of $Na[PhC(NSiMe_3)_2]\cdot 0.5Et_2O$ (**7a**) in THF solution (55% yield) [65]. Similar experiments to synthesize a mercury(II) benzamidinate failed. $HgCl_2$ or $Hg(O_2CCH_3)_2$ did not react with **1a** even after prolonged heating of the components in refluxing acetonitrile. A remarkable disproportionation reaction took place, however, when a suspension of mercury(I) acetate in acetonitrile was treated with **1a** (reaction 89) [133].

$$Hg_2(O_2CCH_3)_2 + \underset{\textbf{1a}}{2PhC({=}NSiMe_3)[N(SiMe_3)_2]}$$

$$\rightarrow \underset{\textbf{121}}{[PhC(NSiMe_3)_2]_2Hg} + Hg + 2Me_3SiOSiMe_3 \tag{89}$$

The elemental mercury formed in this reaction was removed by vacuum distillation. The resulting white, needle-like crystals were characterized by IR spectroscopy and an X-ray structure determination (Fig. 9). Compound **121** forms a nearly centrosymmetric molecule with an sp-hybridized Hg atom (Hg—N 2.07 Å (average), N—Hg—N 174.6(3)°) [133]. This is so far the only example of a coordination compound containing monodentate *N,N'*-bis(trimethylsilyl)benzamidinate ligands.

6. F-ELEMENT CHEMISTRY OF *N,-N'*-BIS(TRIMETHYLSILYL)BENZAMIDINATE LIGANDS

The use of bulky heteroallylic ligands such as the N-silylated benzamidinate anions has had a major impact on rare earth and actinide coordination chemistry in recent years. Several ligand systems such as $[RC_6H_4C(NSiMe_3)_2]^-$, $[PhC(NSiMe_3)_2]^-$ and $[Ph_2P(NSiMe_3)_2]^-$ have been extensively employed in lanthanide and actinide chemistry and found to be highly useful for these elements in

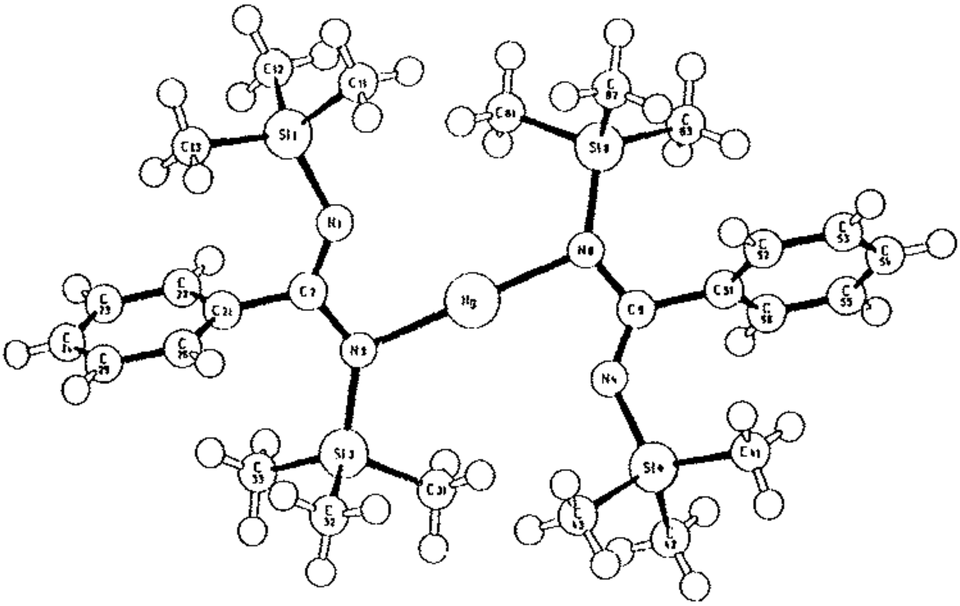
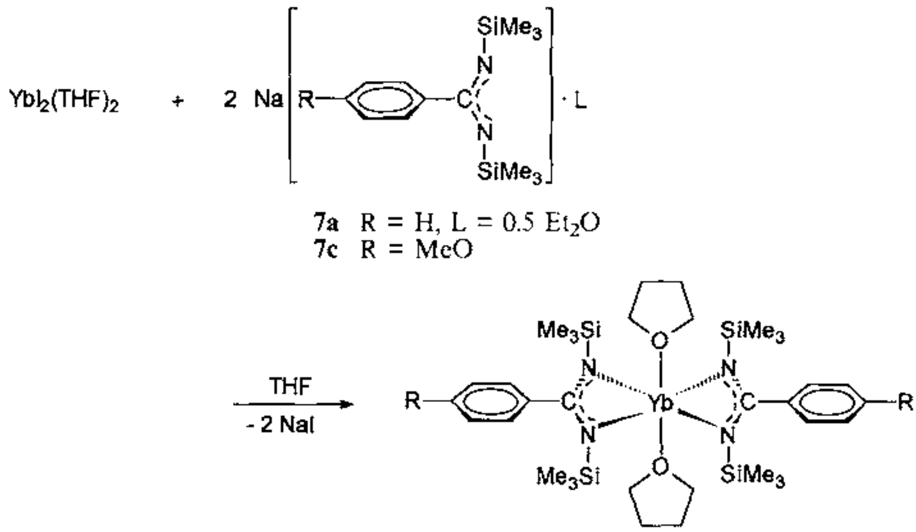


Fig. 9.

particular. Bulky heteroallylic ligands seem to be capable of stabilizing relatively low coordination numbers around the large 4f and 5f ions by forming sterically saturated disubstituted and trisubstituted coordination compounds with these elements. The chemistry of lanthanide complexes has recently been summarized in two review articles [91,92].

Soluble, very reactive ytterbium(II) benzamidinates (**122a,b**) have been prepared by treating freshly prepared YbI_2 in THF solution with two equivalents of sodium *N,N'*-bis(trimethylsilyl)benzamidinates **7** (reaction 90) [134]. The dark red, crystalline complexes **122** are highly air sensitive and remarkably soluble in nonpolar organic solvents such as toluene or even hexane. Aliphatic hydrocarbons are the solvents of choice for recrystallization of these divalent lanthanide complexes. The presence of divalent ytterbium was clearly demonstrated by ^{171}Yb NMR spectroscopy as well as an X-ray structure determination of **122a** (Fig. 10) [134]. The central ytterbium atom is in a distorted octahedral coordination environment with the THF ligands occupying the trans positions. The Si−N−C−N−Si units of the chelating benzamidinate ligands are planar and the dihedral angle between the two planes is 26.3°. This value compares favorably with the torsion angle between the two four-membered CrNCN rings in the chromium(II) benzamidinate **95a** (22.8°) [65]. The Yb−N bond distances (average 2.48 Å) are comparable with those in $Na[Yb^{II}\{N(SiMe_3)_2\}_2]$ (Yb−N 2.38, 2.44, 2.47 Å [135]). A large dihedral angle (77.3°) between the phenyl rings and the amidinate units precludes any conjugation between those two π-systems [134].



(90)

7a R = H, L = 0.5 Et_2O
7c R = MeO

122a R = H
122b R = MeO

A rare example of tetracoordination around ytterbium was observed in the unsolvated ytterbium(II) benzamidinate complex $[PhC_6H_4C(NSiMe_3)_2]_2Yb$ (**123**) [134]. In general, ytterbium(II) compounds are strong reducing agents ($E^0(Yb^{3+}/Yb^{2+}) = -1.15$ V [136]). Both complexes **122a** and **122b** undergo various redox reactions, i.e. with alkyl halides, disulfides, diselenides and ditellurides. In

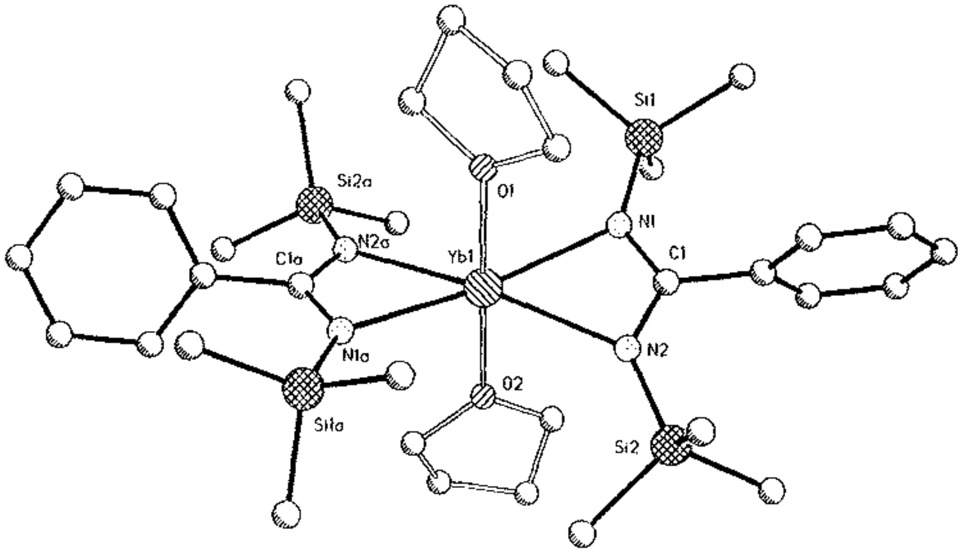
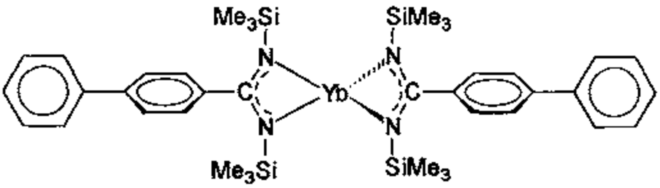


Fig. 10.

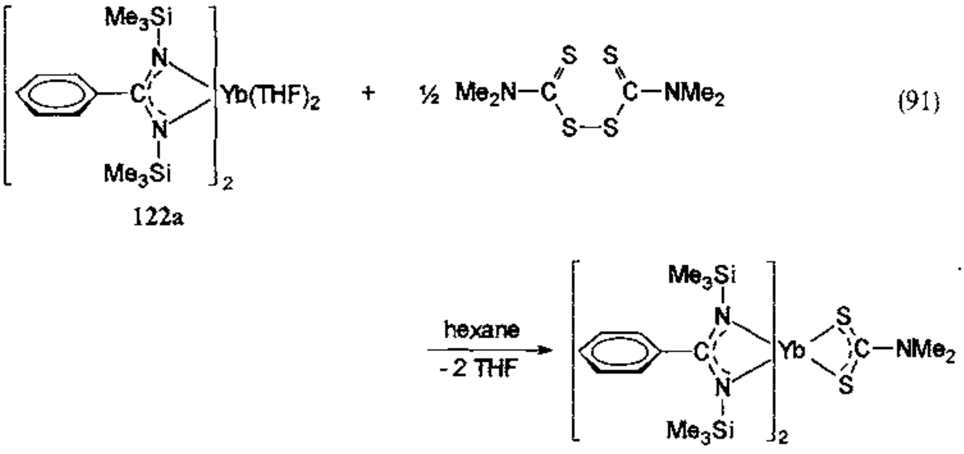


123

particular, the reductive cleavage of E—E bonds has been demonstrated to be an elegant way of preparing lanthanide(III) coordination compounds containing soft donor ligands [137–139]. For example, the sulfur–sulfur bond in $[Me_2NC(S)S]_2$ is readily cleaved on treatment with stoichiometric amounts of **122a**. The resulting ytterbium(III) dithiocarbamate complex **124** can be isolated as a colorless crystalline solid in 33% yield (reaction 91). According to the X-ray structure determination, **124** contains a bent $[PhC(NSiMe_3)_2]_2Yb$ unit and thus somewhat resembles the bent metallocene derivatives containing $(C_5Me_5)_2Ln$ units (Fig. 11). The two trans coordinated THF ligands present in the ytterbium(II) starting material have been replaced by the chelating dimethyldithiocarbamate ligand [134].

Similarly, diaryl diselenides and ditellurides are reductively cleaved by **122a** or **122b** to give stable ytterbium(III) benzamidinate complexes containing Yb—Se or Yb—Te bonds respectively (reaction 92) [134,140].

The chalcogenolate derivatives **124–126** exhibit strongly temperature-dependent ^1H NMR spectra, which have been discussed in detail [140]. In addition, the molecular structures of **125a** and **125b** have been determined by X-ray diffraction. Figure 12 shows the molecular structure of the mesitylselenolate derivative **125b**. Compound **125b** is a rare example of a monomeric ytterbium(III) selenolate. Once



(91)

122a

124

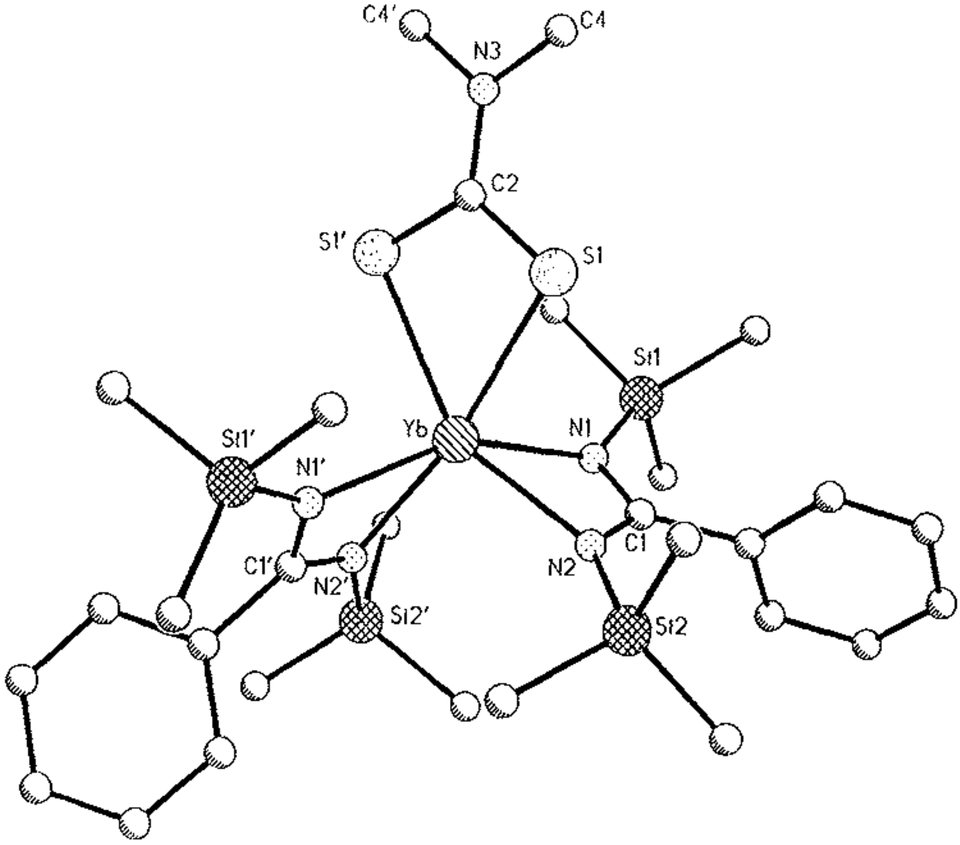
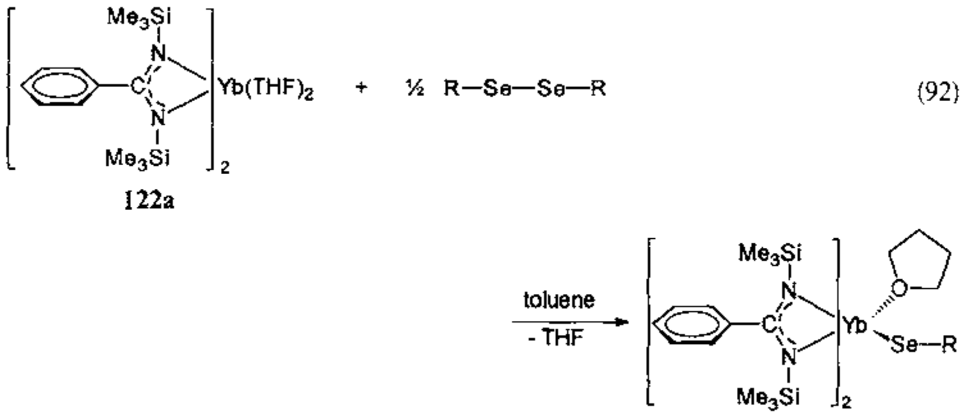


Fig. 11.

again, the $[PhC(NSiMe_3)_2]_2Yb$ unit is bent. The overall asymmetrical structure is retained in solution, as reflected by the ^1H NMR spectrum of **125b** [140].

Starting from anhydrous lanthanide trichlorides and sodium *N,N'*-bis(trimethylsilyl)benzamidinates 7, a large number of homoleptic lanthanide tris-(benzamidinates) (**127**) has been prepared (reaction 93) [17]. All homoleptic lanthanide(III) benzamidinates have in common that they are highly soluble in non-polar organic solvents. In particular, the solubility of $[PhC(NSiMe_3)_2]_3Ln$ and $[CF_3C_6H_4C(NSiMe_3)_2]_3Ln$ in pentane or hexane is very high. In all cases the good solubility in hydrocarbon solvents can be attributed to the presence of six trimethylsilyl groups in the molecules. However, the lanthanide(III) benzamidinates **127** are very susceptible to hydrolysis. Initial experiments have indicated that these complexes may serve as useful precursors for lanthanide-based materials such as Ln_2O_3, Ln_2S_3, Ln_2Se_3 etc. In particular, lanthanide oxides can be prepared from the lanthanide benzamidinates via sol–gel procedures [91,141].

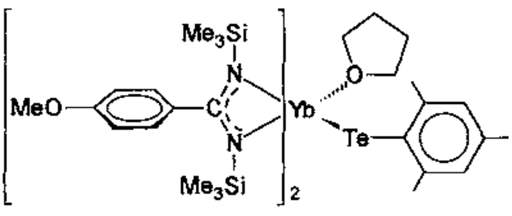
The lanthanide *N,N'*-bis(trimethylsilyl)benzamidinates **127** has been thor-



122a

125a R = Ph
125b R = Mes

(92)



126

oughly studied by various spectroscopic methods [17,142]. Absorption and emission measurements revealed that the three benzamidinate ligands produce an unusually large crystal field which is comparable with that of cyclopentadienyl. The crystal and molecular structure of $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$ has been determined by X-ray crystallography [17]. The coordination geometry around the central six-coordinate praseodymium atom is distorted octahedral. Torsion angles between the phenyl rings and the NCN heteroallylic units are between 66.9° and 88.6°. The Pr—N distances are remarkably short (average 2.48 Å). Pr—N bond distances in other structurally characterized coordination compounds of praseodymium are ca. 0.15–0.30 Å longer than in $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$. Such examples include $[Pr(bipy)_6](ClO_4)_3$ (Pr—N 2.735–2.768 Å [143]) and $[Pr(terpy)Cl(H_2O)_5]Cl_2$ (Pr—N 2.625, 2.635 Å [144]).

The homoleptic lanthanide(III) benzamidinates **127** can be regarded as steric analogs of the well known tris(cyclopentadienyl) complexes $(C_5H_5)_3Ln$ [145]. A characteristic reactivity pattern of the homoleptic cyclopentadienyl complexes is the formation of Lewis base adducts of the type $(C_5H_5)_3Ln(B)$ (B = MeCN, EtCN, THF, $C_6H_{11}NC$, esters etc.) [146]. Most recently it was discovered that the homoleptic lanthanide benzamidinates $[RC_6H_4C(NSiMe_3)_2]_3Ln$ (**127**) form similar adducts

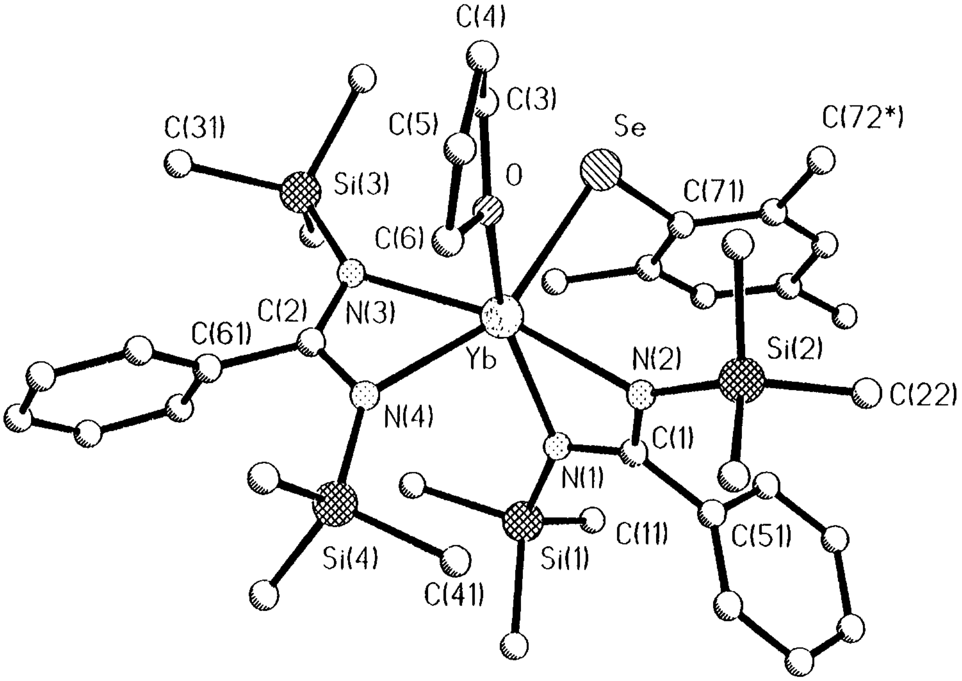
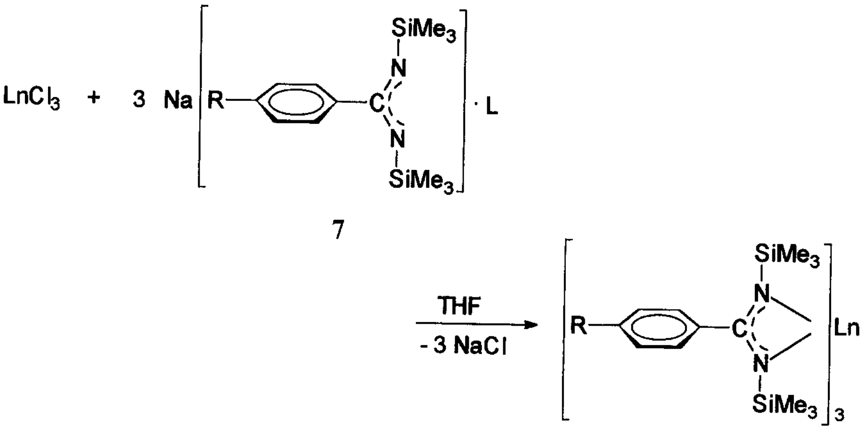


Fig. 12.



(93)

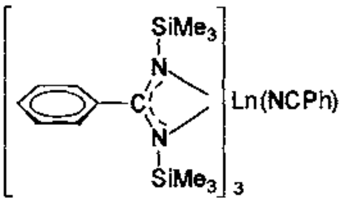
7

127

Ln = Sc, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu

R = H, MeO, CF_3, Ph

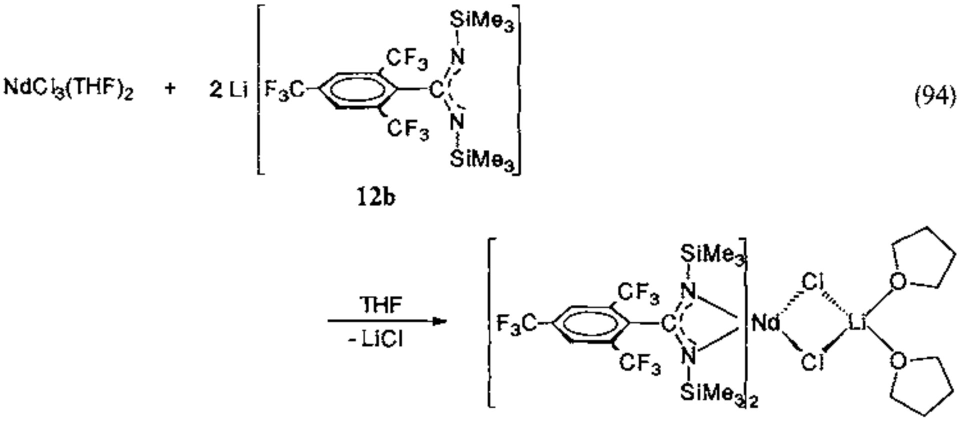
with THF and nitrile ligands such as MeCN and PhCN. The molecular and crystal structures of two benzonitrile adducts (**128a,b**) have been determined [122]. Obviously even three bulky silylated benzamidinate ligands leave enough room in the coordination sphere of the lanthanide ions to allow the addition of "slim" ligands such as MeCN or PhCN.



128a Ln = Sm

128b Ln = Eu

More important for the design of potential new lanthanide catalysts containing benzamidinate and related ligands is the preparation of disubstitution products [147,148]. A rational synthesis of disubstituted lanthanide(III) benzamidinates utilizes the most bulky *N,N'*-bis(trimethylsilyl)benzamidinate ligands, especially the nonafluoromesityl derivative $[(CF_3)_3C_6H_2C(NSiMe_3)_2]^-$. Anhydrous neodymium trichloride reacts with two molar equivalents of $Li[(CF_3)_3C_6H_2C(NSiMe_3)_2]$ (**12b**) to give exclusively the sky-blue neodymium "ate" complex **129** (reaction 94) [149]. Compound **129** can be regarded as an analog of the well known organoneodymium complex $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ [150]. This, in turn, is an important starting material for the synthesis of organoneodymium homogeneous catalysts such as $(C_5Me_5)_2NdCH(SiMe_3)_2$ and $[(C_5Me_5)_2Nd(\mu\text{-}H)]_2$ [151,152]. In this respect compound **129** represents a novel class of precursors for lanthanide-based homogeneous catalysts free of cyclopentadienyl ligands. Initial experiments have already shown



(94)

12b

129

that derivatives such as $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2NdCH(SiMe_3)_2$ (**130**) and $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2NdN(SiMe_3)_2$ (**131**) are available from **129** through simple metathetical reactions [93].

The molecular and crystal structure of **129** has been determined by X-ray diffraction (Fig. 13) [149]. The central neodymium atom is surrounded in a distorted octahedral fashion by two chelating benzamidinate ligands and two chlorine atoms. These chlorine atoms act as bridging ligands between neodymium and lithium. The four-membered Nd—N—C—N rings are almost planar (dihedral angles N—Nd—N/N—C—N 179.6° and 170.8° respectively). The most notable structural feature is the bent arrangement of the two bulky benzamidinate ligands which makes **129** an analog of the bent lanthanide metallocene complexes containing $(C_5Me_5)_2Ln$ units.

An unusual binuclear neodymium(III) benzamidinate was isolated by recrystallizing compound **129** from dimethoxyethane. This resulted in the formation of the

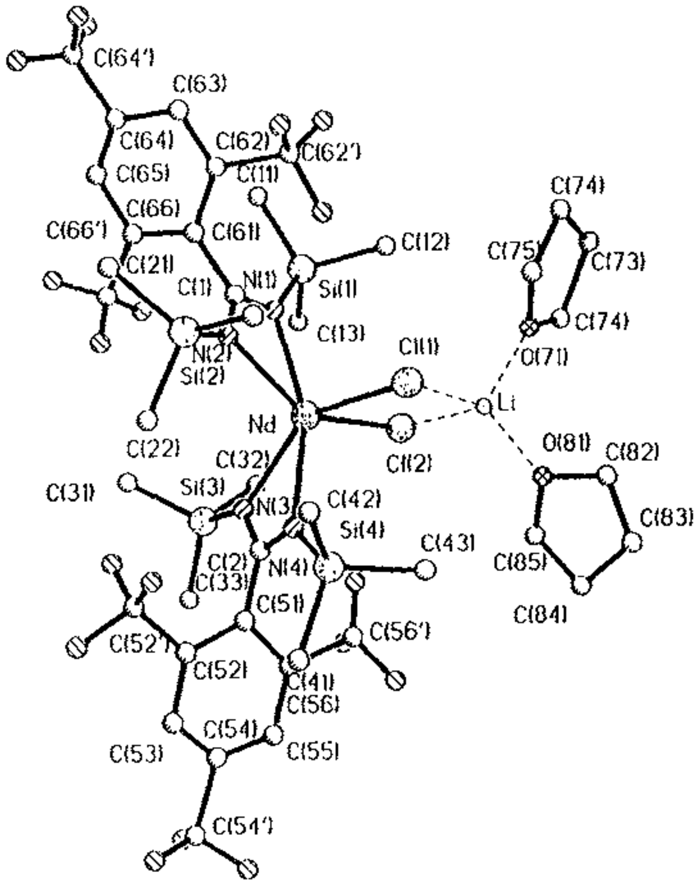


Fig. 13.

DME bridged complex (μ-DME)[{$(CF_3)_3C_6H_2C(NSiMe_3)_2$}$_2$Nd($\mu$-Cl)$_2$Li(THF)]$_2$ (**132**). The molecular structure of this material was determined by X-ray crystallography (Fig. 14) [149].

Uranium(IV) derivatives are the most thoroughly investigated class of actinide metal *N,N'*-bis(trimethylsilyl)benzamidinates [14,153]. Depending on the stoichiometry, anhydrous uranium tetrachloride reacts with lithium or sodium *N,N'*-bis(trimethylsilyl)benzamidinates to give disubstituted or trisubstituted products. The uranium bis(benzamidinates) **133** have been isolated as light green (**133a,c**) or light brown (**133b**) air-sensitive solids by treatment of UCl_4 with two equivalents of lithium *N,N'*-bis(trimethylsilyl)benzamidinates **2** (reaction 95) [14,153]. The straightforward formation of the disubstituted uranium benzamidinates **133** is in marked contrast to the corresponding cyclopentadienyl uranium chemistry. There the complex $(C_5H_5)_2UCl_2$ is unstable with respect to disproportionation and cannot be isolated [154–156]. When UCl_4 is treated with C_5H_5Tl (molar ratio 1:2) in

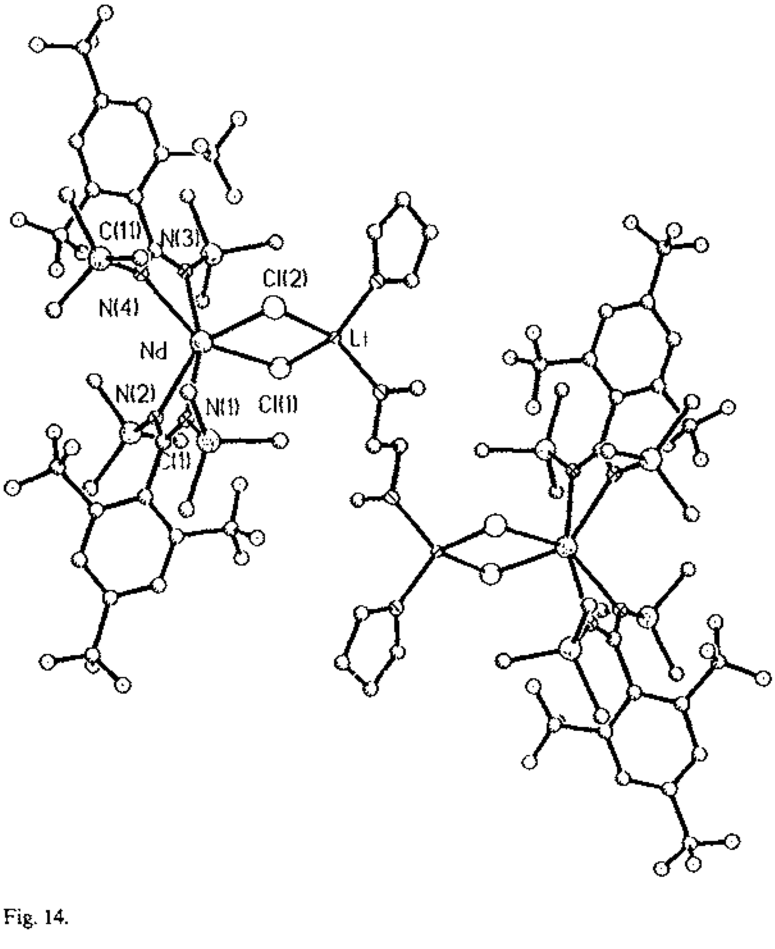


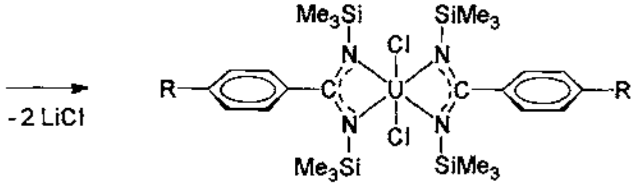
Fig. 14.

$$UCl_4 \; + \; 2\,Li[RC_6H_4C(NSiMe_3)_2] \qquad (95)$$

2a R = H

2b R = Me

2c R = MeO



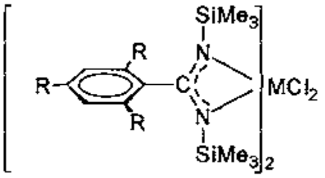
133a R = H

133b R = Me

133c R = MeO

DME solution, a mixture of $C_5H_5UCl_3(DME)$ and $(C_5H_5)_3UCl$ is obtained [155]. A similar ligand redistribution is not observed in the case of the uranium benzamidinates.

Lithium salts of the very bulky N-silylated benzamidinate anions $[(CF_3)_3C_6H_2C(NSiMe_3)_2]^-$ and $[Me_3C_6H_2C(NSiMe_3)_2]^-$ react with UCl_4 to give exclusively the disubstituted complexes **134a** and **134b** [14]. No other uranium-containing products were observed even when the lithium benzamidinates were used in excess. Similarly, the thorium(IV) derivative **134c** was prepared by reacting anhydrous $ThCl_4$ with two equivalents of $Li[(CF_3)_3C_6H_2C(NSiMe_3)_2]$ (**12b**). With respect to the exclusive formation of disubstitution products, the bulky benzamidinate anions very much resemble the pentamethylcyclopentadienyl ligand $C_5Me_5^-$. Uranium and thorium tetrachloride were reported to react with pentamethylcyclopentadienyl reagents to give $(C_5Me_5)_2UCl_2$ and $(C_5Me_5)_2ThCl_2$ as the only organoactinide products [157,158]. Here too, no trisubstituted species were detected.



134a M = U, R = Me

134b M = U, R = CF_3

134c M = Th, R = CF_3

The uranium bis(benzamidinate) **134b** forms yellow-brown, needle-like crystals, which are air sensitive but thermally highly stable. The compound melts without decomposition at 215°C! The molecular structures of **134b** and **134c** have been determined by X-ray crystallography [14]. The coordination geometry in the two isostructural complexes is distorted octahedral. With 2.54 Å the U—Cl bond length is almost identical with the uranium–chlorine distance in $(C_5H_5)_3UCl$. The Cl—M—Cl angles are 99° (**134b**) and 100° (**134c**) and are thus very similar to the corresponding angle in $[PhC(NSiMe_3)_2]_2TiCl_2$ (**80a**, Cl—Ti—Cl 98.6° [48]).

The reaction of anhydrous UCl_4 with three equivalents of lithium or sodium *N,N'*-bis(trimethylsilyl)benzamidinates afforded the tris(benzamidinato)uranium chlorides **135** in high yields (reaction 96) [14,153]. The complexes **135** are obtained as green crystalline solids which are sensitive to air and moisture but thermally highly stable. Owing to their good solubility they can be recrystallized from non-polar organic solvents such as benzene, cyclohexane or hexane. The temperature-dependent ^{1}H NMR spectra of the complexes **135** have been studied in detail. X-ray crystal structure determinations of **135a** and **135d** revealed an interesting "propeller"-like molecular structure (Fig. 15, **135a**) [17].

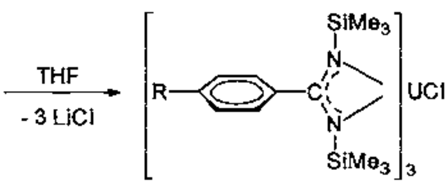
$$UCl_4 + 3Li[RC_6H_4C(NSiMe_3)_2] \qquad (96)$$

2a R = H

2b R = Me

2c R = MeO

2d R = CF_3



135a R = H

135b R = Me

135c R = MeO

135d R = CF_3

The coordination geometry around the seven-coordinate uranium can be described as capped-octahedral. In Fig. 15 the molecule is viewed along the chlorine–uranium axis. Owing to the "propeller"-like structure, three trimethylsilyl groups are in a cis position with respect to the chlorine ligand and the other three are arranged

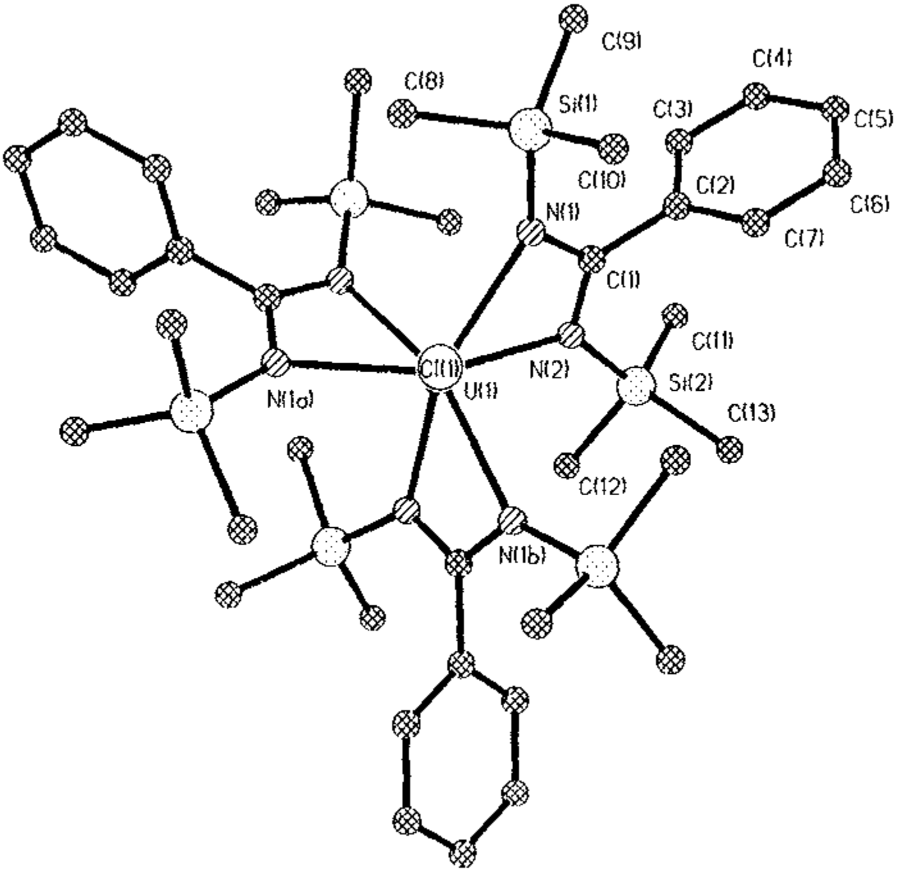
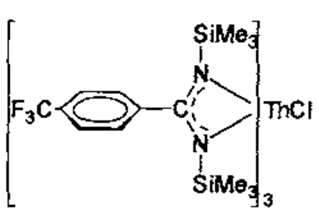


Fig. 15.

on the opposite side of the chlorine. This accounts for the fact that in the ^{1}H NMR spectrum two signals are observed for the $SiMe_3$ protons (e.g. **135a** δ 1.24 and -3.00 ppm [153]). The four-membered U−N−C−N rings deviate even more from planarity than the corresponding ring systems in **129** (dihedral angles N−U−N/N−C−N 167°–173°) [14].

A corresponding thorium(IV) tris(benzamidinate) (**136**) was made in 38% yield



136

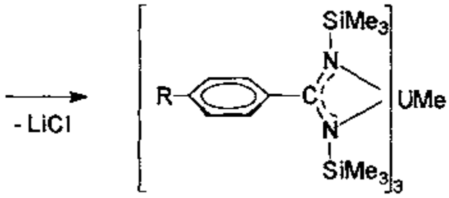
by treating anhydrous $ThCl_4$ with three molar equivalents of **2d**. The colorless crystals are readily soluble in toluene or THF and thermally highly stable. So far no derivative chemistry of the thorium benzamidinates **134c** and **136** have been reported. Several uranium benzamidinates, however, have been found to be interesting starting materials for novel σ-alkyl complexes of uranium stabilized by *N,N'*-bis(trimethylsilyl)benzamidinate ligands. Three stable uranium σ-methyl complexes (**137**) have been prepared by reacting the corresponding chloro complexes with methyllithium followed by recrystallization of the crude products from cyclopentane (reaction 97) [159].

$$[RC_6H_4C(NSiMe_3)_2]_3UCl + MeLi \tag{97}$$

135a R = H

135c R = MeO

135d R = CF_3



136a R = H

137b R = MeO

137c R = CF_3

The benzamidinate-stabilized uranium alkyls form bright green, highly air-sensitive crystals which are thermally very stable. The melting points of all three compounds are around 230°C. Compared with the starting chloro complexes the methyl derivatives exhibit an even better solubility in hexane and other non-polar organic solvents. The presence of a methyl group σ-bonded to uranium is clearly seen in the ^1H NMR spectra of **137** (δ −34.8 (**137a**), −35.9 (**137b**), −29.6 (**137c**) (s, CH_3)). The temperature-dependent ^1H NMR spectra of these complexes have been studied in detail. In addition, the molecular structure of **137a** has been studied by X-ray diffraction [159]. As expected, the molecular structure of **137a** is very similar to that of the parent chloro complex **135a**. The bond distance of the uranium–carbon bond is 2.498(5) Å. This value is in good agreement with previously reported U−C bond lengths (e.g. 2.48 Å in $U[CH(SiMe_3)_2]_3$ [160] and 2.43 Å in $(C_5H_5)_3UMe$ [161]).

A stable dimethyluranium complex, $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2UMe_2$ (**138**), was made similarly by reacting **134b** with two equivalents of methyllithium (55%

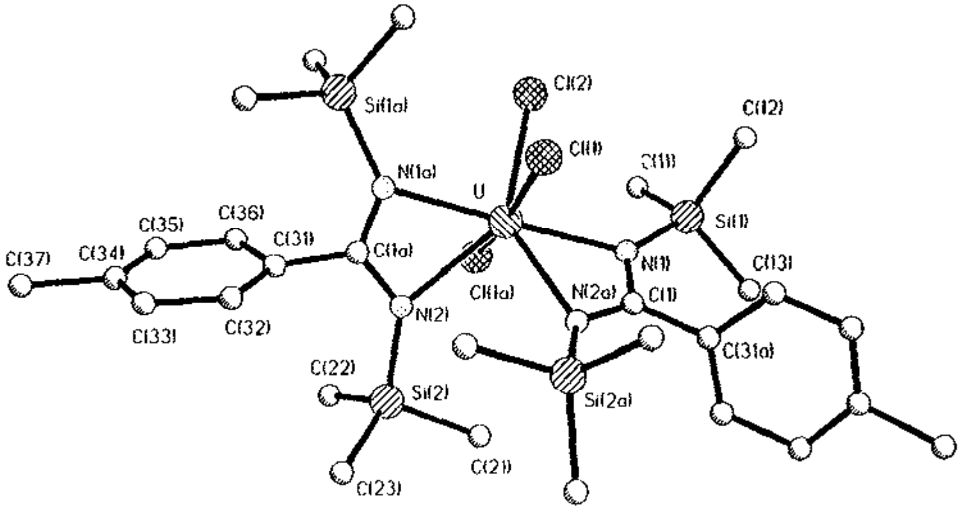


Fig. 16.

yield). Compound **138** can be regarded as a benzamidinate analog of the known complex $(C_5Me_5)_2UMe_2$ [158]. It forms olive-green crystals which are highly soluble in hydrocarbon solvents [159]. The ^1H NMR spectrum shows a signal attributable to the σ-methyl groups at -29.5 ppm.

Two borohydride derivatives of the type $[RC_6H_4C(NSiMe_3)_2]_3UBH_4$ (**139**) have been synthesized by reacting the chloro derivatives with a large excess of $NaBH_4$ in THF solution (reaction 98) [159]. IR data for **139** showed that the borohydride anion acts as tridentate ligand towards uranium. No further derivative chemistry of the complexes **137–139** has been carried out although it can be anticipated that these complexes could serve as very useful starting materials in actinide chemistry.

$$[RC_6H_4C(NSiMe_3)_2]_3UCl + NaBH_4 \rightarrow [RC_6H_4C(NSiMe_3)_2]_3UBH_4 + NaCl \quad (98)$$

135a R = H **139a** R = H

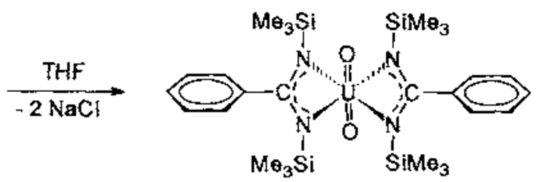
135c R = MeO **139b** R = MeO

Finally, it was found that the *N,N′*-bis(trimethylsilyl)benzamidinate ligands form stable complexes with uranium in high oxidation states [153,162]. An unusual benzamidinate derivative of uranium pentachloride was prepared by reacting UCl_4 with two equivalents of $MeC_6H_4C(=NSiMe_3)[N(SiMe_3)_2]$ (**1b**) followed by controlled air-oxidation of the reaction mixture (reaction 99). Glistening black crystals of **140** have been isolated in 11% yield after recrystallization from hexane. This compound is the first stable substitution product of uranium pentachloride. Its molecular structure was determined by X-ray crystallography (Fig. 16) [162]. The coordination geometry around the seven-coordinated uranium atom can be described as a distorted pentagonal bipyramid. The uranium–chlorine distances (2.527(4) and 2.568(5) Å respectively) are slightly shorter than in the uranium(IV) benzamidinate $[PhC(NSiMe_3)_2]_3UCl$ (**135a**, U–Cl 2.660(9) Å [14]).

$$UCl_4 + 2\underset{\mathbf{1b}}{MeC_6H_4C(=NSiMe_3)[N(SiMe_3)_2]} \xrightarrow{O_2} \underset{\mathbf{140}}{[MeC_6H_4C(NSiMe_3)_2]_2UCl_3} \qquad (99)$$

A stable *N,N'*-bis(trimethylsilyl)benzamidinate derivative of uranium(VI) has been prepared by treatment of uranyl chloride with **7a** (reaction 100). The orange-yellow crystals of **141** are hydrocarbon soluble and only moderately moisture sensitive. *N,N'*-bis(trimethylsilyl)benzamidinate complexes of actinide metals other than uranium and thorium have not been described so far.

$$UO_2Cl_2 + Na[PhC(NSiMe_3)_2] \cdot 0.5Et_2O \qquad (100)$$



141

7. CONCLUSIONS AND FUTURE OUTLOOK

Within a few years N-silylated benzamidines have become very versatile building blocks in main group and coordination chemistry. The neutral species $RC_6H_4C(=NSiMe_3)[N(SiMe_3)_2]$ (**1**) and the lithium or sodium salts of the corresponding anions, $[RC_6H_4C(NSiMe_3)_2]^-$, are excellent precursors for novel inorganic heterocycles as well as various transition metal and f-element complexes. Their synthetic potential in the preparation of inorganic ring systems is far from being exhausted. In addition, very little is known about the reactivity of *N,N'*-bis(trimethylsilyl)benzamidinate ligands coordinated to transition metals. Owing to their excellent solubility, transition metal and f-element benzamidinates appear to be promising precursors in materials science, especially with the use of sol–gel processes. The *N,N'*-bis(trimethylsilyl)benzamidinate ligands discussed in this article combine several favorable properties. First of all, they are promising new observer ligands for transition metals as they contain different NMR-observable nuclei. Most important, however, they are "steric cyclopentadienyl equivalents" and in many respects they match the chemistry of the well known transition metal cyclopentadienyl complexes. Thus the N-silylated benzamidinates and related heteroallylic ligands offer the possibility of designing new homogeneous catalysts without the use of cyclopentadienyl ancillary ligands. This is likely to be the most exciting future application of *N*,*N*′-bis(trimethylsilyl)benzamidinate ligands in transition metal and f-element chemistry.

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