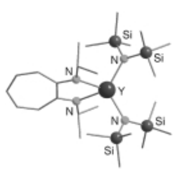
# The co-ordination chemistry of aminotroponiminates†



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**This article reviews recent progress of main group and transition metal complexes of *N,N′*-disubstituted aminotroponiminates and mono-bridged bis(aminotroponiminate)s. Recent developments have shown that aminotroponiminates can stabilise low valent main group metals and that they can be used in early transition metal chemistry as cyclopentadienyl alternatives. The structural properties and the reactivity of these complexes as well as the catalytic and synthetic applications of aminotroponiminate complexes will be outlined in this article.**

## 1 Introduction

Over the past 15 years an enormous progress has been observed in the design and application of organometallic compounds as $\alpha$-olefin polymerisation catalysts. The vast majority of the investigated compounds have been metallocenes and amidocyclopentadienyl (constrained geometry) complexes of group 4 metals. Since it is known that one class of catalysts cannot control all product parameters there is considerable interest in finding a new generation of catalysts.[1] One synthetic approach for the design of the new catalysts is the incorporation of non-cyclopentadienyl ligands into the co-ordination sphere of the metal. It has been shown that some group 4 as well as some late transition metal amido complexes are very active catalysts for olefin polymerisation. The reason for the high activity of these amido complexes compared to metallocenes is a lower electron density at the centre metal which most likely increases its electrophilicity. Today a number of research groups are investigating various main and transition metal complexes with bi- and multidentate amides and amidinates as ligands in the co-ordination sphere.[1,2] Amidinates are mono anionic ligands which formally may be considered as a combination of an amido and an imido donor. The most prominent example of this class are the benzamidinates which form four-membered metallacycles[3,4] and aminotroponiminates which can form five-membered metallacycles upon co-ordination to a metal atom.

Aminotroponiminates ($\{(R)_2ATI\}^-$) (**A**) are bidentate, monoanionic ligands containing a 10 $\pi$-electron backbone. Like 1,4-diazabutadiene, $\{(R)_2ATI\}^-$ can form five-membered metallacycles upon co-ordination to a metal atom. In contrast to 1,4-diazabutadiene, $\{(R)_2ATI\}^-$ is believed to be much less reactive towards electrophiles and nucleophiles. The aminotroponiminate ligand system was introduced into co-ordination chemistry in the 1960s by researchers from DuPont. Between 1961 and 1970 a large number of chromium(II), manganese(II), iron(II), cobalt(II) nickel(II) and copper(II) complexes were prepared in order to study their magnetic moments and NMR contact shifts. However only one complex (manganese) was characterised by single crystal X-ray methods.[5] Bis(aminotroponiminate) complexes of these metals are known, with both square planar and tetrahedral metal geometries. In the case of nickel(II), equilibrium mixtures of the two limiting structures have been characterised by magnetic studies and temperature-dependent NMR experiments for a range of *N,N′*-disubstituted aminotroponiminates. The early work with this ligand was reviewed by R. H. Holm in 1971.[6] For nearly 25 years almost no research in this field has been published. On the other hand, complexes with double bridged aminotroponiminates (tropocoronands $\{H_2(TC\text{-}n,m)\}$) (**B**) have been intensively studied by S. J. Lippard.[7–9] Complexes of the first row transition metals such as manganese, iron, cobalt, nickel, copper, and zinc were the most thoroughly investigated. It was demonstrated that metal tropocoronand complexes have properties of structure and reactivity which are distinct from their porphyrin or salen counterparts. Part of this work was reviewed in 1986.[7] Then, in 1995 the development of a new and convenient $H\{(R)_2ATI\}$ synthesis started a renaissance of the ligand. It was shown that $\{(R)_2ATI\}^-$ acts in co-ordination chemistry in a similar way to other well-known systems such as benzamidinates and guanidinates.[10] Due to the presence of the highly delocalised $\pi$-electron system, the planar $\{(R)_2ATI\}^-$ ligand framework shows minimal reactivity towards most nucleophiles and electrophiles.

The present article deals with metal complexes of *N,N′*-disubstituted aminotroponiminates, $H\{(R)_2ATI\}$, (**A**) as well as of mono bridged bis(aminotroponiminate)s (**C**). This review covers published material from 1995 through to early 2000.

## 2 Complexes of *N,N′*-disubstituted aminotroponiminates

### 2.1 Ligand synthesis

$H\{(R)_2ATI\}$ was originally prepared by a reaction of primary amines with 5,5,6,6-tetrafluoro-1,3-cycloheptadiene, which it-

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† Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday.

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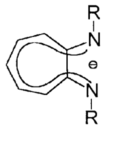
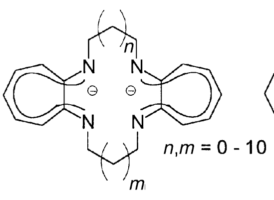
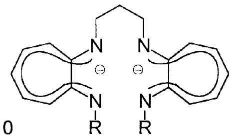


**A**



**B**



**C**

self can be obtained in a two-step synthesis from cyclopentadiene and tetrafluoroethene (Scheme 1).[11]

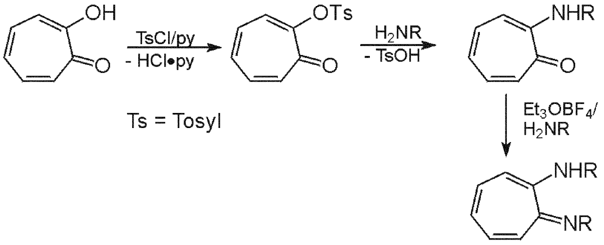
Today H{(R)$_2$ATI} is typically made by a three-step procedure starting with tropolone. In the first step, tropolone is tosylated by reaction with tosyl chloride. The second step involves the direct nucleophilic displacement of the tosyl group on the 2-(tosyloxy)tropone using excess of primary amine. In the third step, the 2-alkylaminotropone is ethylated with $Et_3O{\bullet}BF_4$ and then treated with excess primary amine to obtain H{(R)$_2$ATI} as bright yellow solid (Scheme 2).[10]

## 2.2 Main group metal complexes

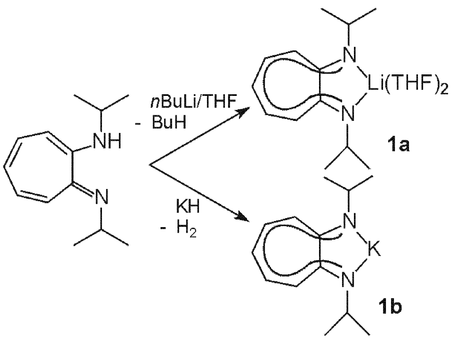
Alkali salts of aminotroponimines are usually obtained by deprotonation of the neutral ligand. Thus, lithium *N*-isopropyl-2-(isopropylamino)troponiminate, [{(*i*Pr)$_2$ATI}Li(THF)$_2$] (**1a**) was prepared by treatment of H{(*i*Pr)$_2$ATI} with 1 equivalent of *n*BuLi in THF (Scheme 3).[12] In a similar procedure, lithium salts of different substituted aminotroponimines {(R)$_2$ATI}Li were obtained. Compound **1a** is the first structurally characterised alkali metal salt of an aminotroponiminate. The molecular structure consists of lithium atom chelated by the aminotroponiminate ligand and to which two THF molecules are co-ordinated. **1a** exhibits a twisted configuration for the $LiN_2C_7$ moiety with a dihedral angle of 16.9° between the $LiN_2C_2$ ring and the seven-membered ring.[12] {(*i*Pr)$_2$ATI}K (**1b**) was synthesised by treatment of the neutral ligand with an excess of KH in THF (Scheme 3).[13,14]

The reaction of **1a** with $CaI_2$ led either to the lithium compound [{(*i*Pr)$_2$ATI}Li$_2$(THF)(I)] or to the ate-complex [{(*i*Pr)$_2$ATI}Ca(THF)$_2$I$_2$Li$_2$(THF)$_2${(*i*Pr)$_2$ATI}] depending on the reaction conditions.[15] Both compounds, in which the lithium atoms occupy positions above and below the plane of an aminotroponiminate ligand, were characterised by single crystal X-ray crystallography. The calcium atom in the ate-complex adopts a pseudo-octahedral geometry with two THF molecules occupying the *trans*-positions, and the iodides in *cis*-co-ordination sites.

The aluminium derivatives, [{(*i*Pr)$_2$ATI}AlH$_2$] (**2a**) and [{(*i*Pr)$_2$ATI}AlR$_2$] (R = Me (**2b**), Et (**2c**), *i*Bu (**2d**)) were synthesised from H{(*i*Pr)$_2$ATI} and $Me_3N{\bullet}AlH_3$ or $AlR_3$ (Scheme 4).[10,16] The compounds **2a,b** are the first structurally characterised main group metal complexes of $\{R_2ATI\}^-$. In the solid state the four co-ordinated aluminium centres adopt a distorted tetrahedral geometry. In contrast to the free ligand, both aluminium derivatives are symmetric with Al–N distances which are equal within the error range. In contrast to **1a**, the aluminium complexes feature a planar heterobicyclic $AlN_2C_7$ ring system.[10] The reaction of **2a,b** with 0.5 equivalents of [Ph$_3$C][B(C$_6$F$_5$)$_4$] resulted in the quantitative formation of dinuclear cationic aluminium complexes of composition [({(*i*Pr)$_2$ATI}AlR)$_2$R][B(C$_6$F$_5$)$_4$] (R = H (**3a**), Me (**3b**)) (Scheme 4).[16] A crystal structure of **3b** shows that the cation contains two {(*i*Pr)$_2$ATI}AlMe units linked by a nearly linear Al–Me–Al bridge (Fig. 1). The μ-Me hydrogens are located in the equatorial plane of the nearly trigonal bipyramidal co-ordinated carbon centre. It was shown that these dimeric cations are labile in solution. The higher alkyl complexes **2c,d** reacted with one equivalent of [Ph$_3$C][B(C$_6$F$_5$)$_4$] *via* β-hydride abstraction to afford base-free cationic complexes of composition [{(*i*Pr)$_2$ATI}AlR][B(C$_6$F$_5$)$_4$] (R = Et (**3c**), *i*Bu (**3d**)). NMR spectroscopic experiments support the monomeric formulation of these compounds. In contrast, the reaction of **2a–d** with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] afforded the amine adducts [{(*i*Pr)$_2$ATI}AlR(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (Scheme 4).



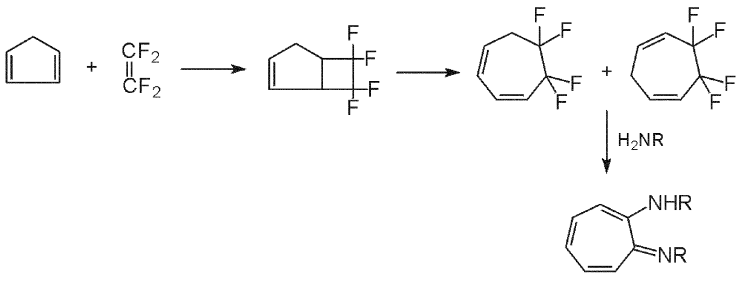
Scheme 2



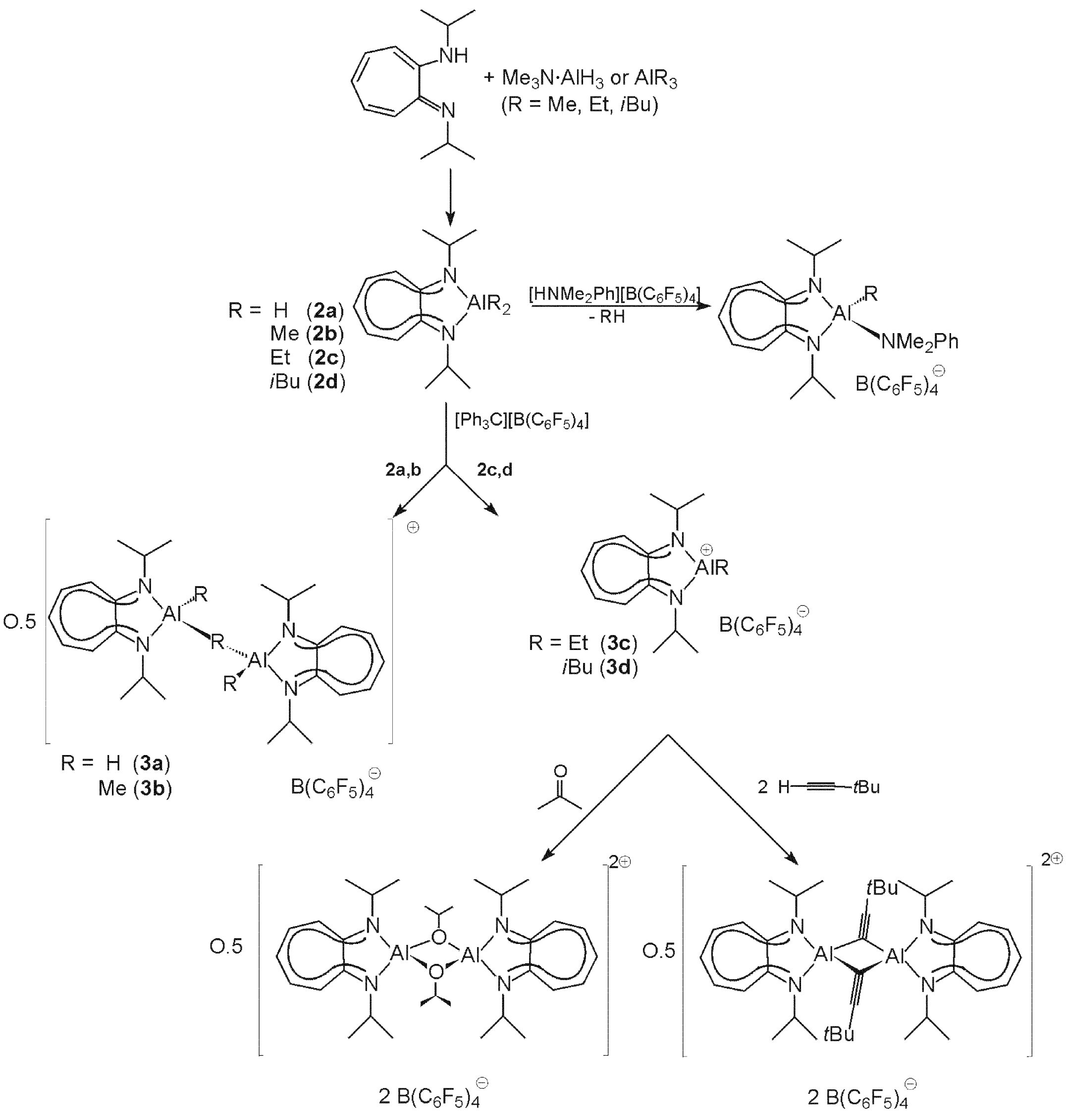
Scheme 3

The base-free compounds **3c,d** exhibited activity for polymerisation of ethylene, while dinuclear cations **3a,b** showed only trace activity. The dinuclear hydride cation **3a** polymerised methyl methacrylate (MMA) to predominately syndiotactic poly(MMA). While the active species and mechanisms of these polymerisations have not yet been established, it is clear that the reactivity of these cationic aluminium species is strongly influenced by their structures.[16]

Further reaction of **3c** with acetone led to the acetone adduct [{(*i*Pr)$_2$ATI}AlR•(O=C(CH$_3$)$_2$][B(C$_6$F$_5$)$_4$] which slowly converted to the ionic isopropoxide complex [{(*i*Pr)$_2$ATI}Al(μ-O*i*Pr)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ by net β-H transfer with release of ethylene



Scheme 1



**Scheme 4**

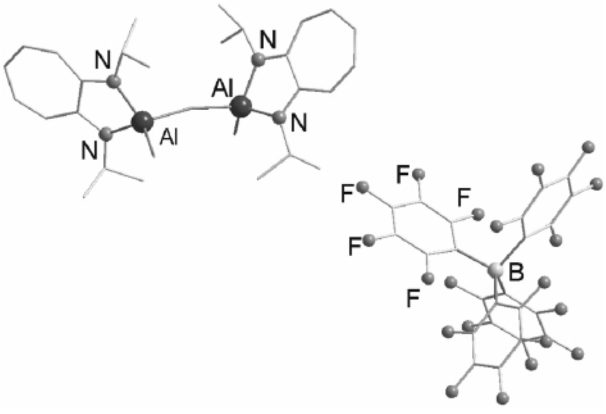


**Fig. 1** Crystal structure of **3b**.

(Scheme 4). The compound **3d** reacted with acetone in a similar manner, however the corresponding intermediates were less stable and were completely converted into the isopropoxide complex.[17] Compounds **3c,d** catalytically dimerise $t$BuC≡CH to the head–tail dimer 2-*tert*-butyl-5,5-dimethylhex-1-en-3-yne. As support for a catalytic mechanism, it was found that the reaction of **3c** with $t$BuC≡CH gave ethylene by β-H transfer and the cationic vinyl compound $[\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{AlCH{=}CH}\text{-}t\mathrm{Bu}][\mathrm{B(C_6F_5)_4}]$, which further reacted with $t$BuC≡CH to yield the dimeric alkynyl complex $[\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{Al}(\mu\text{-}\mathrm{C{\equiv}C}t\mathrm{Bu})]_2[\mathrm{B(C_6F_5)_4}]_2$ (Scheme 4).[17] The crystal structure of the dimeric alkynyl dication consists of two $\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{Al}$ units linked by two unsymmetrical σ,π-bridges.

The treatment of $[\{(\mathrm{Me})_2\mathrm{ATI}\}\mathrm{Sn}]$ with GaI and InCl led to bis(aminotroponiminate)gallium(III) and -indium(III) compounds of composition $[\{(\mathrm{Me})_2\mathrm{ATI}\}_2\mathrm{GaI}]$ (**4a**) and $[\{(\mathrm{Me})_2\mathrm{ATI}\}_2\mathrm{InCl}]$ (**4b**).[18] Whereas most gallium(III) and indium(III) compounds are obtained either by an alkane or hydrogen elimination route, **4a,b** were prepared by a redox reaction. The metal atom in both structures adopts a trigonal bipyramidal geometry, with the halide atom occupying an equatorial site (Fig. 2). The nitrogen atoms of each bidentate ligand occupy an axial and an equatorial site. The NMR spectra of **4a,b** are similar with only minor differences in the chemical shifts, suggesting closely related structures. The methyl groups of the $\{(\mathrm{Me})_2\mathrm{ATI}\}^-$ ligand are equivalent in the NMR spectra. This indicates the possibility of highly fluxional complexes in solution.

Very recently aminotroponiminate compounds of silicon, germanium, tin and lead have been reviewed.[14] Thus, these compounds will be mentioned here only briefly. Tetravalent group 14 compounds such as $[\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{MMe_3}]$ (M = Si, Sn) were obtained by the reaction of $\mathrm{Me_3MCl}$ and **1a**. In an analogous way $[\{(\mathrm{Et})_2\mathrm{ATI}\}\mathrm{SnPh_3}]$ and $[\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{SiCl_3}]$ were prepared from $\mathrm{Ph_3SnCl}$ and $\mathrm{SiCl_4}$, respectively.[14]

The $\{(\mathrm{R})_2\mathrm{ATI}\}^-$ ligand was also used to prepare a number of low-valent group 14 complexes.[19,20] The synthesis of the

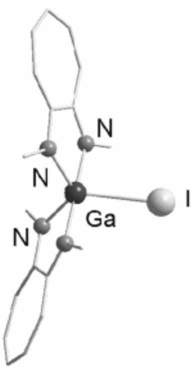


**Fig. 2** Crystal structure of **4a**.

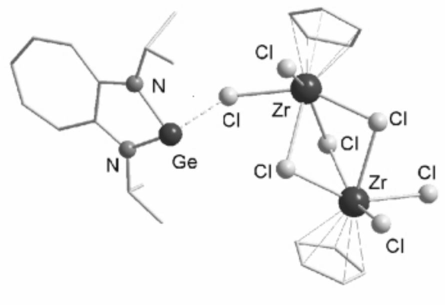


**Fig. 3** Crystal structure of **6b**.

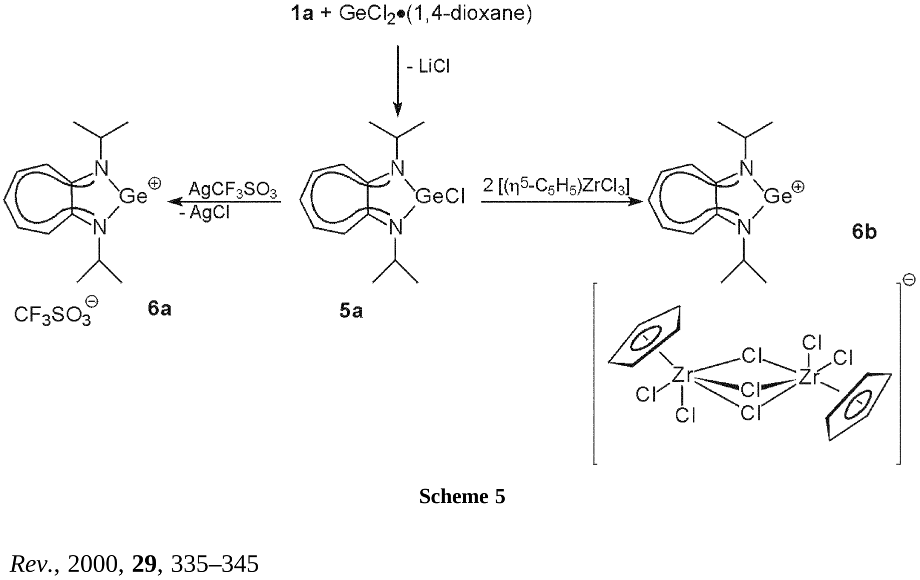
neutral germanium(II) chlorides [{($i$Pr)$_2$ATI}GeCl] (**5a**) (Scheme 5) and [{(Me)$_2$ATI}GeCl] (**5b**) was achieved by the treatment of GeCl$_2$•(1,4-dioxane) with **1a** or {(Me)$_2$ATI}Li.[19] In **5a,b** the germanium centre adopts a pyramidal geometry that is fairly common in germanium(II) chemistry. In order to generate the rare cationic germanium(II) compounds, the chlorine atom in **5a,b** was substituted by weakly co-ordinating anions. The reaction of **5a** with AgCF$_3$SO$_3$ or [($\eta^5$-C$_5$H$_5$)ZrCl$_3$] led to the corresponding ionic complexes [{($i$Pr)$_2$ATI}-Ge]CF$_3$SO$_3$ (**6a**) and [{($i$Pr)$_2$ATI}Ge][($\eta^5$-C$_5$H$_5$)ZrCl$_2$($\mu$-Cl)$_3$ZrCl$_2$($\eta^5$-C$_5$H$_5$)] (**6b**) (Scheme 5) (Fig. 3). In **6b**, weak intermolecular Ge···Cl contacts are observed. On the other hand, no ionic species was obtained by the reaction of **5b** with NaBPh$_4$. Instead the formation of a novel phenyl transfer product of composition [{(Me)$_2$ATI}GePh•BPh$_3$] was observed in which the germanium atom adopts a tetrahedral geometry. Although the NMR data of **6a,b** show notable differences relative to their neutral analogues, the solid-state structures show only minor changes in the C$_7$N$_2$Ge moiety, which is in all cases essentially planar. The Ge–N bond distances of the cations are not indicative of significant Ge–N $\pi$-bonding.

The co-ordination chemistry of tin(II) is comparable to germanium(II). The reaction of **1a** with SnCl$_2$ led to a three co-ordinated tin(II) compound of composition [{($i$Pr)$_2$ATI}SnCl] (**7**).[20] The lead compound [{($i$Pr)$_2$ATI}PbCl] was obtained in an analogous way from PbCl$_2$.[14] The tin centre in **7** adopts a pyramidal geometry in the solid state. As seen in the germanium(II) compound weak intermolecular Sn···Cl interactions are observed. Further reaction of **7** with [($\eta^5$-C$_5$H$_5$)ZrCl$_3$] led to the ionic compound [{($i$Pr)$_2$ATI}Sn][($\eta^5$-C$_5$H$_5$)ZrCl$_2$($\mu_3$-Cl$_3$)ZrCl$_2$($\eta^5$-C$_5$H$_5$)] (**8**). In the solid state, there are two weak interactions between the tin atom of the cation and two terminal chloride atoms of the anion. In solution the $^{119}$Sn NMR data of **8** suggests the presence of two co-ordinate tin(II) species. The crystal structural features of the C$_7$N$_2$Sn moiety in **7** and **8** are very similar. Based on the observed bond distances, the $\pi$-electrons of the C$_7$N$_2$Sn ring system appear to be mostly delocalised over nitrogen and carbon atoms.

## 2.3 Transition metal complexes

All recent publications on aminotroponiminate transition metal complexes deal with early transition metals such as group 3, 4 and the lanthanide elements, whereas the chemistry of the late transition metals was already developed in the 1960s.[6] As already mentioned, the active study of early transition metal chemistry has started since it was realised that {(R)$_2$ATI}$^-$ can be used as cyclopentadienyl alternatives.[1,12,13]

In order to investigate the co-ordination behaviour of the {($i$Pr)$_2$ATI}$^-$ ligand on yttrium and the lanthanide metals, compounds with one, two, or three ligands attached to the metal centre were synthesised (Scheme 6). Since an incorporation of LiCl into the metal complexes is often observed in lanthanide chemistry[21] the potassium compound **1b** was observed to be an ideal transfer reagent for the ligand anion. The homoleptic compounds [{($i$Pr)$_2$ATI}$_3$Ln] (**9**) (Ln = Y, La, Sm) were obtained by transmetallation of **1b** with anhydrous lanthanide trichlorides/triiodides in a 3 : 1 molar ratio (Scheme 6).[13] The NMR spectra of **9** show a diastereotopic splitting of the isopropyl CH$_3$ signals, which is caused by $\Lambda$ and $\Delta$ enantiomers, confirming octahedral co-ordination around the metal centre. Reaction of **1b** with anhydrous yttrium trichloride in a 2.2 : 1 molar ratio or with tris(2,6-di-$t$butylphenoxo)yttrium(III) in a 2 : 1 molar ratio led to [{($i$Pr)$_2$ATI}$_2$YCl] (**10a**)[22] and [{($i$Pr)$_2$ATI}$_2$Y{O(2,6-$t$Bu$_2$C$_6$H$_3$)}] (**10b**),[13] respectively (Scheme 6). Treatment of **1b** with an excess of anhydrous yttrium trichloride in THF (Scheme 6) afforded the corresponding yttrium chloro complex [{($i$Pr)$_2$ATI}YCl$_2$(THF)$_2$]$_2$ (**11**).[13] In the solid-state structure of **11**, the steric influence of the ligand {($i$Pr)$_2$ATI}$^-$ is clearly not sufficient to block all co-ordination sites on the yttrium atom (Fig. 4). Therefore, a dimerisation *via* two chloro-bridges takes place. Co-ordination



**Scheme 5**

of two equivalents of THF completes the seven-membered co-ordination sphere around the yttrium atom. Interestingly, the $\{(i\text{Pr})_2\text{ATI}\}^-$ ligand is attached asymmetrically to the metal centre. Due to the asymmetric attachment, the $C_7N_2Y$ moiety is slightly distorted.[13]

Transmetallation of the yttrium chloro complexes **10a** and **11** with $KN(SiMe_3)_2$ in toluene, afforded the corresponding yttrium amido complexes $[\{(i\text{Pr})_2\text{ATI}\}_2\text{YN}(\text{SiMe}_3)_2]$ (**12**) and $[\{(i\text{Pr})_2\text{ATI}\}\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**13**) as yellow crystalline solids (Schemes 7 and 8).[22] The solid-state structure of **13** was established by single crystal X-ray diffraction (Fig. 5). The structure reveals a distorted tetrahedral arrangement of the ligands around the centre metal. Thus for the yttrium atom the rare co-ordination of four is observed. The compound **12** exhibits a dynamic behaviour in solution which is caused by a rearrangement between a pseudo square-pyramidal and a pseudo trigonal-bipyramidal co-ordination sphere around the yttrium atom.

The catalytic activity of the cyclopentadienyl-free complexes **12** and **13** for the hydroamination/cyclization of aminoalkynes was investigated (Scheme 9). The catalytic hydroamination/cyclization of aminoolefins and aminoalkynes has been pioneered by T. J. Marks with a variety of lanthanocene catalysts.[23,24] The reaction of the catalysts with dry, degassed aminoalkynes (catalyst : substrate ≈ 1 : 50) proceeds regiospecifically (> 95%) to completion in benzene. On the other hand, the catalytic activity of **12** is about a factor five to seven slower than for the established analogous lanthanocene catalysts. Kinetic studies of both **12** and **13** indicate zero-order behaviour in substrate over a tenfold concentration range and so a mechanism for **12** close to the established one of $[(\eta^5\text{-}C_5Me_5)_2\text{LnCH}(\text{SiMe}_3)_2]$ was suggested.[22,23]

Reaction of **11** with potassium pentamethylcyclopentadienyl yielded the corresponding dicyclopentadienyl complex $[\{(i\text{Pr})_2\text{ATI}\}\text{Y}(\eta^5\text{-}C_5Me_5)_2]$ (**14a**) (Scheme 10).[25] **14a** has also been obtained by the 'classical' route from the reaction of $[(\eta^5\text{-}C_5Me_5)_2\text{Y}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2]$ with **1b**. The room temperature NMR spectra point to a symmetrical co-ordination of the $\{(i\text{Pr})_2\text{ATI}\}^-$ ligand in solution, which is in agreement with the co-ordination observed in the solid state. In contrast to the anionic dicyclopentadienyl diazadiene complex of lanthanum, $[(\eta^5\text{-}C_5Me_5)_2\text{La}(\text{DAD})]^-$ {DAD = (Ph)N=C(Ph)C(Ph)=N(Ph)}, **14a** does not show a rapid dynamic exchange of the chelating ligand in solution at room temperature. Whereas DAD complexes show a rapid migration of the $(\eta^5\text{-}C_5Me_5)_2M$ unit from one side of the reduced DAD ligand to the other, the rigid geometry of the $\{(i\text{Pr})_2\text{ATI}\}^-$ ligand prevents such a facile movement of the $(\eta^5\text{-}C_5Me_5)_2Y$ moiety. The crystal structure of **14a** shows that the steric demand of the $\{(i\text{Pr})_2\text{ATI}\}^-$ ligand is somewhat similar to that of the well-known cyclopentadienyl group and diazadiene ligand. The structure reveals a pseudo-tetrahedral arrangement of the ligands around the yttrium atom, in which the $C_7N_2Y$ moiety is significantly twisted.

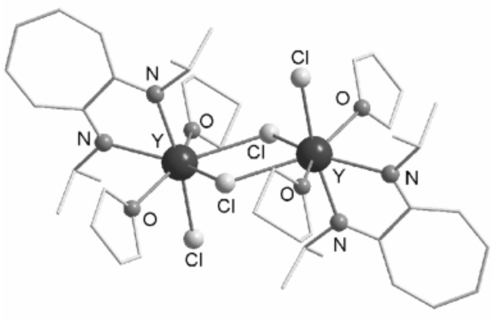
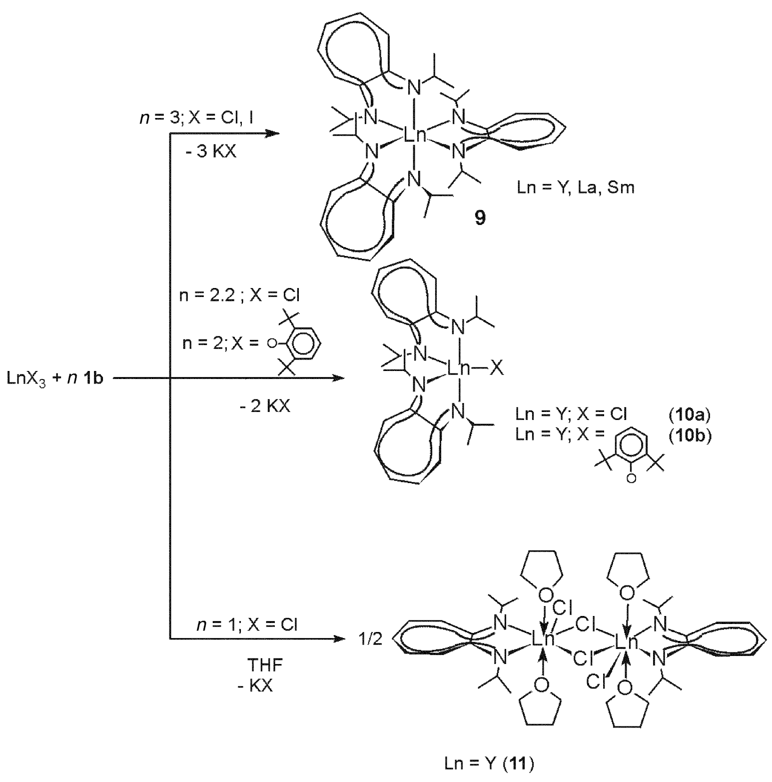


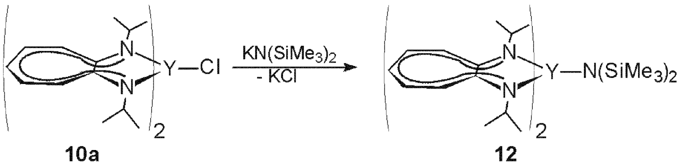
**Fig. 4** Crystal structure of **11**.

The bis[di-1,3-(trimethylsilyl)cyclopentadienyl] complex $[\{(i\text{Pr})_2\text{ATI}\}\text{Y}\{C_5H_3(\text{SiMe}_3)_2\}_2]$ (**14b**) was prepared in a similar way to **14a** (Scheme 10).[25] In contrast to **14a** the $^1H$ NMR spectrum of **14b** shows a dynamic behaviour in solution, which is caused by rotation of the cyclopentadienyl group rather than by migration of the $\{(i\text{Pr})_2\text{ATI}\}^-$ ligand.

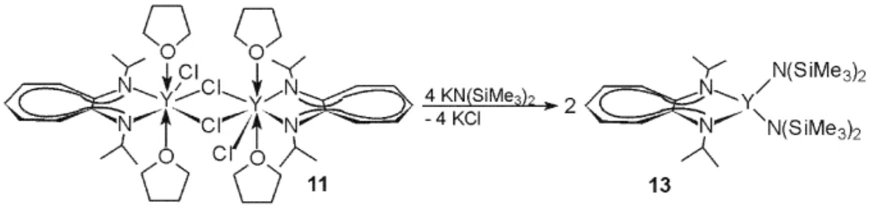
$\{(\text{Me}_2)\text{ATI}\}^-$ complexes of titanium were prepared by reaction of $[\text{TiCl}_2(\text{NMe}_2)_2]$ with two equivalents of $\text{H}\{(\text{Me}_2)\text{ATI}\}$ to yield $[\{(\text{Me}_2)\text{ATI}\}_2\text{TiCl}_2]$ (**15**) as an insoluble powder (Scheme 11). Reaction of **15** with $Me_3SiOTf$ (Tf = triflate), MeMgBr, or PhMgBr yielded the corresponding complexes $[\{(\text{Me}_2)\text{ATI}\}_2\text{Ti}(\text{OTf})_2]$, $[\{(\text{Me}_2)\text{ATI}\}_2\text{TiMe}_2]$ (**16**), and $[\{(\text{Me}_2)\text{ATI}\}_2\text{TiPh}_2]$ (**17**), respectively (Scheme



**Scheme 6**



Scheme 7



Scheme 8

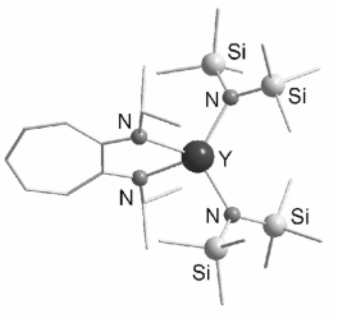
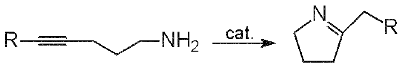


**Fig. 5** Crystal structure of **13**.



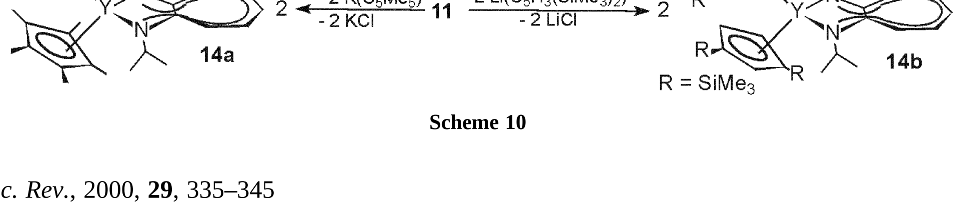
Scheme 9

11).[26] The mixed alkyl–aryl complex $[\{(Me_2)ATI\}_2Ti(Me)Ph]$ was prepared by treating **15** sequentially with MeMgBr and PhMgBr. The mono-alkyl complex $[\{(Me_2)ATI\}_2Ti(Cl)CH_2SiMe_3]$ was obtained by reaction of **15** and one equivalent of $Me_3SiCH_2MgCl$ (Scheme 11).[27] The solid-state structures of these alkyl and aryl complexes were determined by single crystal X-ray diffraction and confirmed the expected six-coordinated titanium geometry. Attempts to prepare alkyl complexes containing β-hydrogen atoms resulted instead in titanium(III) compounds. Thus, reaction of **15** with *n*BuLi resulted in $[\{(Me_2)ATI\}_3Ti]$, whereas reaction of **15** with *i*BuMgBr gave $[\{(Me_2)ATI\}_4Ti_2Cl_2]$ (Scheme 11).[27] Because of the modest steric requirements of the $[\{(Me_2)ATI\}_2Ti]^{2+}$ fragment, five coordinated titanium(IV) complexes were only generated with a bulky σ–2π donor ligand, $[\{(Me_2)ATI\}_2Ti(N\text{-}2,6\text{-}iPr_2C_6H_3)]$ being a specific example, which was obtained by the reaction of **15** with two equivalents of $Li(NH\text{-}2,6\text{-}iPr_2C_6H_3)$ (Scheme 11). Attempts to prepare the isoelectronic oxo analogue afforded only dimeric $[\{(Me_2)ATI\}_4Ti_2O_2)]$.[27]

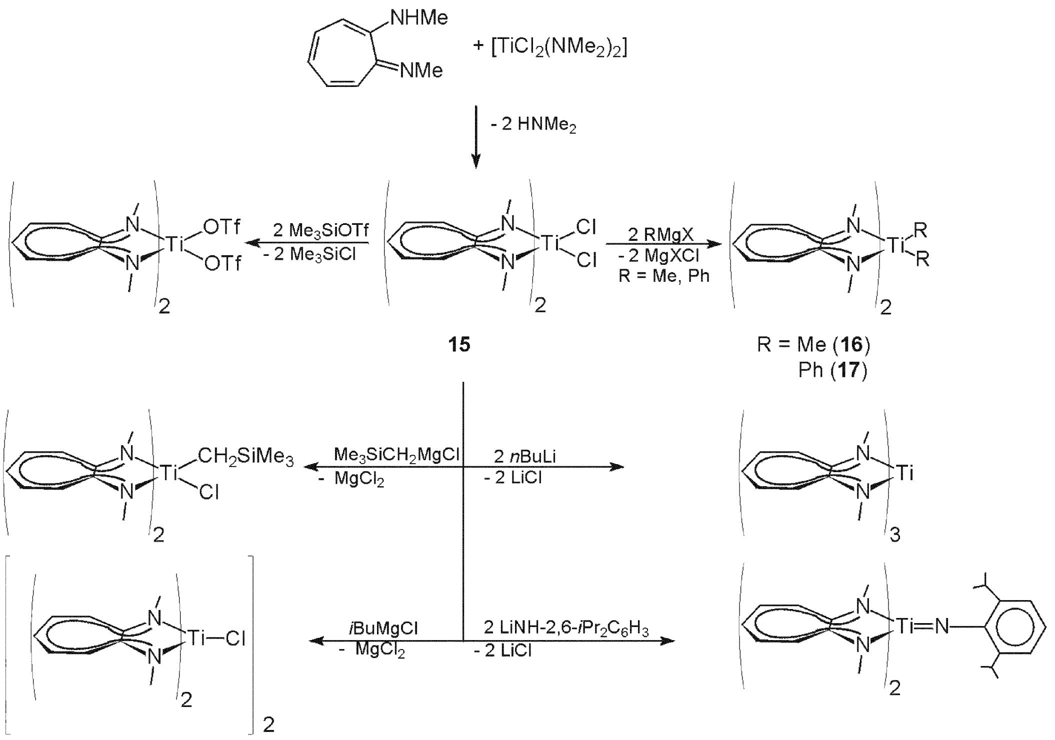
Since it was known that zirconium and hafnium troponcoronand dialkyl complexes react with CO to form stable η²-ketone complexes, which add to chalcone, cyclohexenone and cyclohexyl phenyl ketone to yield unsymmetrical zirconium diolates,[28] compound **16** was similarly treated with CO. However, it was not possible to characterise any metal complexes. On the other hand the reaction of **16** or **17** with aldehydes or ketones and CO yielded unsymmetrical diolate complexes of the general formula $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCR_2CR^1R^2O)]$ (**18**) (Scheme 12). The formulation of **18** as a diolate complex was confirmed by single crystal X-ray crystallography. The free vicinal diols could be isolated by treatment of **18** with 3 M aqueous HCl. Thus, the titanium system does not require any additives and yields diolates from alkyl complexes. The unique nature of the $\{(R)_2ATI\}^-$ ligand system for this carbonyl coupling is further demonstrated by the fact that neither the {salenTi} nor $\{(\eta^5\text{-}C_5H_5)_2Ti\}$ fragments will likely mediate this reaction.[26]

Reaction of **16** with phenyl acetylene and CO cleanly afforded the oxametallacyclopentene complex $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCMe_2CH{=}CPh)]$. The spectroscopic data of this complex are consistent with alkyne insertion where the phenyl group is directed away from the two methyl groups of the acetone η²-unit.[29] In contrast, reaction of isocyanides with **16** yielded imines. The formation of imines suggested that reduction to afford a low-valent titanium species had occurred. Trapping of this intermediate with benzaldehyde or benzil afforded the titanium diolate $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCHPhCHPhO)]$ or enediolate complex $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCPh{=}CPhO)]$, respectively (Scheme 13). The addition of two equivalents of benzophenone and *t*BuCN to a solution of **16** afforded the diolate complex $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCPh_2CPh_2O)]$. When one equivalent of benzophenone and either one equivalent of acetone or *N*-tosylbenzaldimine were added to the intermediate $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCMe_2CPh_2O)]$ and $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCPh_2CHPhN(SO_2Tol)]$, respectively, were obtained (Scheme 13). The titanium thiolatoalkoxide complex $[\{(Me_2)ATI\}_2Ti(\eta^2\text{-}OCMe_2CPh_2S)]$ was prepared by use of thiobenzophenone and acetone (Scheme 13).[29]

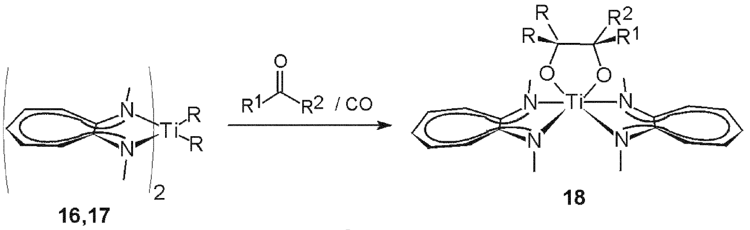
In order to use $\{(R)_2ATI\}^-$ as cyclopentadienyl alternative in group 4 chemistry, zirconium and hafnium complexes of composition $[\{(iPr)_2ATI\}_2MCl_2]$ (M = Zr (**19a**), Hf (**19b**)) were prepared (Scheme 14).[12] These compounds were obtained



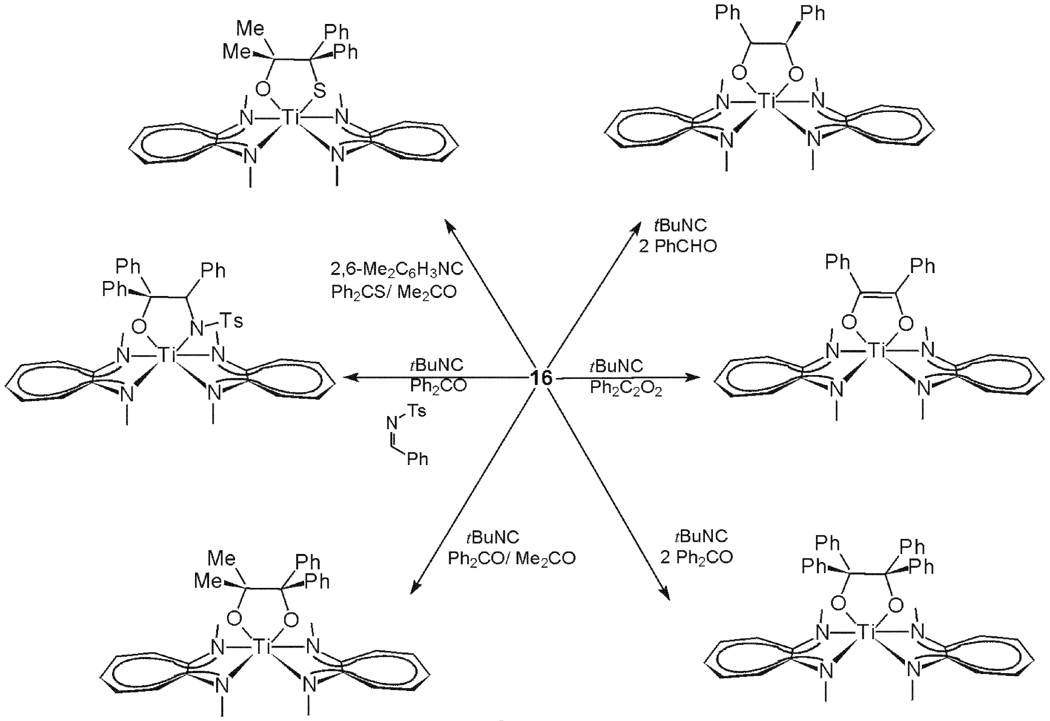
Scheme 10



Scheme 11

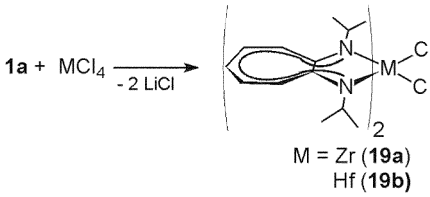


Scheme 12



Scheme 13

by the reaction of **1a** with $MCl_4$ (M = Zr, Hf). The crystal structures of **19a,b** are almost isostructural (Fig. 6). The sixfold co-ordinated metal centres of the monomeric complexes adopt a distorted octahedral geometry in which the chlorine atoms occupy *cis* co-ordination sites. As seen in **11** and **14a**, the heterobicyclic $C_7N_2M$ framework in **19a,b** shows a notable



Scheme 14

deviation from planar structure. The similarities in the structural parameters of **19a,b** and [($\eta^5$-$C_5H_5$)$_2$$ZrCl_2$] are even closer than those found between [($\eta^5$-$C_5H_5$)$_2$$ZrCl_2$] and amidinates. The amidinate ligands have been noted to have steric properties similar to those of the cyclopentadienyl ligand.[3,4] The simple room temperature NMR spectra of **19a,b** suggest that they have stereochemical non-rigid structures in solution. The solid-state structures, if retained in solution, should lead to diastereotopic pairs of ligand signals, which were not observed in the NMR. The synthesis of the dialkyl derivative [{(*i*Pr)$_2$ATI}$_2$Zr($CH_2SiMe_3$)$_2$] was achieved by treating [Zr($CH_2SiMe_3$)$_4$] with two equivalents of the neutral ligand H{(*i*Pr)$_2$ATI}. As indicated by the NMR spectra, the molecule appears to be fairly symmetric.

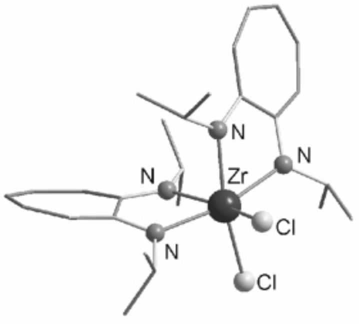


**Fig. 6** Crystal structure of **19a**.

## 3 Complexes of mono-bridged bis (aminotroponiminate)s

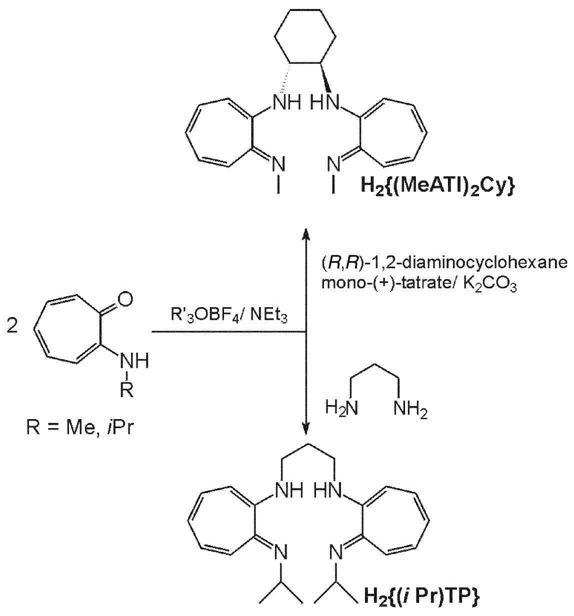
### 3.1 Ligand synthesis

Mono-bridged aminotroponiminates can be obtained by a three-step procedure starting from tropolone. The first two steps, the preparation of 2-alkylaminotropone, are the same as for the preparation of H{(R)$_2$ATI} (Scheme 2). The third step involves the alkylation of 2-alkylaminotropone with $R_3O{\bullet}BF_4$ (R = Me or Et) followed by treatment with excess of a diaminoalkyl reagent to obtain the desired mono-bridged ligand. Recently, by using this method, two mono-bridged aminotroponiminates were prepared. These are the *n*-propyl- and the (*R,R*)-1,2-diaminocyclohexane-bridged bis(aminotroponimine)s (H$_2${(*i*Pr)TP} and H$_2${(MeATI)$_2$Cy}, respectively) (Scheme 15).[30,31]

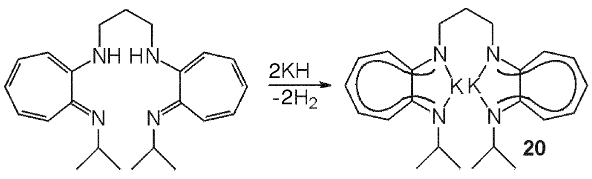
### 3.2 Main group metal complexes

The main group chemistry of bridged bis(aminotroponimine)s is still limited to group 1 and 13 complexes. Reaction of H$_2${(*i*Pr)TP} with a potassium hydride suspension in THF affords the dipotassium salt K$_2${(*i*Pr)TP} (**20**) as an orange solid (Scheme 16).[30] **20** was characterised by spectroscopic methods but not by single crystal X-ray diffraction. The spectroscopic data show that **20** was obtained solvent free.

The bimetallic aluminium complexes [($R_2Al$)$_2${(*i*Pr)TP}] (R = Me (**21a**), Et (**21b**), *i*Bu (**21c**)) were synthesised by reactions



Scheme 15



Scheme 16

of the neutral ligand H$_2${(*i*Pr)TP} with the corresponding dialkyl aluminium hydrides $R_2AlH$ in hexane (Scheme 17).[32] The solid-state structures of **21a** and **21c** (Fig. 7) were investigated by single crystal X-ray diffraction. In contrast to most other known structures in which the {(*i*Pr)TP}$^{2-}$ ligand co-ordinates in a chelating fashion (see below), **21a–c** show a metal bridging co-ordination mode. In the solid state, the four co-ordinated aluminium centres adopt a distorted tetrahedral geometry which is comparable to **2a,b**. In contrast to **21a**, in which the two metal centres are located in a *cisoid* arrangement, in **21c** the two metal centres are found in *transoid* conformation in the solid state. This is mainly caused by the increased steric demand of the *i*Bu substituents of the aluminium atoms.

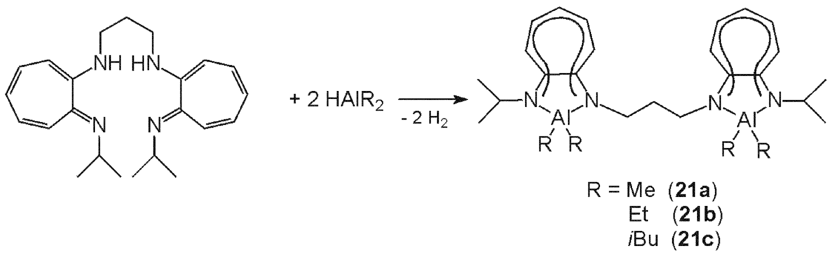
In a straightforward synthesis, the complexes [{(*i*Pr)TP}MCl] (M = Ga (**22a**), In (**22b**)) can be obtained by transmetallation of **20** with the metal trichlorides in a 1:1 molar ratio in THF (Scheme 18).[33] The co-ordination polyhedron **22b** is best described in terms of a distorted tetragonal pyramid with the chlorine atom in the apex (Fig. 8). The two seven-membered rings of the {(*i*Pr)TP}$^{2-}$-ligand in **22b** are approximately 20° twisted with respect to each other.

Transmetallation of **22b** with MeLi, $LiCH_2SiMe_3$ or KO*t*Bu led to the corresponding alkyl and alkoxide complexes of the general formula [{(*i*Pr)TP}In–R] (R = Me, $CH_2SiMe_3$, O*t*Bu).

### 3.3 Transition metal complexes

All reports regarding mono-bridged aminotroponiminate transition metal complexes have dealt with early transition metals. In group 3 and lanthanide chemistry the {(*i*Pr)TP}$^{2-}$-ligand was used as an *ansa*-metallocene alternative.[30]

Transmetallation of **20** with anhydrous lanthanum trichloride in a 3:2 molar ratio in THF afforded the corresponding dinuclear lanthanum complex [{(*i*Pr)TP}$_3$La$_2$(THF)$_2$] (**23**)



**Scheme 17**

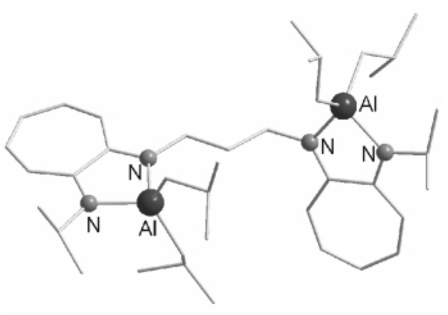


**Fig. 7** Crystal structure of **21c**.

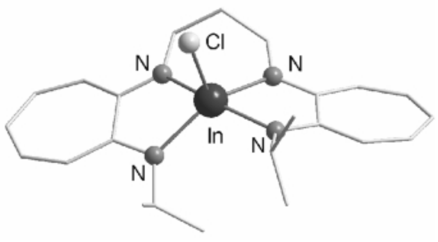
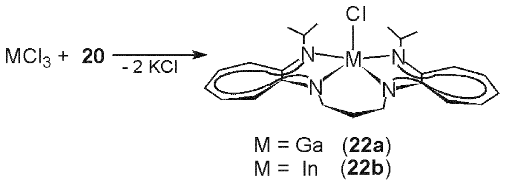


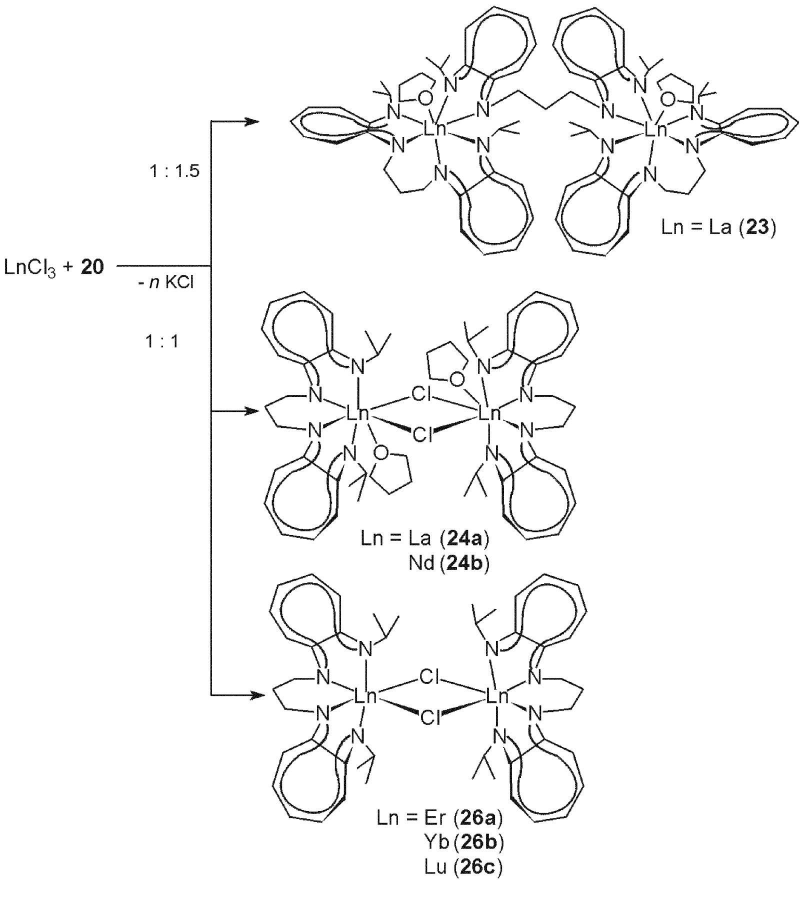
**Fig. 8** Crystal structure of **22b**.



**Scheme 18**

(Scheme 19).[30] **23** is a dimeric complex in which the $\{(i\text{Pr})\text{TP}\}^{2-}$ anion exhibits two different co-ordination modes (Fig. 9). Two $\{(i\text{Pr})\text{TP}\}^{2-}$ units are co-ordinated as tetradentate chelating ligand anions, whereas the third unit bridges the two lanthanum centres. Both kinds of co-ordination were observed earlier for *ansa*-metallocenes of the lanthanides.[21] The structure reveals a seven-membered co-ordination sphere of the ligands around the lanthanum atom. Thus, one lanthanum atom is co-ordinated by 1.5 $\{(i\text{Pr})\text{TP}\}^{2-}$ units and one THF molecule. As observed for **11**, the aminotroponiminate moieties are asymmetrically co-ordinated to the metal centre.

In order to obtain mono-substituted complexes of the lighter lanthanide elements with $\{(i\text{Pr})\text{TP}\}^{2-}$, **20** and anhydrous



**Scheme 19**

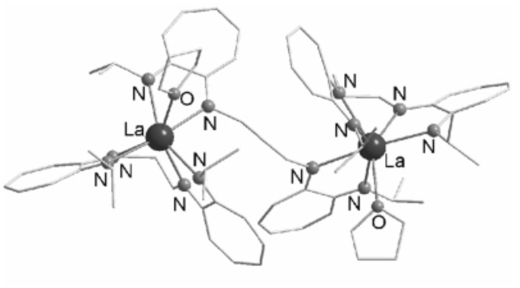


**Fig. 9** Crystal structure of **23**.

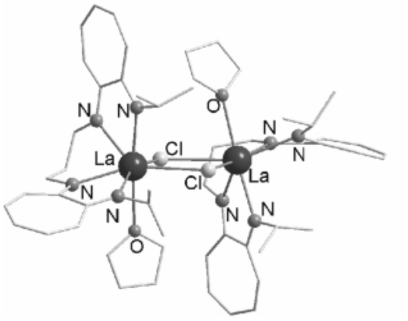
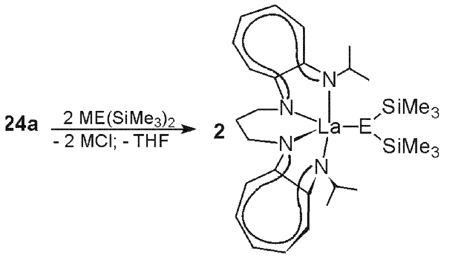


**Fig. 10** Crystal structure of **24a**.

lanthanum and neodymium trichloride, respectively, in THF were reacted in a 1 : 1 molar ratio to give, selectively, products of composition [{(*i*Pr)TP}LnCl(THF)]$_2$ (Ln = La (**24a**), Nd (**24b**)) (Scheme 19).[30,34] The NMR spectra of **24a** indicate a symmetrical co-ordination of the {(*i*Pr)TP}$^{2-}$ anion in solution. The crystal structures of **24a,b** are isostructural (Fig. 10). The compounds **24a,b** are dimeric complexes in which two metal atoms are symmetrically bridged by two μ-chlorine atoms. The {(*i*Pr)TP}$^{2-}$ units are co-ordinated as tetradentate chelating ligand anions. Additionally, on each metal atom one equivalent of THF is co-ordinated. Thus, the structure reveals a sevenfold co-ordination sphere of the ligands around the metal atoms. A further reaction of **24a** with LiCH(SiMe$_3$)$_2$ or KN(SiMe$_3$)$_2$ in toluene yielded the alkyl or amide derivatives [{(*i*Pr)TP}LaE(SiMe$_3$)$_2$] (E = CH (**25a**), N (**25b**)) (Scheme 20).



E = CH, M = Li (**25a**)
E = N, M = K (**25b**)

**Scheme 20**

To study the co-ordination behaviour of the {(*i*Pr)TP}$^{2-}$-dianion with the heavier lanthanides, which feature a smaller ionic radius in oxidation state +3 compared to lanthanum and neodymium, the reaction of **20** with anhydrous erbium, ytterbium and lutetium trichloride in a 1 : 1.3 molar ratio in THF was investigated. As products, compounds of composition [{(*i*Pr)TP}LnCl]$_2$ (Ln = Er (**26a**), Yb (**26b**), Lu (**26c**)) were obtained (Scheme 19).[34,35] The solid-state structures were established by single crystal X-ray diffraction (Fig. 11). Owing to the similar ionic radiis of the central atoms of **26a–c** the crystal structures of all three compounds are isostructural. They are dimeric complexes in which the metal centres are bridged by two μ-chlorine atoms resulting in a sixfold co-ordination sphere of the ligands around the lanthanide atoms. Due to the smaller ionic radii of erbium, ytterbium and lutetium compared to neodymium and lanthanum, no additional co-ordination of THF to the centre atom is observed.

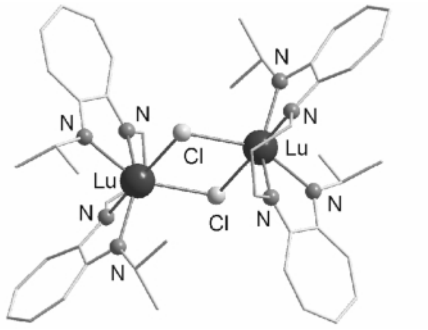


**Fig. 11** Crystal structure of **26c**.

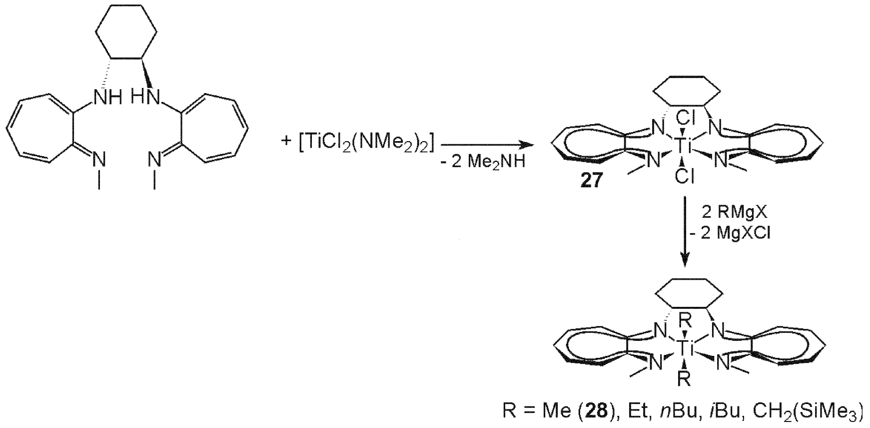
To study the reactivity of **26c** some selected derivatives were synthesised by a substitution of the chlorine atom of **26c**.[35] Transmetallation of **26c** with KN(SiMe$_3$)$_2$, LiCH$_2$(SiMe$_3$), NaBH$_4$, and NaC$_5$H$_5$, respectively led to the corresponding alkyl, amide, η$^3$-borohydride and η$^5$-cyclopentadienyl complexes of composition [{(*i*Pr)TP}Lu–R] (R = N(SiMe$_3$)$_2$, CH$_2$(SiMe$_3$), η$^3$-BH$_4$, η$^5$-C$_5$H$_5$).[35]

By using the *C*$_2$-symmetric {(MeATI)$_2$Cy}$^{2-}$-ligand a number of titanium complexes were accessible that cannot be obtained using the {(Me$_2$)ATI}$^-$-ligand system (see above). Thus, rare examples of thermally stable titanium diethyl and di-*n*-butyl as well as η$^2$-imine complexes were obtained.[31] Reaction of H$_2${(MeATI)$_2$Cy} with [TiCl$_2$(NMe$_2$)$_2$] led to [{(MeATI)$_2$Cy}TiCl$_2$] (**27**) (Scheme 21). Reaction of **27** with various alkyl Grignard reagents RMgCl (R = Me, Et, *n*Bu, *i*Bu, CH$_2$(SiMe$_3$)) gave the corresponding dialkyl complexes of composition [{(MeATI)$_2$Cy}TiR$_2$]. The co-ordination geometry of the methyl compound [{(MeATI)$_2$Cy}TiMe$_2$] (**28**) in the solid state is best described as a skew trapezoidal bipyramidal in contrast to the *cis*-octahedral geometry of the unlinked complex **16**. Further reaction of **28** with *t*BuNC resulted in the η$^2$-imine complex [{(MeATI)$_2$Cy}Ti{η$^2$-Me$_2$CN(*t*Bu)}] (**29**) (Scheme 22).[31] The solid state structure of **29** is best described as square pyramidal, with the four nitrogen atoms of the ligand comprising the base of a square pyramid and the η$^2$-imine ligand occupying the axial position. The stabilising effect of the {(MeATI)$_2$Cy}$^{2-}$-ligand is seen by the difference in isocyanide reactivity with the analogous compound **16**. Thus, the reduced titanium species formed by a reaction of **16** with *t*BuNC is unstable towards loss of imine. The change in stability was attributed in part to steric factors. Further reaction of **29** with Ph$_2$CO gave the diolate complex [{(MeATI)$_2$Cy}Ti(η$^2$-OCPh$_2$CPh$_2$O)].

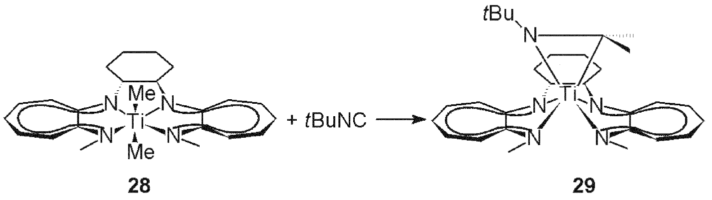
Mono-bridged aminotroponiminate complexes of zirconium and hafnium were obtained by a ligand degradation reaction of zirconium or hafnium tropocoronand complexes. Thermal decomposition of [M(CH$_2$SiMe$_3$)$_2$(TC-4,4)] (M = Zr, Hf) afforded a dimeric product in which one of the nitrogen–carbon bonds of one of the alkyl linker chains was cleaved.[8]

## 4 Conclusions

It has been shown that aminotroponiminates and mono-bridged bis(aminotroponiminate)s are versatile ligands in main group and in transition metal (*d*- and 4*f*-elements) chemistry. In contrast to the older work, which was mainly limited to manganese(II), iron (II), cobalt(II) and nickel(II) complexes,[6] the recent work has focused on main group and early transition elements. It has been shown by different research groups that



Scheme 21



Scheme 22

aminotroponiminates can stabilise low-valent main group metals and that they can be used in early transition metal chemistry as cyclopentadienyl alternatives. A significant number of the new compounds have been characterised by single crystal X-ray diffraction. Depending on the ionic radius of the centre metal the heterobicyclic $C_7N_2M$ framework of the aminotroponiminate ligand shows either a symmetrical co-ordination or a notable deviation from planar structure. Some of the new complexes can be used in homogenous catalysis or for synthetic purposes. In summary, it can be emphasised that the aminotroponiminates offer a pathway to a rich co-ordination chemistry, which includes application in catalysis and synthesis.

## 5 Acknowledgements

I am deeply grateful to my co-worker M. R. Bürgstein who is named on our joint publications cited in this review. This work was supported by the Deutsche Forschungsgemeinschaft (Habilitation- and Heisenberg-Stipendium) and the Fonds der Chemischen Industrie (Liebig-Stipendium). Additionally, generous support from Prof. Dr. D. Fenske is gratefully acknowledged.

## 6 References

1 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem.*, 1999, **111**, 448–468; G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 428–447, and references therein.
2 R. Kempe, *Angew. Chem.*, 2000, **112**, 478–504; R. Kempe, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 468–493, and references therein.
3 F. T. Edelmann, *Top. Curr. Chem.*, 1996, **179**, 113–148, and references therein.
4 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403–481, and references therein.
5 M. Bartlett and G. J. Pelenik, *J. Chem. Soc., Chem. Commun.*, 1970, 416.
6 R. H. Holm, *Prog. Inorg. Chem.*, 1971, **14**, 241–401, and references therein.
7 G. M. Villacorta and S. J. Lippard, *Pure Appl. Chem.*, 1986, **58**, 1477–1484, and references therein.
8 M. J. Scott and S. J. Lippard, *Inorg. Chim. Acta*, 1997, **263**, 287–299.
9 K. J. Franz and S. J. Lippard, *J. Am. Chem. Soc.*, 1998, **120**, 9034–9040.
10 H. V. R. Dias, W. Jin and R. E. Ratcliff, *Inorg. Chem.*, 1995, **34**, 6100–6105.
11 W. R. Brasen, H. E. Holmquist and R. E. Benson, *J. Am. Chem. Soc.*, 1960, **82**, 995–996.
12 H. V. R. Dias, W. Jin and Z. Wang, *Inorg. Chem.*, 1996, **35**, 6074–6079.
13 P. W. Roesky, *Chem. Ber.*, 1997, **130**, 859–862.
14 H. V. Dias, Z. Wang and W. Jin, *Coord. Chem. Rev.*, 1998, **176**, 67–86.
15 H. V. R. Dias and W. Jin, *J. Chem. Cryst.*, 1997, **27**, 353–358.
16 E. Ihara, V. G. Young and R. F. Jordan, *J. Am. Chem. Soc.*, 1998, **120**, 8277–8278.
17 A. V. Korolev, I. A. Guzei and R. F. Jordan, *J. Am. Chem. Soc.*, 1999, **121**, 11605–11606.
18 H. V. R. Dias and W. Jin, *Inorg. Chem.*, 1996, **35**, 6546–6551.
19 H. V. R. Dias and W. Jin, *J. Am. Chem. Soc.*, 1997, **119**, 4650–4655.
20 H. V. R. Dias and W. Jin, *J. Am. Chem. Soc.*, 1996, **118**, 9123–9126.
21 F. T. Edelmann in: *Comprehensive Organometallic Chemisty II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, and references therein.
22 M. R. Bürgstein, H. Berberich and P. W. Roesky, *Organometallics*, 1998, **17**, 1452–1454.
23 Y. Li and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 9295–9306.
24 T. E. Müller and M. Beller, *Chem. Rev.*, 1998, **98**, 675–703, and references therein.
25 P. W. Roesky, *Eur. J. Inorg. Chem.*, 1998, 593–596.
26 D. P. Steinhuebel and S. J. Lippard, *Organometallics*, 1999, **18**, 109–111.
27 D. P. Steinhuebel and S. J. Lippard, *Inorg. Chem.*, 1999, **38**, 6225–6233.
28 M. J. Scott and S. J. Lippard, *J. Am. Chem. Soc.*, 1997, **119**, 3411–3412.
29 D. P. Steinhuebel and S. J. Lippard, *J. Am. Chem. Soc.*, 1999, **121**, 11762–11772.
30 P. W. Roesky, *Inorg. Chem.*, 1998, **37**, 4009–4013.
31 D. P. Steinhuebel and S. J. Lippard, *Organometallics*, 1999, **18**, 3959–3961.
32 S. Schulz, M. Nieger, H. Hupfer and P. W. Roesky, *Eur. J. Inorg. Chem.*, 2000, 1623–1626.
33 M. R. Bürgstein, N. P. Euringer and P. W. Roesky, *J. Chem. Soc., Dalton Trans.*, 2000, 1045–1048.
34 P. W. Roesky and M. R. Bürgstein, *Inorg. Chem.*, 1999, **38**, 5629–5632.
35 P. W. Roesky, *J. Organomet. Chem.*, 2000, **603**, 161–166.