Journal of Alloys and Compounds, 207/208 (1994) 182–188
JALCOM 3087

Rare earth complexes with heteroallylic ligands and their use as precursors for lanthanide-based homogeneous catalysts

Frank T. Edelmann

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen (Germany)

Abstract

Bulky heteroallylic ligands are shown to be very promising alternatives for cyclopentadienyl ligands in lanthanide chemistry. In particular, the easily accessible silylated benzamidinate ligands $[RC_6H_4C(NSiMe_3)_2]^-$ (NCN) may soon rival $C_5H_5^-$ and $C_5Me_5^-$ in their high versatility. Heteroallylic ligands are capable of stabilizing reactive lanthanide(II) complexes (*e.g.* $[RC_6H_4C(NSiMe_3)_2]_2Yb(THF)_2$ (**1**, **2**)) as well as homoleptic complexes of the type $[RC_6H_4C(NSiMe_3)_2]_3Ln$, the latter being useful precursors for lanthanide-based materials (Ln_2O_3, Ln_2S_3, Ln_2Se_3). Of special interest for future applications are functionalizable bis(ligand) lanthanide halides and triflates (*e.g.* $[Ph_2P(NSiMe_3)_2]_2LnCl(THF)$ (**11**) and $[RC_6H_4C(NSiMe_3)_2]_2Y(O_3SCF_3)$ (**18**)). Implications for the development of novel homogeneous catalysts are discussed.

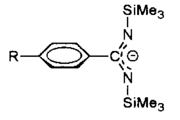
1. Introduction

Due to the numerous industrial applications of the rare earth elements and their compounds [1–3], modern lanthanide chemistry is an area of vigorous research. This is especially true for organolanthanide chemistry [4], which has produced an impressive number of highly active homogeneous catalysts [5,6]. Various olefin transformations are effectively catalyzed by organolanthanide complexes [6]. Typically the most active catalysts are compounds of the type $(C_5Me_5)_2LnX$, where X is a hydride ligand or a hydrocarbyl ligand such as methyl or bis(trimethylsilyl)methyl [7–14]. The organolanthanide hydrides are usually dimerized through bridging hydride ligands.

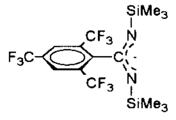
Surprisingly little is known about catalytically active lanthanide complexes containing other ancillary ligands than $C_5H_5^-$ or $C_5Me_5^-$ [15–17]. In fact, an estimated 90% of all organolanthanide complexes contain supporting ligands of the cyclopentadienyl type [4,18]. Therefore our research activities are directed towards the development of alternative ligand systems which eventually may rival the cyclopentadienyl ligands in their high versatility.

2. Results and discussion

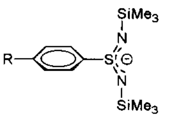
Recent work in our lab has focused on the chemistry of lanthanide complexes with bulky heteroallylic ligands. These ligands have been shown to behave as "steric cyclopentadienyl equivalents" [19], *i.e.* their cone angle is very similar to that of $C_5H_5^-$ or $C_5Me_5^-$. The following heteroallylic anions have been successfully employed:



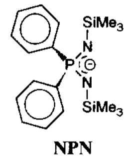
NCN
R = H, Me, OMe, CF_3, Ph



NCN*



NSN



NPN

These anionic ligands combine several unique features that make them extremely useful for lanthanide chemistry:

(1) The cone angle of NCN and NSN is roughly comparable with that of $C_5H_5^-$ or monosubstituted cyclopentadienyl ligands. On the other hand the chemistry of $C_5Me_5^-$ can be matched by using the very bulky ligands NCN* and NPN.
(2) The trimethylsilyl substituents at nitrogen provide the necessary steric saturation around the large lanthanide ions and assure a high solubility of the products in non-polar organic solvents.
(3) Just like cyclopentadienyl ligands, the heteroallylic ligands are kinetically more inert than halide, hydride, or alkyl ligands and thus allow facile sub-

SSDI 0925-8388(93)03087-Y

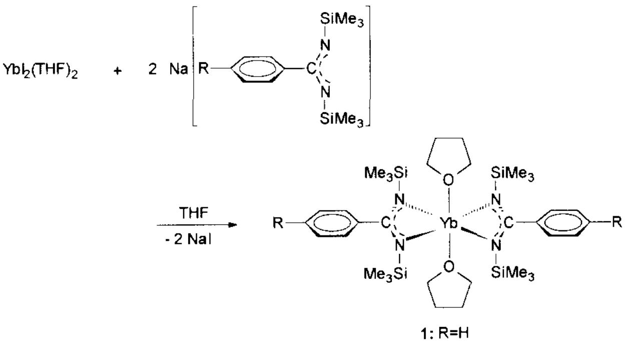
stitution reactions at other reactive sites of the molecules.

(4) The *N*-silylated heteroallylic ligands are easily accessible in large quantities through one- or two-step preparations. They can be isolated either in the form of lithium or sodium salts or as fully silylated neutral species.

(5) The heteroallylic anions are ideal new observer ligands for lanthanides as they contain several NMR-observable nuclei (^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P).

2.1. Lanthanide(II) derivatives

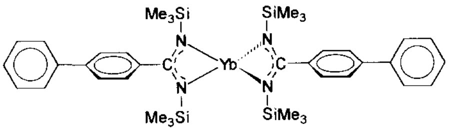
Like $C_5H_5^-$ and $C_5Me_5^-$, the heteroallylic ligands NCN and NPN have been found to give stable though highly reactive lanthanide(II) complexes [20,21]:



1: R=H
2: R=MeO

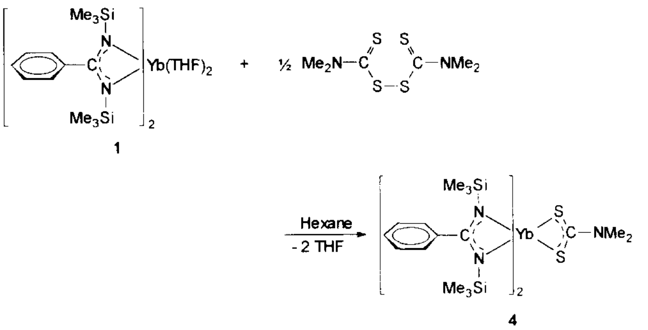
A crystal structure determination of **1** revealed a distorted octahedral geometry with the THF ligands occupying the *trans* positions (Fig. 1) [20].

Four-coordinate ytterbium was observed in the unsolvated species $PhC_6H_4C(NSiMe_3)_2]_2Yb$ (**3**):

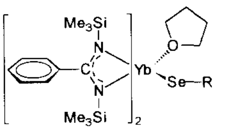


3

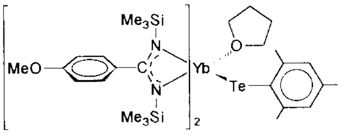
Both **1** and **2** are hydrocarbon-soluble and undergo various redox reactions, *i.e.* with alkyl halides, disulfides, diselenides and ditellurides. The reductive cleavage of E–E bonds (E = S,Se,Te) in the presence of divalent ytterbium provides a good access to lanthanide(III) complexes containing soft donor ligands. Cleavage of the sulfur–sulfur bond in $[Me_2NC(S)S]_2$ by **1** gave the ytterbium(III) dithiocarbamate **4** (Fig. 2) [20]:



A comparable pentamethylcyclopentadienyl derivative, $(C_5Me_5)_2Yb(S_2CNEt_2)$ was described by Andersen *et al.* in 1982. The ytterbium(III) selenolate complexes **5** and **6** were prepared analogously from **1** and diphenyldiselenide or dimesityldiselenide, respectively [20,21].



5: R = Ph
6: R = Mes



7

The preparation of **7** clearly showed that even stable compounds with lanthanide–tellurium bonds are easily accessible using this method. The molecular structures of both **5** and **6** (Fig. 3) have been determined by X-ray diffraction [20,21].

A ytterbium(II) diiminophosphinate **8** [22] was obtained by the following synthetic route:

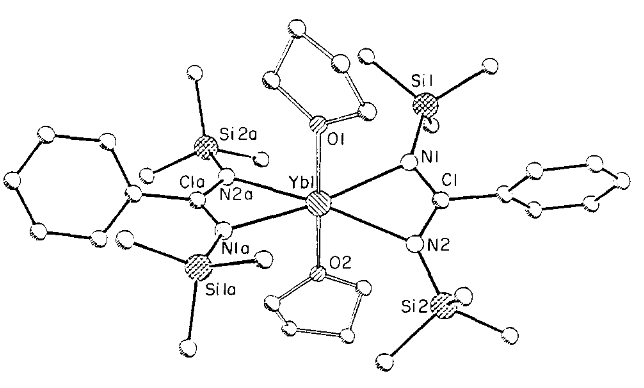


Fig. 1. Molecular structure of $[PhC(NSiMe_3)_2]_2Yb(THF)_2$.

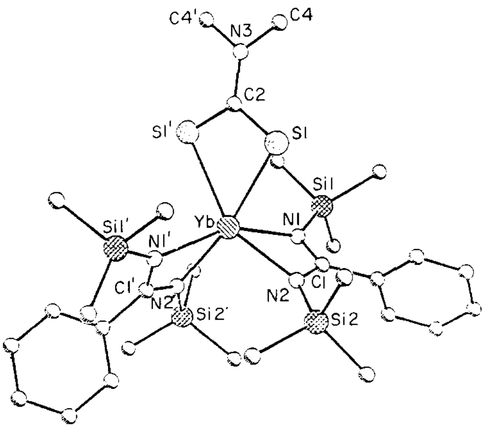


Fig. 2. Molecular structure of $[PhC(NSiMe_3)_2]_2Yb(S_2CNMe_2)$.

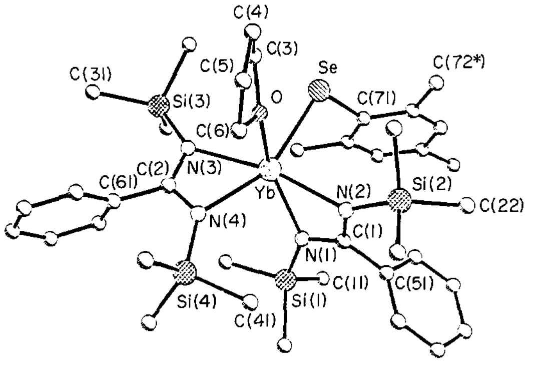


Fig. 3. Molecular structure of $[PhC(NSiMe_3)_2]_2Yb(SeMes)(THF)$.

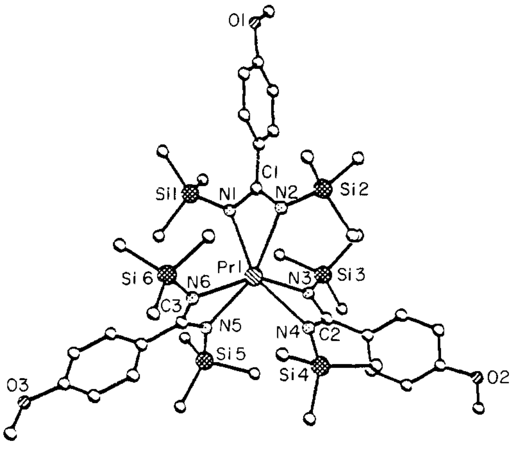
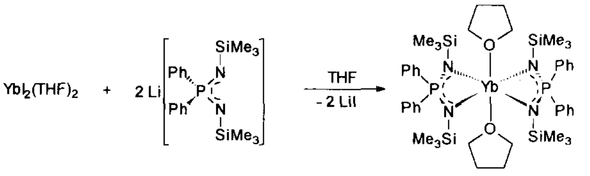


Fig. 4. Molecular structure of $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$.



8

Compound **8** was the first ytterbium(II) complex for which a ytterbium–phosphorus coupling constant was determined by NMR spectroscopy (**8** $\delta(^{171}Yb) = 521.2(d)$ ppm, $^2J_{Yb-P} = 67$ Hz) [21].

2.2. Lanthanide(III) complexes

Both NCN and NPN form homoleptic lanthanide complexes of the type $[RC_6H_4C(NSiMe_3)_2]_3Ln$ [23] and $[PhS(NSiMe_3)_2]_3Ln$ [24]. These highly soluble compounds have been described for many lanthanide elements. The molecular structure of the praseodymium derivative $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$ (**9**) was determined by X-ray diffraction (Fig. 4) [23].

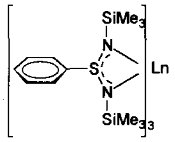
The coordination geometry in **9** was found to be distorted octahedral. Due to their high solubility in organic solvents, the homoleptic lanthanide benzamidinates $[PhC(NSiMe_3)_2]_3Ln$ are promising precursors for lanthanide based materials. The formation of lanthanide oxides Ln_2O_3 using the sol-gel technique has been studied [25].

$$[PhC(NSiMe_3)_2]_3Ln + 6H_2O \longrightarrow$$

$$\begin{array}{l} Ln(OH)_3 + 3PhC({=}NH)NH_2 + 3Me_3SiOSiMe_3 \\ \quad\downarrow \\ Ln_2O_3 \end{array}$$

Preliminary experimental results indicate that other lanthanide chalcogenides (Ln_2S_3, Ln_2Se_3) may also be accessible by a similar procedure [25].

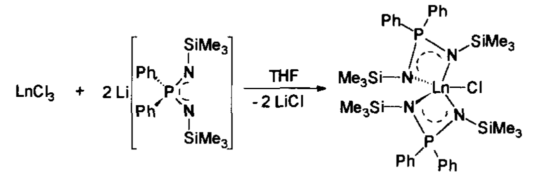
Homoleptic lanthanide complexes containing the $[PhS(NSiMe_3)_2]^-$ ligand were prepared analogously from anhydrous lanthanide trichlorides and $Li[PhS(NSiMe_3)_2]\cdot 0.5Et_2O$ [24]:



10: Ln = Sc, Nd

As expected, the physical properties of the sulfur derivatives **10** are very similar to those of the corresponding lanthanide(III) benzamidinates.

An interesting difference in reactivity was observed when anhydrous lanthanide trichlorides were reacted with 3 equiv. of $Li[Ph_2P(NSiMe_3)_2]$. Regardless of the stoichiometry (1:2 or 1:3), the disubstituted complexes **11** were found to be the only isolable products [26]. In the exclusive formation of disubstituted products, the diiminophosphinate ligand NPN very much resembled the pentamethylcyclopentadienyl ligand. In fact this was the first indication that the very bulky ligands NCN* and NPN might behave as steric equivalents of $C_5Me_5^-$.



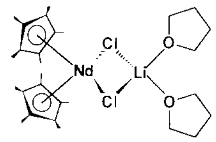
11: Ln = Pr, Nd

In cyclopentadienyl lanthanide chemistry, disubstituted complexes are probably the most important compounds as they contain reactive halide ligands [4,18]. These can be replaced by various other substituents such as hydride, alkyl, amide or alkoxide ligands. Thus, the bis(cyclopentadienyl)lanthanide chlorides represent one of the most versatile classes of reactive precursors in organolanthanide chemistry. These compounds exist in several different structural types depending on the size of the ligands and on the ionic radius of the lanthanide element. In the case of the unsubstituted cyclopentadienyl ligand, dimeric complexes of the type $[Cp_2LnCl]_2$ can be isolated for almost any lanthanide element. For $C_5Me_5^-$ and other bulky substituted cyclopentadienyl ligands (*e.g.* $(Me_3Si)_2C_5H_3^-$, $(^tBu)_2C_5H_3^-$) chlorine-bridged dimers have been isolated with the early lanthanide elements. In some cases, the THF solvates $(C_5Me_5)_2LnCl(THF)$ are formed. Obviously the fragments $(C_5Me_5)_2LnCl$ (coordination number 7) are coordinatively unsaturated and exhibit a strong tendency to increase the coordination number around the lanthanide atom. Formal eight-coordination is achieved in the above-mentioned dimers and THF solvates. The third possibility is the formation of "ate" complexes through incorporation of lithium halide. This results in complexes of the general type $(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(S)_2$ where S is a solvent molecule such as diethyl ether, THF or 1/2 DME. These compounds containing a four-membered $Ln(\mu\text{-}Cl)_2Li$ ring are very characteristic and common in pentamethylcyclopentadienyl lanthanide chemistry. In fact, this type of complex was known originally only for organolanthanide complexes containing the $C_5Me_5^-$ ligand [4,18]. Thus, it was an important finding that the bulky heteroallylic ligands are able to form very similar disubstituted lanthanide(III) complexes containing a four-membered $Ln(\mu\text{-}Cl)_2Li$ ring as the central structural unit. Together with numerous other analogies it confirms our theory that the *N*-silylated heteroallylic ligands are steric cyclopentadienyl equivalents, especially in the case of lanthanide and actinide elements [23,27,28].

Just as the $(C_5Me_5)_2LnCl$ derivatives are highly useful precursors in organolanthanide chemistry, the bis(benzamidinate)lanthanide chlorides should also develop into some very useful starting materials. Thus, considerable research effort is currently being directed towards rational syntheses of these compounds. For many metal/ligand combinations, it was found that the homoleptic lanthanide benzamidinates $[RC_6H_4C(NSiMe_3)_2]_3Ln$ were the preferred reaction products. In these cases, mixtures of products were obtained when the reactions were carried out in a 2:1 ligand-to-metal molar ratio. From this, it was concluded that two factors should increase the chance of isolating pure disubstitution products. Disubstitution should be more favorable if either very bulky ligands are used (*i.e.*NCN*) or if the ionic radius of the metal ion is small (*i.e.* Sc, Y, Yb, Lu). Both assumptions were subsequently confirmed through experiments.

In an early paper by Evans and Wayda [29], it was reported that LiC_5Me_5 reacts with anhydrous neodymium trichloride in refluxing THF to give exclusively the disubstituted complex **12**:

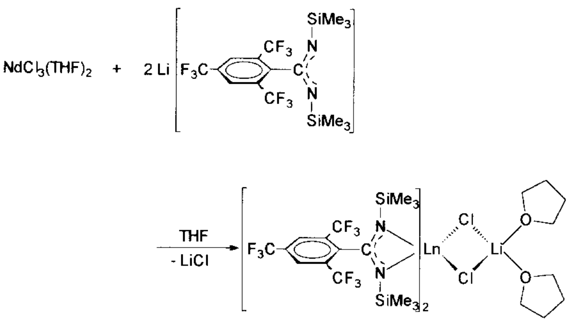
$$NdCl_3 + 2\,LiC_5Me_5 \xrightarrow[-\,LiCl]{THF} \underset{\mathbf{12}}{(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2}$$



12

Compound **12** is formally an "ate" complex in which 1 equiv. of LiCl is retained in the product in order to increase the coordination number at the neodymium atom. Neodymium and lithium are bridged by two chlorine atoms and the coordination sphere at lithium is completed by two THF ligands.

An entirely analogous reaction occurs when anhydrous neodymium trichloride is reacted under similar conditions with 2 equiv. of $Li[(CF_3)_3C_6H_2C(NSiMe_3)_2]$. In this reaction, the very bulky benzamidinate ligand behaves like a steric equivalent of $C_5Me_5^-$:



13

The molecular structure of **13** was confirmed by X-ray diffraction [30]. Just as in the corresponding C_5Me_5 derivatives, a four-membered $Nd(\mu\text{-}Cl)_2Li$ ring forms the central part of the molecule (Fig. 5).

Initial reactivity studies showed that **13** can serve as a useful starting material for further reactions [31]. For example, the reactive chlorine atom can be replaced

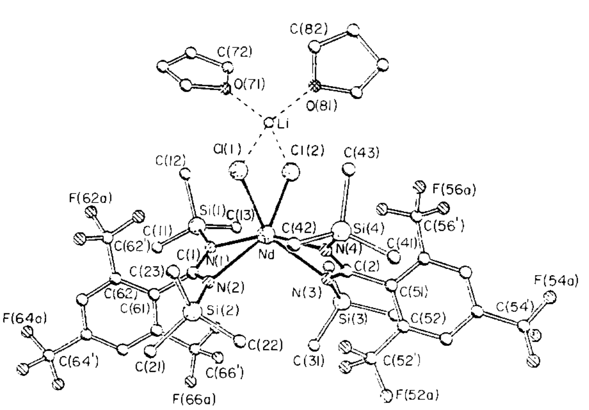
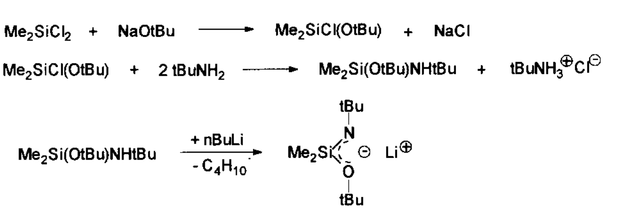


Fig. 5. Molecular structure of $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2Nd(\mu\text{-}Cl)_2Li(THF)_2$.

by amido or alkyl ligands such as $-\mathrm{N(SiMe_3)_2}$ or $-\mathrm{CH(SiMe_3)_2}$ to give the products $[\mathrm{(CF_3)_3C_6H_2C(NSiMe_3)_2}]_2\mathrm{NdN(SiMe_3)_2}$ and $[\mathrm{(CF_3)_3C_6H_2C(NSiMe_3)_2}]_2\mathrm{NdCH(SiMe_3)_2}$, respectively. These correspond to the known organoneodymium complexes $\mathrm{(C_5Me_5)_2NdN(SiMe_3)_2}$ and $\mathrm{(C_5Me_5)_2NdCH(SiMe_3)_2}$.

The ionic radius of the lanthanide atom is another important factor governing the formation and successful synthesis of well-defined disubstituted complexes. This can be nicely illustrated by the example of the closely related ligand $[\mathrm{Me_2Si(O^tBu)(N^tBu)}]^-$. This anionic ligand has been frequently employed by Veith *et al.* [32]. The lithium salt $\mathrm{Li[Me_2Si(O^tBu)(N^tBu)]}$ is easily obtained in a straightforward preparation starting with $\mathrm{Me_2SiCl_2}$ [33]:

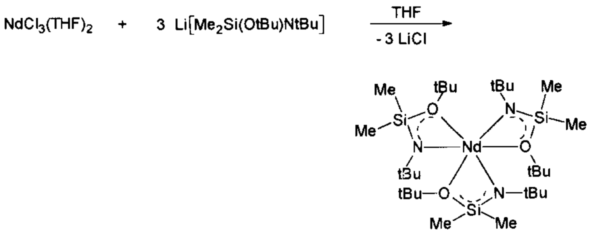


$$\mathrm{Me_2SiCl_2 + NaOtBu \longrightarrow Me_2SiCl(OtBu) + NaCl}$$

$$\mathrm{Me_2SiCl(OtBu) + 2\,tBuNH_2 \longrightarrow Me_2Si(OtBu)NHtBu + tBuNH_3^{\oplus}Cl^{\ominus}}$$

$$\mathrm{Me_2Si(OtBu)NHtBu \xrightarrow[-C_4H_{10}]{+\,nBuLi} Me_2Si(N{tBu})(O{tBu})^{\ominus}\,Li^{\oplus}}$$

The large ionic radius of neodymium as a typical representative of the early lanthanide elements allowed the formation of a homoleptic tris(alkoxysilylamide) complex [34]:



$$\mathrm{NdCl_3(THF)_2 + 3\,Li[Me_2Si(OtBu)NtBu] \xrightarrow[-3\,LiCl]{THF}}$$

14

Compound **14** was isolated as a sky-blue crystalline solid which is highly soluble in non-polar organic solvents. The molecular structure of **14** was determined by a single crystal X-ray analysis. It showed the neodymium atom in a distorted octahedral coordination environment (Fig. 6) [34]. Dark red crystalline $[\mathrm{Me_2Si(O^tBu)(N^tBu)}]_3\mathrm{Eu}$ was prepared analogously [35].

A marked difference in reactivity is observed with the smaller ytterbium ion. Even if an excess of the ligand is used, ytterbium trichloride reacts with $\mathrm{Li[Me_2Si(O^tBu)(N^tBu)]}$ selectively in a 1:2 molar ratio to give a high yield of the disubstituted product **15** (Fig. 7) [34]. Not even traces of the homoleptic complex $[\mathrm{Me_2Si(O^tBu)(N^tBu)}]_3\mathrm{Yb}$ were formed in this reaction.

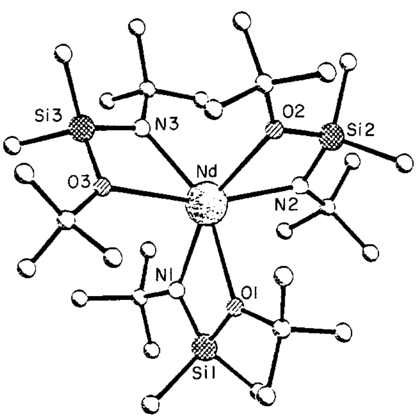


Fig. 6. Molecular structure of $[\mathrm{Me_2Si(O^tBu)(N^tBu)}]_3\mathrm{Nd}$.

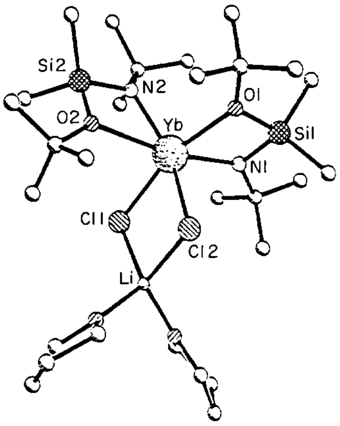


Fig. 7. Molecular structure of $[\mathrm{Me_2Si(O^tBu)(N^tBu)}]_2\mathrm{Yb}(\mu\text{-}\mathrm{Cl})\mathrm{Li(THF)_2}$.

$$\mathrm{YbCl_3 + 2Li[Me_2Si(O^tBu)(N^tBu)] \xrightarrow[-\,LiCl]{THF}}$$

$$[\mathrm{Me_2Si(O^tBu)(N^tBu)}]_2\mathrm{Yb}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(THF)_2}$$

15

Once again the typical chloro-bridged "ate" complex known so far only from $\mathrm{C_5Me_5}$ lanthanide chemistry was realized with a bulky chelating ligand. This example clearly showed that the selective formation of disubstituted complexes could be achieved also by adjusting the ionic radius of the metal atom to the steric requirements of the ligands. To test this hypothesis, scandium and yttrium were chosen to synthesize well-defined complexes of the type $[\mathrm{RC_6H_4C(NSiMe_3)_2}]_2\mathrm{MCl(THF)}$ (M = Sc,Y). Indeed, treatment of either $\mathrm{ScCl_3(THF)_3}$ or $\mathrm{YCl_3(THF)_{3.5}}$ with 2 equiv. of the silylated benzamidinate ligands resulted in a clean formation of the desired disubstitution products [25]:

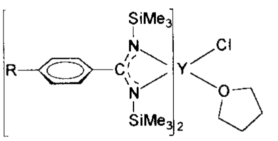
$$\mathrm{ScCl_3 + 2Li[RC_6H_4C(NSiMe_3)_2] \xrightarrow[-\,2LiCl]{THF}}$$

$$[\mathrm{RC_6H_4C(NSiMe_3)_2}]_2\mathrm{ScCl(THF)}$$

16: R = H, MeO, $\mathrm{CF_3}$

$$YCl_3(THF)_{3.5} + 2\,Li[RC_6H_4C(NSiMe_3)_2] \xrightarrow[-2\,LiCl]{THF} [RC_6H_4C(NSiMe_3)_2]_2YCl(THF)$$

17: R = H,MeO,CF_3



17

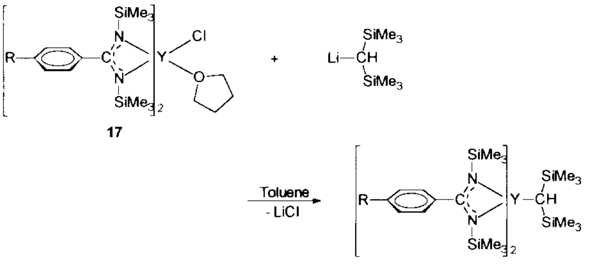
The products **16** and **17** were isolated as colorless, crystalline solids. Thus far the use of scandium and yttrium appears to be the best entry into the chemistry of disubstituted complexes with bulky heteroallylic ligands. Even higher yields (*ca.* 80–90%) of such disubstituted complexes are obtained when anhydrous yttrium triflate is used as precursor. Treatment of $Y(O_3SCF_3)_3$ with 2 equiv. of $Li[RC_6H_4C(NSiMe_3)_2]$ yields the novel bis(ligand) yttrium triflates **18** [25]:

$$Y(O_3SCF_3)_3 + 2Li[RC_6H_4C(NSiMe_3)_2] \xrightarrow[-2LiO_3SCF_3]{THF}$$

$$[RC_6H_4C(NSiMe_3)_2]_2Y(O_3SCF_3)$$

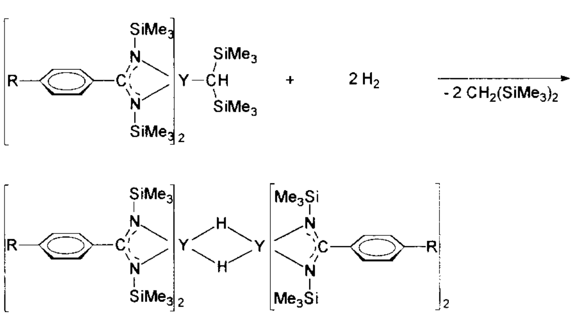
18: R = H, MeO, CF_3

All these new scandium and yttrium complexes may serve as versatile starting materials for highly reactive alkyl and hydride derivatives [25]. For example, the chlorine atom in **16** and **17** is easily replaced by bulky anionic ligands such as $-N(SiMe_3)_2$ or $-CH(SiMe_3)_2$. More recently it was found that the yttrium triflates **18** are even better suited for this type of substitution reaction because LiO_3SCF_3 is more easily separated from the reaction mixtures than LiCl. The yttrium alkyls **19** have been prepared either from **17** or **18** by treatment with $LiCH(SiMe_3)_2$ in toluene solution:



19: R = H,MeO,CF_3

Hydrogenation of **19** under mild conditions yields the dimeric yttrium hydrides **20**:



20: R = H,MeO,CF_3

The hydrides **20** have been found to polymerize ethylene and react with a variety of protic reagents [25].

3. Conclusions

Bulky heteroallylic ligands of the type NCN, NCN*, NSN and NPN have been found to be highly versatile observer ligands for lanthanide elements in their di- and trivalent oxidation states. Surprising parallels between the lanthanide complexes with heteroallylic ligands and the corresponding cyclopentadienyl complexes have been discovered. Several important advantages make the ligand systems NCN, NCN*, NSN and NPN very promising alternatives to the well-known cyclopentadienyl ligands. Initial investigations have shown that lanthanide complexes with heteroallylic ligands may be very useful as precursors for lanthanide-based materials as well as homogeneous catalysts.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Dr. Otto Röhm-Gedächtnisstiftung is gratefully acknowledged.

References

1 B.T. Kilbourn, *Inorg. Chim. Acta, 140* (1987) 335.
2 L. Niinistö, *Inorg. Chim. Acta, 140* (1987) 339.
3 R. Reisfeld, *Inorg. Chim. Acta, 140* (1987) 345.
4 H. Schumann, *Angew. Chem., 96* (1984) 475; *Angew. Chem., Int. Ed. Engl., 23* (1984) 474.
5 P.L. Watson and G.W. Parshall, *Acc. Chem. Res., 18* (1985) 51.
6 K.N. Harrison and T.J. Marks, *J. Am. Chem. Soc., 114* (1992) 9220 and refs. therein.
7 H. Mauermann, P.N. Swepston and T.J. Marks, *Organometallics, 4* (1985) 200.
8 G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann and T.J. Marks, *J. Am. Chem. Soc., 107* (1985) 8091.

9 G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T.J. Marks, *J. Am. Chem. Soc., 107* (1985) 8111.

10 M.R. Gagné and T.J. Marks, *J. Am. Chem. Soc., 111* (1989) 4108.

11 M.R. Gagné, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc., 114* (1992) 275.

12 H.J. Heeres and J.H. Teuben, *Organometallics, 10* (1991) 1980.

13 T. Sakakura, H.-J. Lautenschlager and M. Tanaka, *J. Chem. Soc., Chem. Commun.,* (1991) 40.

14 J. Renkema and J.H. Teuben, *Rec. Trav. Chim. Pays-Bas, 105* (1986) 241.

15 J. Sieler, A. Simon, K. Peters, R. Taube and M. Geitner, *J. Organomet. Chem., 362* (1989) 297.

16 Z. Shen, *Inorg Chim. Acta, 140* (1987) 7.

17 M. Brunelli, S. Poggio, U. Pedretti and G. Lugli, *Inorg. Chim. Acta, 131* (1987) 281.

18 F.G.A. Stone, G. Wilkinson and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, London, 1982.

19 T.V. Lubben, P.T. Wolczanski and G.D. van Duyne, *Organometallics, 3* (1984) 977.

20 M. Wedler, M. Noltemeyer, U. Pieper, H.-G. Schmidt, D. Stalke and F.T. Edelmann, *Angew. Chem., 102* (1990) 941; *Angew. Chem., Int. Ed. Engl., 29* (1990) 894.

21 M. Wedler, A. Recknagel, J.W. Gilje, M. Noltemeyer and F.T. Edelmann, *J. Organomet. Chem., 426* (1992) 295.

22 A. Recknagel, A. Steiner, S. Brooker, D. Stalke and F.T. Edelmann, *J. Organomet. Chem., 415* (1991) 315.

23 M. Wedler, F. Knösel, U. Pieper, D. Stalke, F.T. Edelmann and H.-D. Amberger, *Chem. Ber., 125* (1992) 2171.

24 F. Knösel, M. Noltemeyer and F.T. Edelmann, *Z. Naturforsch., 44b* (1989) 1171.

25 J. Richter and F.T. Edelmann, unpublished results.

26 A. Recknagel, M. Witt and F.T. Edelmann, *J. Organomet. Chem., 371* (1989) C40.

27 M. Wedler, F. Knösel, M. Noltemeyer, F.T. Edelmann and U. Behrens, *J. Organomet. Chem., 388* (1990) 21.

28 M. Wedler, F. Knösel, F.T. Edelmann and U. Behrens, *Chem. Ber., 125* (1992) 1313.

29 A.L. Wayda and W.J. Evans, *Inorg. Chem., 19* (1980) 2190.

30 A. Recknagel, F. Knösel, H. Gornitzka, M. Noltemeyer, F.T. Edelmann and U. Behrens, *J. Organomet. Chem., 417* (1991) 363.

31 F.T. Edelmann, unpublished results.

32 M. Veith, *Angew. Chem., 99* (1987) 1; *Angew. Chem,. Int. Ed. Engl., 26* (1987) 1.

33 M. Veith and R. Rösler, *J. Organomet. Chem., 229* (1982) 131.

34 A. Recknagel, A. Steiner, S. Brooker, D. Stalke and F.T. Edelmann, *J. Organomet. Chem., 415* (1991) 315.

35 U. Kilimann and F.T. Edelmann, unpublished results.