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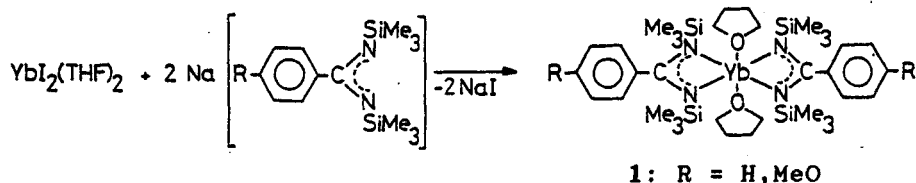
INORGANIC RING SYSTEMS CONTAINING LANTHANIDE ELEMENTS

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Abstract Lanthanide complexes containing four-membered N-C-N-Ln, N-S-N-Ln and N-P-N-Ln rings have been synthesized by treatment of lanthanide halides with bulky anionic chelating ligands. Similar ring systems containing four different elements (N-Si-O-Ln) have been obtained by reacting anhydrous lanthanide trichlorides with $\text{Li}[\text{Me}_2\text{Si}(\text{O}^t\text{Bu})(\text{N}^t\text{Bu})]$. A twelve-membered inorganic ring is formed during the reaction of $\text{Cp}^*_2\text{Sm}(\text{THF})_2$ with $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$.

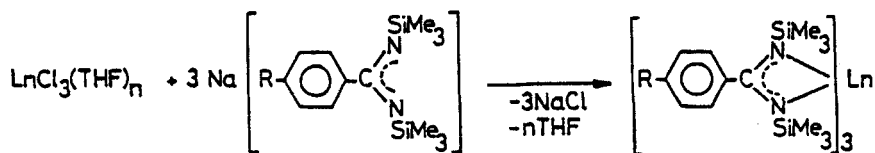
In previous studies we have demonstrated that certain bulky chelating ligands can be regarded as steric cyclopentadienyl equivalents.¹⁻⁵ Typical examples are the silylated benzamidinate anions $[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]^-$ ($\text{R} = \text{H}, \text{Me}, \text{MeO}, \text{CF}_3, \text{Ph}$), whose cone angle (ca. 137°) resembles that of Cp. Thus treatment of ytterbiumdiodide with $\text{Na}[\text{RC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]$ yields the highly reactive dark red ytterbium(II) benzamidinates **1**:



The p-phenyl derivative $[\text{PhC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2]_2\text{Yb}$ crystallizes without THF and represents a rare example of a four-coordinated ytterbium(II) complex.

Reduction of sulfur-sulfur and selenium-selenium bonds by the ytterbium(II) species **1** leads to the formation of novel ytterbium(III) thiolates and selenolates.

Homoleptic lanthanide(III) benzamidinates **2** are prepared analogously from anhydrous LnCl_3 and three equivalents of silylated sodium benzamidinates:

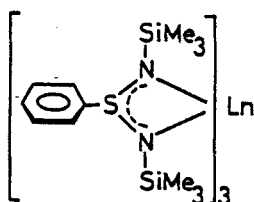
2: R = H, MeO, CF₃, Ph

Ln = Sc, Ce, Pr, Nd, Sm,

Eu, Gd, Yb, Lu

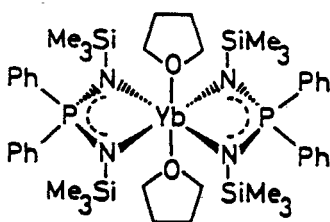
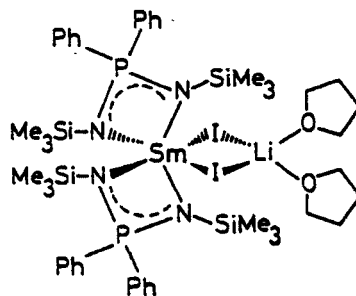
The crystalline complexes **2** are moisture-sensitive and highly soluble in unpolar organic solvents. A crystal structure determination of [MeOC₆H₄C(NSiMe₃)₂]₃Pr shows that the four-membered N-C-N-Ln rings are nearly planar.

A similar synthetic route was used to prepare lanthanide complexes containing four-membered N-S-N-Ln and N-P-N-Ln rings. The diiminosulfinate derivatives **3** are obtained by treatment of LnCl₃ with Li[PhS(NSiMe₃)₂] (molar ratio 1:3):



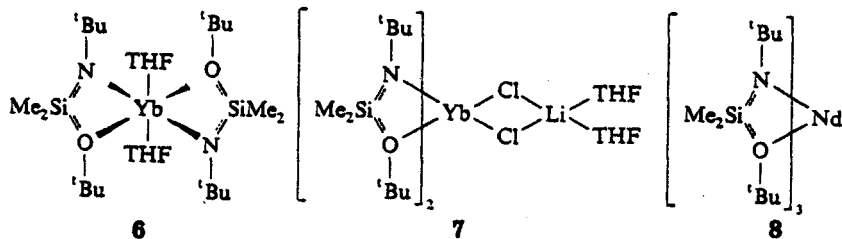
3: Ln = Sc, Nd

The steric bulk of the diiminophosphinate anion [Ph₂P(NSiMe₃)₂]⁻ is comparable to that of Cp*. In this case only disubstituted lanthanide derivatives can be isolated. Typical examples are **4** and **5**:

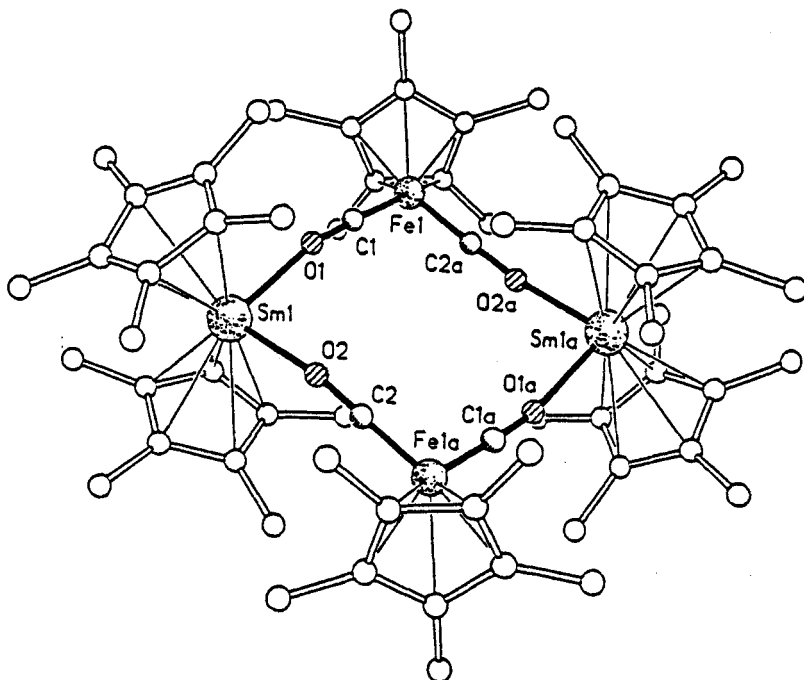
**4****5**

The alkoxysilylamide anion [Me₂Si(O^tBu)(N^tBu)]⁻ allow the synthesis of inorganic ring systems containing four

different elements (N-Si-O-Ln). Di- and trivalent lanthanide derivatives (6 - 8) have been prepared by treatment of various lanthanide halides with stoichiometric amounts of $\text{Li}[\text{Me}_2\text{Si}(\text{O}^t\text{Bu})(\text{N}^t\text{Bu})]$:



An unusual twelve-membered ring system containing samarium was found in $[\text{Cp}^*\text{Sm}(\mu\text{-OC})_2\text{FeCp}^*]$.⁶ This compound was made by reacting $\text{Cp}^*\text{Sm}(\text{THF})_2$ with $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$. The samarium and iron atoms are connected via Σ -carbonyl bridges. The twelve membered ring adopts a flat chair conformation.



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REFERENCES

1. M. Wedler, H.W. Roesky and F. Edelmann, J. Organomet. Chem., **345**, C1 (1988).
2. F. Knösel, M. Noltemeyer and F.T. Edelmann, Z. Naturforsch., **44b**, 1171 (1989).
3. A. Recknagel, M. Witt and F.T. Edelmann, J. Organomet. Chem., **371**, C40 (1989).
4. M. Wedler, F. Knösel, M. Noltemeyer, F.T. Edelmann and U. Behrens, J. Organomet. Chem., **388**, 21 (1990).
5. M. Wedler, M. Noltemeyer, U. Pieper, H.-G. Schmidt, D. Stalke and F.T. Edelmann, Angew. Chem., **102**, 941 (1990); Angew. Chem., Int. Ed. Engl., **29**, 894 (1990).
6. A. Recknagel, A. Steiner, S. Brooker, D. Stalke and F.T. Edelmann, Chem. Ber., **124**, 1373 (1991).