Heterocyclopentadienyl Complexes of Group-3 Metals

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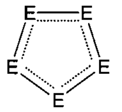
Keywords: Lanthanides / Actinides / Coordination modes / Heteroelements / Cyclopentadienes

Heterocyclopentadienyl complexes of group-3 metals (scandium, yttrium, lanthanum and the lanthanides, and uranium) are compounds in which one or more –CH units of a cyclopentadienyl-like ligand have been replaced by a heteroelement (nitrogen, phosphorus, arsenic, or antimony). These ligands can have very diverse substitution patterns, notably with bridged and cavitand-like structures. In addition to the classical η^5-coordination behaviour, the heterocyclopentadienyl ligand can adopt a very large array of coordination patterns. Some complexes have a very promising chemistry since they have been found to activate small molecules such as nitrogen and ethylene.

I. Introduction

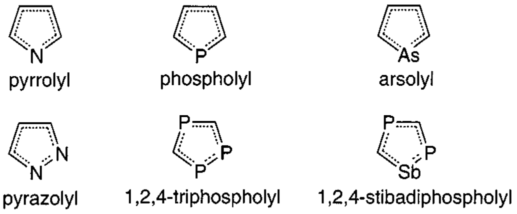
Cyclopentadienyl π-complexes of group-3 metals (including scandium, yttrium, lanthanum and the lanthanides, and the actinides) have received a tremendous amount of attention in the past few years.[1] These metals can achieve very high coordination numbers (c.n.) (up to 12), but it is possible to obtain stable complexes with lower coordination numbers by increasing the steric bulk on the cyclopentadienyl ligand. For instance, introduction of the η^5-pentamethylcyclopentadienyl (Cp*) ligand, which has become ubiquitous in this chemistry, has allowed for the isolation of stable complexes such as $Cp^*_2LnX_2^-$ (X = halogen, c.n. = 8), Cp^*_2LnR (R = alkyl, c.n. = 7), or even the divalent lanthanide complexes Cp^*_2Ln (Ln = Sm, Eu, c.n. = 6). In addition, some of these complexes are highly efficient homogeneous catalysts.[2]

Another possibility for modifying a cyclopentadienyl ligand is the replacement of one or several carbon atoms of this ring by a group-15 heteroelement; an isoelectronic heterocyclopentadienyl ligand is thus obtained.



E = CH, N, P, As, Sb, Bi

Several such heterocyclopentadienyl ligands have been used in group-3 metal chemistry. They include the pyrrolyl, phospholyl, and arsolyl ring systems with one heteroelement in the ring, the pyrazolyl ligand with two heteroelements and the 1,2,4-triphospholyl and 1,2,4-stibadiphospholyl ligands with three heteroelements. Like the cyclopentadienyl anion, all these ligands, in the anionic form, formally derive from the corresponding pyrrole, phosphole, arsole, pyrazole, 1,2,4-triphosphole and 1,2,4-stibadiphosphole ring systems, respectively, by deprotonation.



Of course many types of substituents have been introduced on these rings, notably by benzoannelation such as in

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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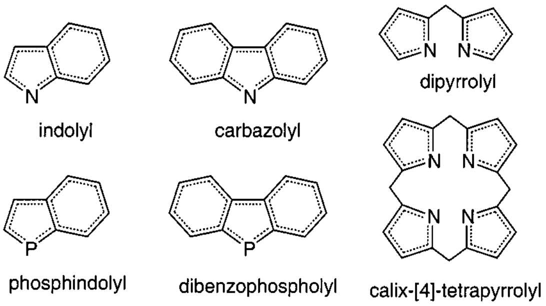
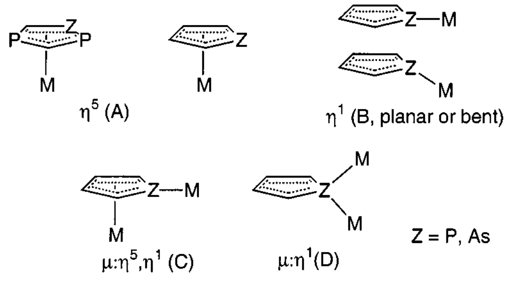
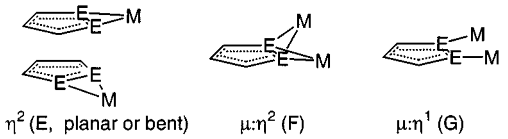
indolyl, phosphindolyl, carbazolyl, and dibenzophospholyl ligands. Bridged ligands have also been used: Complexes with chelating or cavitand-like pyrrolyl ligands such as bipyrrolyl or calix[4]tetrapyrrolyl (porphynogen) have recently been prepared (it is worth noting that a cavitand structure based on cyclopentadienyl has not been made yet).



All these 5-membered ring systems, except for pyrazolyl, have been shown to behave as "true" heterocyclopentadienyl ligands in the sense that complexes displaying the η^5-coordination mode (A), which is typical of the cyclopentadienyl group, have been isolated. Since the heteroatom in the ring still possesses a lone pair of electrons, other coordination patterns are possible, namely the η^1-mode (B, planar or bent), in which there is a σ bond with the group-3 metal, the μ:η^5,η^1-mode (C), in which both the ring and the lone pair are coordinated, and the μ:η^1-bridging mode (D).



The proximity of two heteroatoms in the pyrazolyl, 1,2,4-triphospholyl, and 1,2,4-stibadiphospholyl ligands can give rise to other coordination modes: η^2-(E, planar or bent), μ:η^2-(F) and μ:η^1-(G).



Heterocyclopentadienyl complexes of group-3 metals have been studied less than the cyclopentadienyl complexes. However, many references have appeared in the past few years and so this field is rapidly expanding.

Interest in the structure and reactivity of these complexes stems from:

a) coordination mode A and comparison with analogous cyclopentadienyl complexes,

b) the additional possibilities offered by coordination modes C and E for mononuclear complexes,

c) coordination modes D, F, and G which give rise to polynuclear complexes,

d) heterocyclopentadienyl complexes based on pyrrolyl ligands with bridging or cavitand structures, and

e) synthetic pathways possibly different from those of cyclopentadienyl complexes.

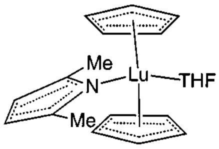
This review will tentatively cover the complexes of group-3 metals (scandium, yttrium, lanthanum and the lanthanides, and uranium) with heterocyclopentadienyl ligands as described above. Group-3 metal complexes with ligands that have extended delocalised structures, such as porphyrin, or with pyrazolylborates, in which the formal negative charge does not reside on the heterocyclic ring, will not be considered in this survey.

II. Complexes with Nonbridged Ligands

A. Monocyclic Pyrrolyl, Phospholyl and Arsolyl Complexes

1. Pyrrolyl Complexes

In contrast to the cyclopentadienyl ligand, there is a dissymmetry in the ligand ring electron density of the heterocyclopentadienyl ligand, owing to the fact that the heteroatom bears a larger part of the overall electronic density than the carbon atoms. This effect is more important for the pyrrolyl ligand because of the higher electronegativity of the nitrogen atom. Considering the strong electrophilicity of group-3 metals, one would thus expect mostly the η^1-bonding mode between the pyrrolyl ligand and these elements. As an illustration, Schumann et al. have prepared a series of complexes containing both the Cp or Cp* ligand and the pyrrolyl (pyr) or the 2,5-dimethylpyrrolyl (Dmpyr) ligand:[3] [(η^5-Cp)$_2$(η^1-L)Lu(THF)] (L = pyr, Dmpyr) and [(η^5-Cp*)$_2$(η^1-pyr)Y(THF)]. X-ray data on [(η^5-Cp)$_2$(η^1-Dmpyr)Lu(THF)] (**1**) and NMR evidence show that in these complexes, the pyrrolyl ligand is indeed σ-bonded to the group-3 metal.



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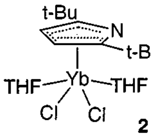
However, π-coordination of the pyrrolyl ligand can be also achieved. In a seminal paper, Marks[4] prepared [U(Dmpyr)$_4$] by reaction of KDmpyr with UCl$_4$. Although no structural data are available for this compound, a VT NMR study suggests that the low-temperature structure of this fluxional complex is that of [U(η^1-Dmpyr)$_3$(η^5-Dmpyr)]. Presumably, [U(Dmpyr)$_4$] with all the Dmpyr ligands σ-bonded would be sterically too unsaturated (c.n. =

4) and so one of the ligands is π-bonded in order to decrease this unsaturation.

Schumann et al. then introduced the 2,5-di-*tert*-butylpyrrolyl ligand (Dtpyr) in group-3 metal chemistry. It was expected that for steric reasons, the two *tert*-butyl groups would inhibit coordination with the nitrogen lone pair and indeed mostly η^5-coordinated complexes have been obtained with this ligand, such as the bis(pyrrolyl)Ln^{II} complexes [(η^5-Dtpyr)$_2$Ln(THF)] (Ln = Sm, Yb),[5] the (pyrrolyl)Yb^{III} compound [(η^5-Dtpyr)YbCl$_2$(THF)$_2$][6] (**2**), and the mixed (cyclooctatetraenyl/pyrrolyl)Ln^{III} complexes [(η^8-COT)(η^5-Dtpyr)Sm(THF)] (**3**) and [(η^8-COT)(η^5-Dtpyr)Ln] (Ln = Tm, Lu).[7] However, σ,π complexation of the Dtpyr ligand is also possible since the nitrogen lone pair of this ligand is coordinated with sodium in the neodymate(III) dimer [{(η^5-Dtpyr)(μ:η^5,η^1-Dtpyr)(μ^2-Cl)(μ^3-Cl)Na(THF)}$_2$][5] (**4**).



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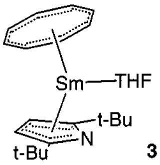

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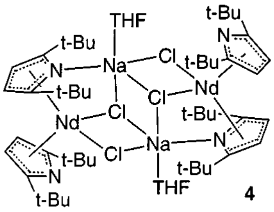

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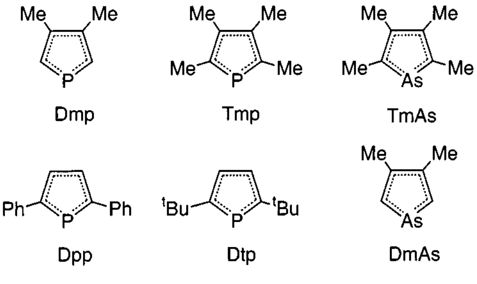
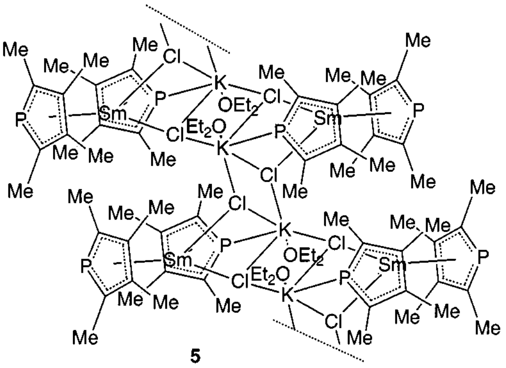
2. Phospholyl and Arsolyl Complexes

In contrast to pyrrolyl, one would expect mostly η^5- or μ:η^5,η^1-bonding modes of the phospholyl (or arsolyl) ligand owing to the close electronegativities of the =CH− and =P− (or =As−) entities (the so-called diagonal analogy).[8] We will see that this is not always so. The following phospholyl and arsolyl ligands have been used.



With the Tmp and TmAs ligands, one can usually obtain the same types of η^5-complexes as those described with the Cp* ligand. For instance, classical Ln^{III} ate complexes such as [(η^5-Tmp)$_2$LnCl$_2$Li(solv)$_2$][9] [Ln = Y, Lu, solv = Et$_2$O, dimethoxyethane (DME)] or [(η^5-Tmp)$_2$LnCl$_2$K] (Ln = Nd, Sm)[10] have been prepared by the reaction of the appropriate alkali metal phospholide with LnCl$_3$. In the case of [(η^5-Tmp)$_2$YCl$_2$Li(Et$_2$O)$_2$], it has been possible to observe the coupling of ^{31}P with ^{89}Y by NMR. From the small value of this coupling and from the triplet pattern in the ^{89}Y spectrum, it has been suggested that this complex retains the η^5-structure in solution. The polymeric crystal structure of [{(η^5-Tmp)(μ:η^5,η^1-Tmp)Ln(μ_3-Cl)$_2$K(Et$_2$O)}$_n$] (**5**), while similar to that of [{(η^5-Cp*)$_2$Ce(μ_3-Cl)$_2$K(THF)}$_n$],[11] shows additional coordination of the lone pair of one Tmp ligand to potassium. As was the case with their Cp* analogues, [(η^5-Tmp)$_2$LnCl$_2$K] could be transformed into the neutral alkyl complexes [(η^5-Tmp)$_2$LnCH(SiMe$_3$)$_2$] (Ln = Nd, Sm) by reaction with LiCH(SiMe$_3$)$_2$.



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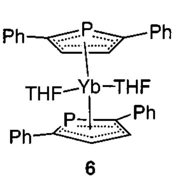
Divalent lanthanide chemistry with phospholyl ligands is also similar to that observed with the Cp* ligand. Thus, [(η^5-L)$_2$Ln(THF)$_2$] (Ln = Yb, Sm, L = Tmp, TmAs, Dpp)[12] could be obtained by the classical metathesis reaction of the potassium phospholides with LnI$_2$(THF)$_2$. More interestingly, these molecules could also be prepared by insertion of metallic ytterbium or samarium (in the form of the commercial powders) into the P−P bond of a 1,1′-biphospholyl or -biarsolyl.[13] Once again, investigation of the ytterbium complexes by multinuclear (^{31}P, ^{171}Yb) NMR suggests π-complexation of the phospholyl ligand with Yb. The structure of [(η^5-Dpp)$_2$Yb(THF)$_2$] (**6**) has been determined by X-ray crystallography.

In [(η^5-L)$_2$Ln(THF)$_2$] (L = Tmp, TmAs, Ln = Sm, Yb), THF is very easily lost under vacuum, with the formation of decomposition products L$_2$Ln, which are insoluble in nonpolar solvents.[13] In contrast, it is known that [(η^5-Cp*)$_2$Sm(THF)$_2$] sublimes by heating under high vacuum, to give unsolvated toluene-soluble [(η^5-Cp*)$_2$Sm].[14] Although the structures of L$_2$Ln are still unknown, it is suspected that these materials are polymers, with Ln−P or Ln−As σ-bonds. However, L$_2$Ln compounds are reactive in nonpolar solvents: [Tmp$_2$Yb] reacts in toluene with a stable nucleophilic carbene such as *N*,*N*-diisopropyl-2,3-dimethylimida-



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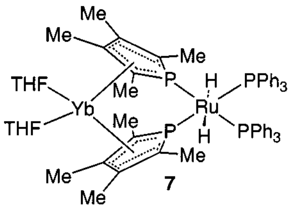

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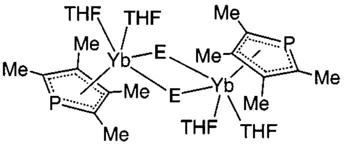
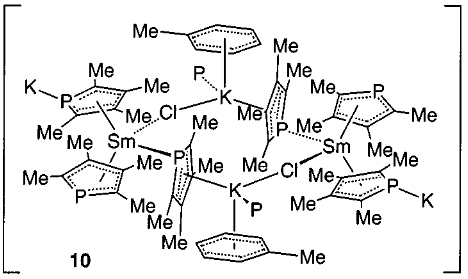
zolylidene (carb) to give the adduct $[(\eta^5\text{-Tmp})_2\text{Yb(carb)}]$.[15] Since the Tmp_2Yb moiety still possesses two lone pairs at the phosphorus atoms, it can act as a chelating ligand in the heterobimetallic Yb/Ru complexes, $[(\text{L})_2\text{Yb}(\mu{:}\eta^5,\eta^1\text{-Tmp})_2\text{RuH}_2(\text{PPh}_3)_2]$ [L = THF (**7**), Carb].[15,16]

The use of zerovalent Yb as a precursor to phospholyl complexes could be extended to the synthesis of monophospholyl Yb complexes. Insertion of Yb metal into the P−Cl bond of 1-chloro-2,3,4,5-tetramethylphosphole or the P−S bond of 1-phenylthio-2,3,4,5-tetramethylphosphole afforded the corresponding Yb^{II} dimers $[\{(\eta^5\text{-Tmp})\text{Yb}(\mu\text{-E})(\text{THF})_2\}_2]$ [E = Cl (**8**), SPh (**9**)].[17]



E = Cl (**8**), SPh (**9**)

The following examples illustrate how the substitution pattern on the heterocyclopentadienyl ring can influence its coordination chemistry. Compounds such as $[(\eta^5\text{-Cp*})_3\text{M}]$ (M = Nd, Sm, U)[18] exist but they cannot be synthesised by the metathesis reaction of MX_3 (X = halogen) with the appropriate alkali metal salts, because these reactions often require donor solvents such as THF which can react with the sterically overcrowded $\text{Cp*}_3\text{M}$ intermediates. However, removal of just one methyl group on the Cp* ring allows for the easy synthesis of $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_3\text{Ln}]$ (Ln = La, Sm, Tb) by the metathesis route.[19] In a way, the Tmp ligand may be regarded as looking more like $\text{C}_5\text{Me}_4\text{H}$ than Cp*: The lone pair on the phosphorus atom in the Tmp ligand is sterically more similar to a C−H bond in Cp than to a $\text{C}-\text{CH}_3$ bond in Cp*. However, reaction of three equivalents of KTmp with SmCl_3 in toluene did not give $[(\eta^5\text{-Tmp})_3\text{Sm}]$. An ate complex of polymeric two-dimensional structure, which retains KCl, was obtained instead. Its X-ray structure has been determined and is that of $[\{(\eta^5\text{-Tmp})\text{Sm}(\mu{:}\eta^5,\eta^1\text{-Tmp})_2(\mu\text{-Cl})\text{K}(\eta^6\text{-toluene})\}_n]$[20] (**10**).



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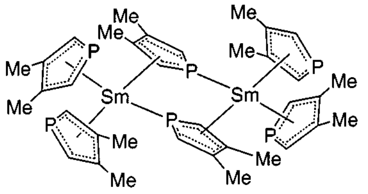
This complex looks like a reaction intermediate towards a hypothetical $[(\eta^5\text{-Tmp})_3\text{Sm}]$ since the Sm atom in **10** is complexed with three Tmp ligands, but KCl has not been eliminated. Under the same conditions with the Dmp ligand, a neutral tris(Dmp) dimer, $[\{(\eta^5\text{-Dmp})_2(\mu{:}\eta^5,\eta^1\text{-Dmp})\text{Sm}\}_2]$ (**11**), was obtained[20]. In this case, since the Dmp ligand is smaller, the Sm atom can achieve a c.n. of 10.



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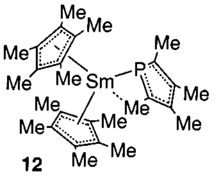
It thus seemed interesting to study the coordination of the phospholyl ligand around Sm in complexes of composition $\text{Cp*}_2\text{Sm(L)}$ (L = phospholyl, arsolyl), that is, when the Sm atom is in a very crowded environment imposed by two Cp* ligands. $\text{Cp*}_2\text{Sm(L)}$ (L = Tmp, Dmp, Dmas, Dtp) was prepared by reductive cleavage of the P−P or As−As bonds of the corresponding 1,1′-biphospholyls or -biarsolyls by $\text{Cp*}_2\text{Sm}$.[21] Three types of structures were obtained.

With Tmp as ligand, the structure is that of $[(\eta^5\text{-Cp*})_2(\eta^1\text{-Tmp})]$ (**12**). The Tmp ligand is only σ-bonded to Sm, but since this atom is still coordinatively unsaturated (c.n. = 7), it will look for additional electronic density through an interaction with one of the α-methyl groups of the σ-Tmp ligand, which thus becomes unsymmetrically bonded to Sm.

With Dmp or Dmas as ligands, the structure is that of an unsymmetrical dimer, $[(\eta^5\text{-Cp*})_4\text{Sm}_2(\eta^1\text{-L})(\mu{:}\eta^5,\eta^1\text{-L})]$ [L = Dmp (**13**), Dmas (**14**)]. Apparently, there is enough room around the Sm atom to achieve π-coordination with the less bulky Dmp or Dmas. However, the lone pair on this π-ligand is still available for complexation with another $\text{Cp*}_2\text{Sm}$ unit, which then only needs σ-coordination with another Dmp or Dmas ligand to achieve the optimum c.n. of 8. With Dtp as ligand, the lone pair is sterically hindered, so only π-coordination is possible and the structure is that of $[(\eta^5\text{-Cp*})_2(\eta^5\text{-Dtp})]$ (**15**).



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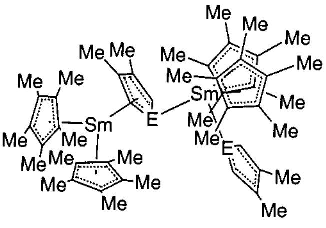
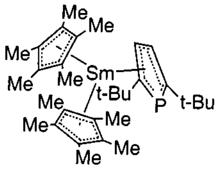


E = P (**13**), As (**14**)



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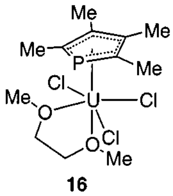
The Tmp ligand has been extensively used in actinide chemistry, in which most of its chemistry parallels that observed with the Cp* ligand. Mono- or bis(phospholyl)U^{IV} complexes such as $[(\eta^5\text{-Tmp})\text{UCl}_3(\text{DME})]$[22] (**16**), $[(\eta^5\text{-Tmp})_2\text{UCl}_2]$,[22] $[(\eta^5\text{-Tmp})_2\text{U(BH}_4)_2]$[23] (**17**), and $[(\eta^5\text{-}$

Tmp)U(BH_4)$_3$][24] could be prepared by reaction of UCl_4 or U(BH_4)$_4$ with KTmp. A mixed Tmp/Cp* complex, [(η^5-Tmp)(η^5-Cp*)U(BH_4)$_2$],[22,25] could also be obtained from KTmp and [(η^5-Cp*)U(BH_4)$_3$]. These Tmp complexes could, in turn, be converted into [(η^5-Tmp)UX_3(DME)], [(η^5-Tmp)(η^5-Cp*)UX_2], and [(η^5-Tmp)$_2UX_2$] (X = alkyl, alkoxy) by reaction with the appropriate nucleophiles.[22] However, contrary to the case with the Cp* ligand, tris(phospholyl)U^{IV} complexes can be obtained: [(η^5-Tmp)$_3$UCl] (**18**) was prepared from KTmp and UCl_4 and this compound was transformed into [(η^5-Tmp)$_3$UMe] and [(η^5-Tmp)$_3$UH].[26] Here, the Tmp ligand behaves similarly to the C_5Me_4H ligand since [(η^5-C_5Me_4H)$_3$UCl][27] has been prepared and its structure determined by X-ray.



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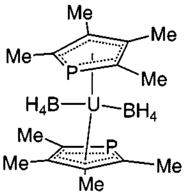

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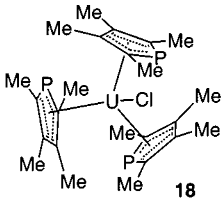

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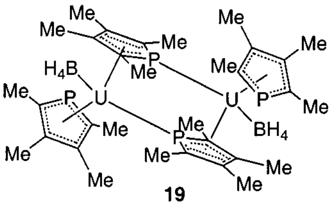
Low-valent (phospholyl)U^{III} complexes could also be obtained either by reduction of the corresponding U^{IV} complexes with sodium amalgam or by reaction of TmpK with the U^{III} precursor [(η^6-mesitylene)U(BH_4)$_3$].[23] When these reactions were performed in THF, U^{III} ate complexes such as [{(η^5-Tmp)$_2$U(BH_4)$_2$}(M)] and [{(η^5-Tmp)U(BH_4)$_3$}(M)] (M = Na, K) were obtained. However, reduction of [(η^5-Tmp)$_2$U(BH_4)$_2$] or [(η^5-Tmp)(η^5-Cp*)U(BH_4)$_2$] in toluene led to the precipitation of $NaBH_4$ and to the isolation of neutral U^{III} dimers [{(η^5-Tmp)(μ:η^5,η^1-Tmp)U(BH_4)}$_2$] (**19**) and [{(η^5-Cp*)(μ:η^5,η^1-Tmp)U(BH_4)}$_2$], respectively. In these compounds, the ^{31}P NMR signal of the bridging Tmp ligand was detected very far downfield ($\delta \approx 3500-3900$). The structure of **19** has been determined by an X-ray crystal structure analysis.[25]



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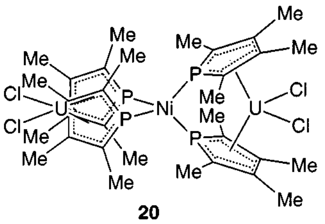
A comparison of the electronic properties of the Tmp and Cp* ligand has been made by electrochemical measurements. The following one-electron reversible potentials (vs. ferrocene/ferricinium) were found for [(η^5-Tmp)$_2$U(BH_4)$_2$] (−1.49 V), [(η^5-Tmp)(η^5-Cp*)U(BH_4)$_2$] (−1.66 V), and [(η^5-Cp*)$_2$U(BH_4)$_2$] (−1.83 V). These results clearly show that the Tmp ligand is less electron-rich than the Cp* ligand. An additional piece of evidence for this is the fact that only [(η^5-Tmp)$_2$U(BH_4)$_2$] was reduced when an equimolar mixture of [(η^5-Tmp)$_2$U(BH_4)$_2$] and [(η^5-Cp*)$_2$U(BH_4)$_2$] was treated with 0.5 equivalents of sodium amalgam. The chemistry of (phospholyl)uranium complexes is therefore not only influenced by steric but also by electronic factors.[22]

Finally, further evidence for the accessibility of the phosphorus lone pairs was found by the X-ray characterisation of two U−Ni heterobimetallic compounds: [Cl_2U(μ:η^5,η^1-Tmp)$_2$Ni] (**20**) and [{Cl_2U(μ:η^5,η^1-Tmp)$_2$(μ-Tmp)Ni}$_2$][28] (**21**).



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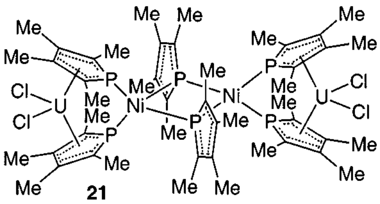
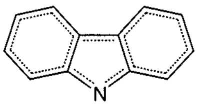


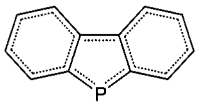
21

B. Ring-Fused Pyrrolyl and Phospholyl Complexes

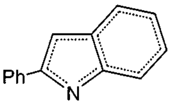
Another opportunity for comparing the phospholyl and pyrrolyl ligands is the study of the effect of benzoannelation on the coordinating properties of these ligands. The following ligands have been used, mostly in Ln^{II} chemistry.



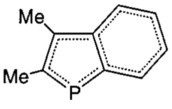
Carbazolyl (Cbz)



Phosphafluorenyl (Pflu)

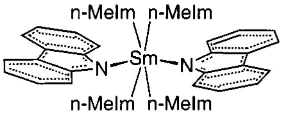


2-Phenylindolyl (PhInd)



2,3-dimethylphosphindolyl (DMPind)

In general, the Ln^{II} complexes are 6-coordinate octahedral or distorted octahedral complexes of general formula [(η^1-L)$_2$Ln(D)$_4$] (L = PhInd, Cbz; Ln = Sm, Eu, Yb; D = donor). Planarity or near-planarity at the nitrogen atom is achieved and thus coordination of type B (planar) is present. The ligands L can be either axial, e.g. in [(η^1-Cbz)$_2$Sm(*N*-MeIm)$_4$][29] (**21**, *N*-MeIm = *N*-Methylimidazole) and [(η^1-PhInd)$_2$Yb(THF)(diglyme)][30] (**23**) or equatorial, e.g. in $[(\eta^1\text{-Cbz})_2\text{Ln(THF)}_4]$ [Ln = Eu[31] (**24**), Sm[29] (**25**)] and $[(\eta^1\text{-Cbz})_2\text{Yb(THF)}_2\text{(DME)}]$[32] (**26**). The steric bulk of the PhInd ligand probably causes the lability of the THF ligand in $[(\text{PhInd})_2\text{Yb(THF)}_4]$. Heating this compound in toluene in the presence of DME produced a five-coordinate dimer, $[\{(\eta^1\text{-PhInd})(\mu{:}\eta^1\text{-PhInd})\text{Yb(DME)}\}_2]$ (**27**), in which there is an unprecedented coordination of type E for one of the PhInd ligands.[30] A single Sm^{III} complex, $[(\text{PhInd})_3\text{Sm(THF)}]$, has been mentioned but its structure is unknown.[31]



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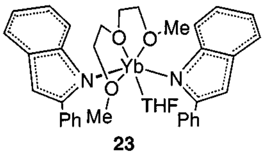

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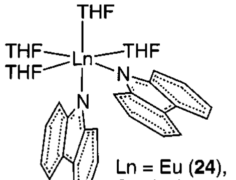
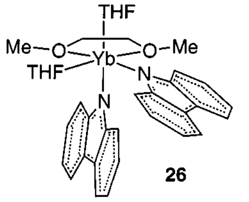


Ln = Eu (**24**), Sm (**25**)



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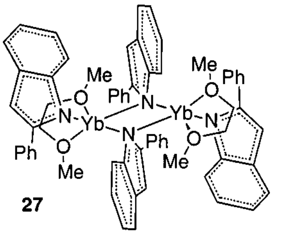

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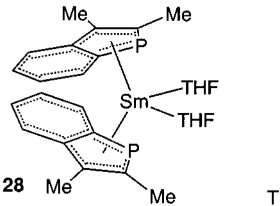
The phosphorus analogues of the indolyl and carbazolyl ligands have a completely different behaviour. The DMPind (2,3-dimethylphosphindolyl) ligand is still π-complexed with the Sm atom in $[(\eta^5\text{-DMPind})_2\text{Sm(THF)}_2]$[33] (**28**) while this is no longer the case in the octahedral phosphafluorenyl complexes, $[(\eta^1\text{-Pflu})_2\text{Ln(THF)}_4]$ [Ln = Sm[33] (**29**), Yb[34] (**30**)], which display type B (bent) coordination. Remarkably, the Pflu ligands in **29** are axial while in **30** they are equatorial, which points to a probable small energy difference between the two forms.



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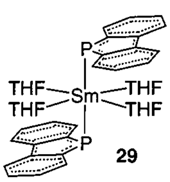

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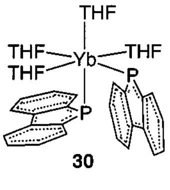

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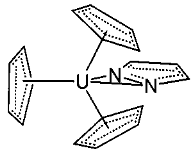
The difference in coordination behaviour between the phosphindolyl and phosphafluorenyl ligands is due to the weaker electron density of the 5-membered ring in the phosphafluorenyl ligand (because of the double benzoannelation), that prevents π-coordination by this ring, so only σ-coordination of the phosphafluorenyl ligand is possible. However, unlike the carbazolyl ligand, the phosphafluorenyl ligand is bent at the phosphorus atom because of the greater tendency of phosphorus to form pyramidal compounds. However, indenyl and fluorenyl complexes of Sm^{II} are both η^5-coordinated.[35]

C. Pyrazolyl, Triphospholyl and Stibadiphospholyl Complexes

Raymond and Eigenbrodt, Jr. were the first to demonstrate the planar η^2-coordination mode of the pyrazolyl ligand (mode E) in uranium chemistry. The metathesis reactions of $[\text{Cp}_3\text{UCl}]$ and $[\text{Cp*}_2\text{UCl}_2]$ with potassium pyrazolate afforded $[\text{Cp}_3\text{U(pz)}]$[36] (**31**, pz = pyrazolate) and $[\text{Cp*}_2\text{U(pz)}_2]$[37] (**32**) or $[\text{Cp*}_2\text{U(Cl)(pz)}]$[37] (**33**), respectively (depending on the stoichiometry).



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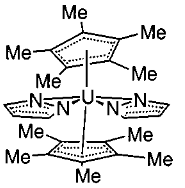

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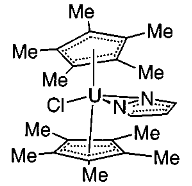
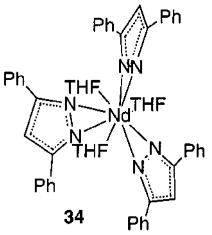


33

Early experiments involved the reaction of lanthanide halides with sodium pyrazolate or 3,5-dimethylpyrazolate (Dmpz). Polynuclear sodium pyrazolyllanthanoidates such as $[\text{Ln}_3(\mu\text{-Dmpz})_6(\eta^2\text{-Dmpz})_2(\mu^3\text{-O})\text{Na}_2(\text{THF})_2]$ (Ln = Y, Ho, Yb, Lu) were obtained, in which the interstitial oxygen atom most likely originated from water present as an impurity in the solvents. Here, the Dmpz ligand can be found in coordination modes E and G.[38]

In almost all other group-3 pyrazolate metal complexes, coordination mode E is present for at least one of the pyrazolyl ligands. In $[\text{LnL}_3(\text{D})_n]$ (L = substituted pyrazolyl; D = donor ligand), the coordination mode of the remaining pyrazolyl ligands depends on the substitution pattern of the pyrazolyl ring. With ligands possessing a group with relatively low steric bulk, such as Dmpz, both coor-



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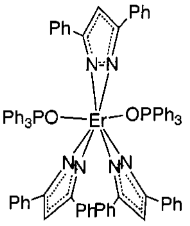

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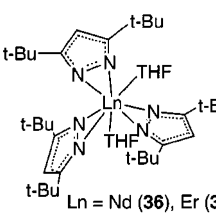
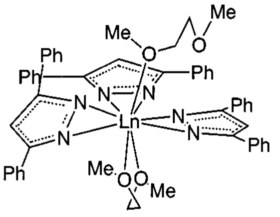


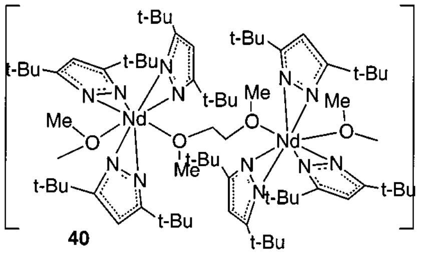
Ln = Nd (**36**), Er (**37**)

dination modes E and G can be found, e.g. in [{(η^2-Dmpz)$_2$(μ:η^1-Dmpz)Nd(μ-THF)}$_2$].[39] With bulkier pyrazoyls such as 3,5-diphenylpyrazolyl (Dppz) or 3,5-di-*tert*-butylpyrazolyl (Dtpz), only type E is encountered in [(η^2-Dppz)$_3$Nd(THF)$_3$] (**34**), [(η^2-Dppz)$_3$Ln(OPPh$_3$)$_2$] [Ln = La, Nd, Er (**35**)],[40] and [(η^2-Dtpz)$_3$Ln(THF)$_2$] [Ln = Y, La, Nd (**36**), Sm, Gd, Dy, Er (**37**), Yb, Lu].[41]

It should be noted that because Dppz is sterically less bulky than Dtpz, the coordination number for the Nd atom in **34** (c.n. = 9) is greater than in **36** (c.n. = 8). Likewise, there are two DME ligands (one chelating and one η^1) in 9-coordinate [(η^2-Dppz)$_3$Ln(η^2-DME)(η^1-DME)] [Ln = Er[42] (**38**), Nd[43] (**39**)] while the structure of 8-coordinate [{(η^2-Dtpz)$_3$Nd(μ-DME)}$_n$] is polymeric, with one bridging DME ligand[42] (**40**).



Ln = Er (**38**), Nd (**39**)



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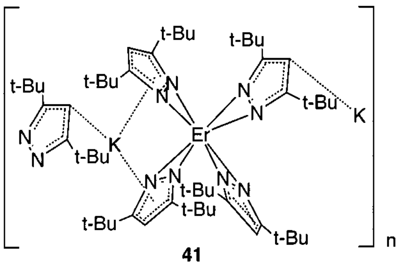
In the absence of donor solvents, the reaction of erbium chloride with KDtpz in toluene gave polymeric [{K(μ-Dtpz)$_3$Er}$_n$] (**41**) displaying an unprecedented η^3-interaction of the Dtpz ligand with the potassium atom. Adding 18-C-6 and DME to this polymer resulted in the isolation of a homoleptic 8-coordinate erbate complex, [{K(18-C-6)(DME)(Toluene)}$^+$ · {(η^2-Dtpz)$_4$Er}$^-$] (**42**).[44]



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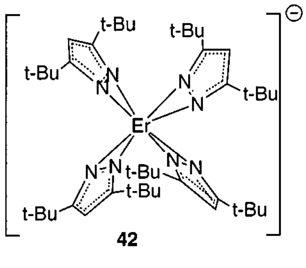
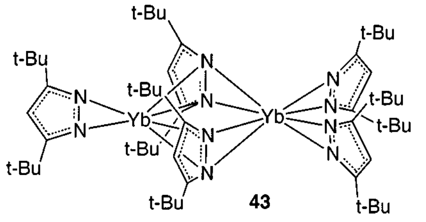


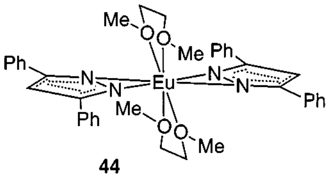
42

Neutral homoleptic complexes could be obtained under harsher conditions: Reaction of neat neutral HDtpz with the lanthanide metal in the presence of Hg metal at 220 °C had a different outcome, depending on the metal. The following compounds were obtained: complexes of Nd^{III} and Sm^{III}, [Ln(Dtpz)$_3$] (Ln = Sm, Nd), an Eu^{II} complex, [Eu(Dtpz)$_2$], and an interesting mixed valence Yb^{II,III} complex, [(η^2-Dtpz)$_3$(μ:η^2-Dtpz)$_2$Yb$_2$] (**43**) with coordination modes E and F. Coordination mode F is also present in [(η^2-Dtpz)$_4$(μ:η^2-Dtpz)$_2$Nd$_2$][45]



43

Ln^{II} complexes could be prepared by several routes, notably by redox-transmetallation reactions involving lanthanide powders and mild oxidants such as thallium or mercury pyrazolates or even diphenylmercury in the presence of pyrazoles. With DME as donor ligand, all complexes have the structure of 8-coordinate [(η^2-L)$_2$Ln(DME)$_2$] {Ln = Sm, Eu (**44**), Yb, L = Dtpz, Dppz, and 4,5-dihydro-2*H*-benz[*g*]indazolyl (**45**)}. The pyrazolyl ligands generally have the *cis* configuration, except in [(η^2-Dppz)$_2$Eu(DME)$_2$] in which they are *trans*.[46]



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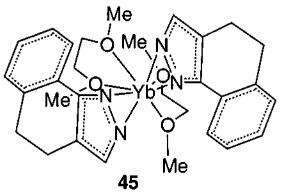

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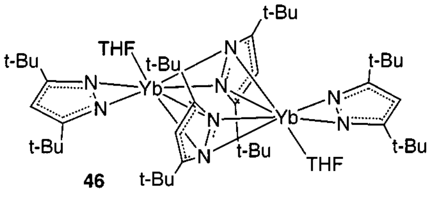
In the case of Yb and with THF as donor ligand, there is only one coordinated THF, and both coordination types E and F are present in [(η^2-Dtpz)$_2$(μ:η^2-Dtpz)$_2$Yb$_2$(THF)$_2$][47] (**46**).



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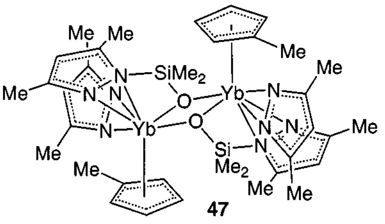
Organolanthanide complexes containing the pyrazolyl ligand have also been prepared. The reaction of [(η^5-MeC$_5$H$_4$)$_3$Ln] with Dmpz gave [(MeC$_5$H$_4$)Ln(Dmpz)$_2$] (Ln = Nd, Gd, Dy, Yb). These compounds reacted with silicone grease, and insertion of a dimethylsilanone unit into an Ln−N bond took place, thus affording dimeric [{(η^5-MeC$_5$H$_4$)(η^2-Dmpz)(μ:η^1,η^2-OSiMe$_2$-Dmpz)Ln}$_2$] [Ln = Yb[48a] (**47**), Dy[48b]]. In this oxygen-bridged dimer, both

Dmpz moieties display the type F (planar) coordination mode.[48]



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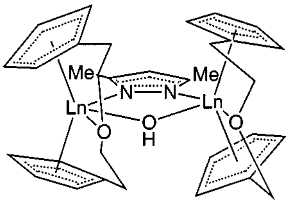
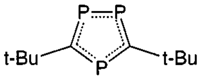
A bridged dicyclopentadienyl ligand containing an ether linkage can bind to a lanthanide through both Cp rings and the oxygen lone pair, thus filling seven coordination sites, such as in [η-{O($C_5H_4CH_2CH_2)_2$}LnCl]. The idea here is that this rigid arrangement should increase the stability of solvent-free organolanthanide complexes. The reaction of [η-{O($C_5H_4CH_2CH_2)_2$}LnCl] (Ln = Y, Lu) with NaDmpz afforded [η-{O($C_5H_4CH_2CH_2)_2$}Ln(Dmpz)], which by controlled hydrolysis gave a dimer with both μ-hydroxo and μ-pyrazolyl (type G) ligands, [({η-{O(C_5H_4-$CH_2CH_2)_2$}Ln$)_2$(μ-Dmpz)(μ-OH)][49] [Ln = Y, Lu (**48**)].

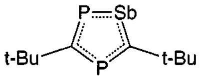


Ln = Y, Lu (**48**)

An interesting comparison has recently been made between the coordinating modes of the pyrazolyl ligand and that of the analogous 1,2,4-di-*tert*-butyltriphospholyl (Dttp) and 1,4,2-di-*tert*-butylstibadiphospholyl (Dtsbp).[43]



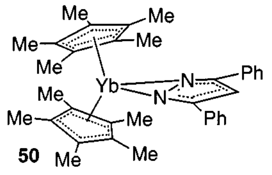
Dttp



Dtsbp

One-electron oxidation of [(η^5-Cp*$)_2$Yb(THF)] with TlDppz afforded [(η^5-Cp*$)_2$Yb(η^2-Dppz)] (**50**) in which the Dppz ligand has the usual type G (planar) coordination mode. In the same type of reaction, [(η^5-Cp*$)_2$Sm(THF$)_2$] reacted with TlDttp to give [(η^5-Cp*$)_2$Sm(η^2-Dttp)(THF)] (**51**), in which the Dttp ligand also displays type G coordination (η^2). However, the ligand is now bent towards the metal centre; reaction of TlDtsbp with Yb metal in the presence of LiDtsbp gave a homoleptic ytterbate(II) complex, [{Li(THF$)_4$}$^+$ · {(η^5-Dtsbp$)_2$(η^2-Dtsbp)Yb}$^-$] (**52**), while the reaction of KDttp with MI_3 in apolar solvents gave [(η^5-Dttp$)_2$(η^2-Dttp)M] [M = Sc, Y, U (**53−55**)].[50] Reduction of the Sc^{III} complex with KC_8 gave a formal Sc^{II} complex, [(Dttp$)_2$Sc], the structure of which is under investigation.[51]

The electron density of the pyrazolyl ligands mostly resides in the in-plane sp^2-hybridized nitrogen lone pairs, which explains the type G (planar) coordination mode for this ligand in **50**. The lone pairs on the heteroelements in Dttp and Dtspb are much more diffuse and less directive, and thus the P and Sb atoms have a greater propensity to be pyramidal. The type G (bent) coordination mode is therefore observed for the Dttp ligand in **51**, for one of the Dtsbp ligands in **52**, and for one of the Dttp ligands in **53−55**. On the other hand, because of the similar electronegativities of the P, Sb, and C atoms in Dttp and Dtsbp, these heterocyclopentadienyl ligands can also be coordinated in the η^5-mode (which is typical for the Cp ligand) in **52−55**. The reaction of *t*BuC≡P with Sc atoms gave a triple-decker Sc^I complex, [{(η^5-Dttp)Sc$\}_2$(μ:η^6,η^6-$P_3C_3t Bu_3$)], in which π-coordination of the Dttp ligand is observed[52] (**56**).



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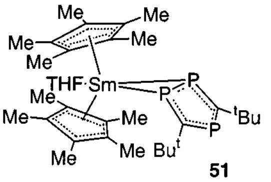

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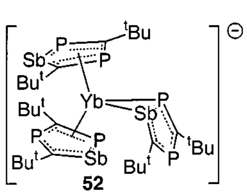

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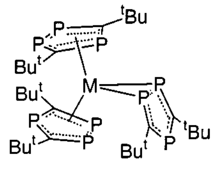
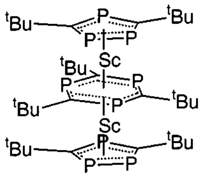


M = Sc, Y, U
(**53**, **54**, **55**)



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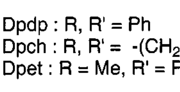
II. Complexes with Bridged Pyrrolyl Ligands

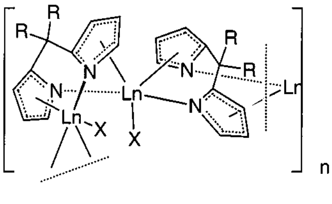
A. Dipyrrolyl Complexes

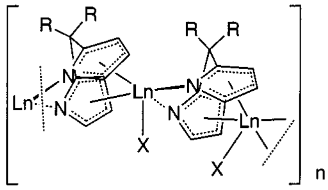
Dipyrrolyl ligands in which the two pyrrolyl moieties are linked at the 2-position by a one-carbon unit have very recently been introduced in lanthanide chemistry. They include bis(2-pyrrolyl)diphenylmethane (Dpdp), 1,1-bis(2-pyrrolyl)cyclohexane (Dpch) and [1,1-bis(2-pyrrolyl)ethyl]-benzene (Dpet).



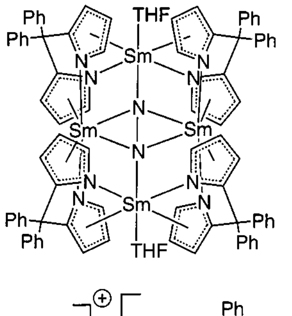
Dpdp : R, R' = Ph
Dpch : R, R' = $-(CH_2)_5-$
Dpet : R = Me, R' = Ph

Almost all compounds described so far with this type of ligand display σ,π-complexation of both pyrrolyl rings to a lanthanide metal centre, and thus polynuclear complexes are obtained, frequently in cyclic structures. Generally, the two π-complexing rings belong to two different bridged ligands, but there is one example in which the lanthanide metal centre is π-complexed to two rings belonging to the same ligand.





The proximity of the metal centres in these polynuclear complexes allow for the cooperative behaviour of the metallic centres: Reaction of K_2Dpdp with $SmI_2(THF)_2$ in the presence of nitrogen irreversibly gave a tetranuclear Sm^{III}−nitrogen (formally N_2^{4-}) complex, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpdp})Sm\}_4(\mu{:}\eta^1,\eta^1,\eta^2,\eta^2\text{-}N_2)]$ (**57**). In the absence of nitrogen, a compound of global composition $[\{(Dpdp)Sm\}_7 \cdot SmI_2]$ was obtained; it is in fact a zwitterionic Sm^{II} species, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpdp})Sm\}_5(\mu_5\text{-I})^- \cdot \{(\mu{:}\eta^5,\eta^1\text{-Dpdp})\}_2Sm_3(THF)_3(\mu_3\text{-I})^+]$ (**58**). Reduction of this zwitterion with KH in the presence of N_2 yielded the nitrogen compound **57**.[53]



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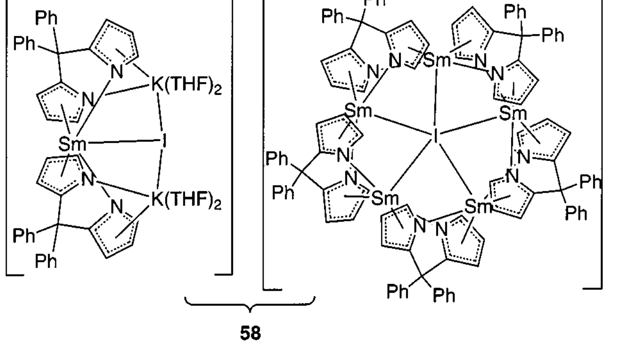

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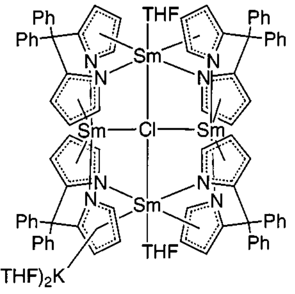
The reaction of K_2Dpdp with $SmCl_3(THF)_3$ gave a yellow compound (presumably [DpdpSmCl]) which was further reduced with alkali metals under argon; surprisingly, the outcome of this reduction was different, depending on the alkali metals used. With potassium, a tetrameric samarium(II) compound, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpdp})Sm\}_4(\mu_4\text{-Cl})K(THF)_2]$ (**59**), was obtained, which displays η^5-coordination of potassium with one pyrrolyl ring. With lithium and sodium, the reduction was not complete and mixed-valent $Sm^{II,III}$ octameric anionic complexes **60**, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpdp})Sm\}_8(\mu_4\text{-Cl})_4Li\}^{2-} \cdot \{Li_2Cl(THF)_4\}^+ \cdot \{Li(THF)_4\}^+]$, and **61**, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpdp})Sm\}_8(\mu_4\text{-Cl})_4Na\}^- \cdot \{Na(THF)_5\}^+]$, respectively, were obtained. While the overall structures of **60** and **61** are similar, the reduction surprisingly occurred to a greater extent with lithium than with sodium since **60** displays one Sm^{III} and seven Sm^{II} atoms whereas in **61** there are two Sm^{III} and six Sm^{II} atoms. The reaction of **60** and **61** with KH in the presence of N_2 gave the above-mentioned tetranuclear Sm nitrogen complex **57**.[54]



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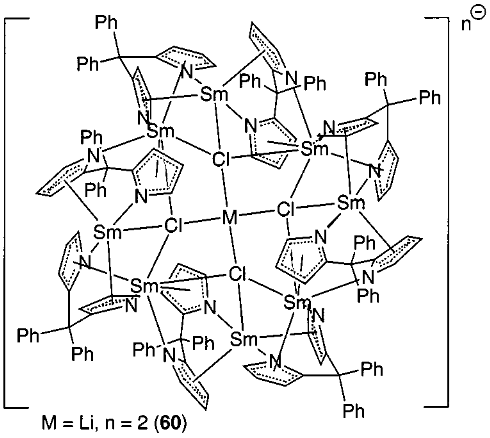
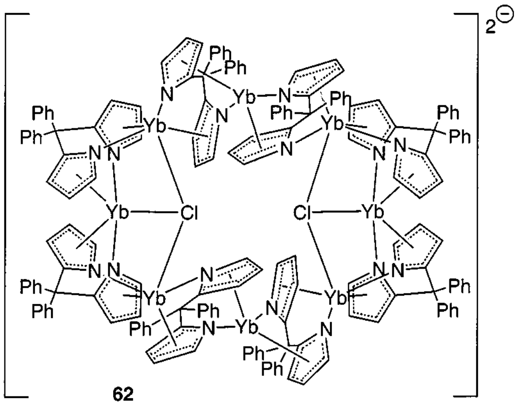


M = Li, n = 2 (**60**)
M = Na, n = 1 (**61**)

The reaction of Li_2Dpdp with $YbCl_3(THF)_3$ gave a yellow-orange compound (presumably [DpdpYbCl]) that was further reduced to Yb^{II} complexes with alkali metals. With lithium an octameric ytterbium(II) dianionic species, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpdp})Yb\}_8(\mu_3\text{-Cl})_2Li\}^{2-} \cdot \{[Li(THF)_4]^+\}_2]$ (**62**) was obtained, whereas with sodium a monomeric ytterbate(II) complex, $[(\mu{:}\eta^5,\eta^1\text{-Dpdp})YbNa_2(THF)_4]$ (**63**), was isolated displaying $\mu{:}\eta^5,\eta^1$-type coordination both to ytterbium and to sodium.[55]



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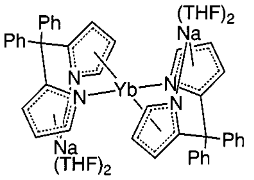

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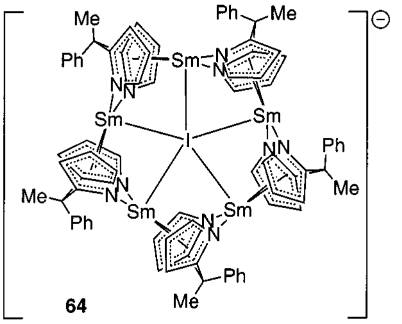
Structural variations of the dipyrrolyl ligand included the use of the Dpch and Dpet ligands in samarium chemistry. The reaction of K_2Dpet with $SmI_2(THF)_2$ gave a pentanuclear μ-iodo anionic complex, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpet})Sm\}_5(\mu_5\text{-}I)^- \cdot K(THF)_6{}^+]$ (**64**), similar to that observed with the Dpdp ligand. Each metal centre is now π-bonded to pyrrolyl rings belonging to the same ligand. The results obtained with the Dpch ligands are different since reaction of K_2Dpch with $SmI_2(THF)_2$ or of Na_2Dpch with $SmCl_3(THF)_3$ followed by reduction with sodium metal afforded a mixed-valence complex, $[\{(\mu{:}\eta^5,\eta^1\text{-Dpch})Sm\}_4(\mu_2\text{-}O)(THF)_2]$ (**65**). Presumably, the oxygen atom comes from a THF molecule. It thus seems that the modifications on the ligand greatly affect the redox potential of the coordinated metal centres.[56]



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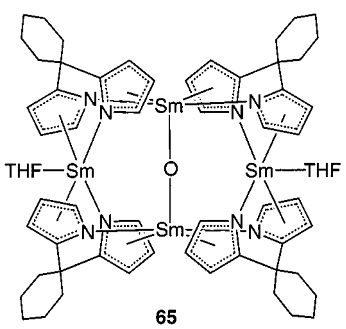

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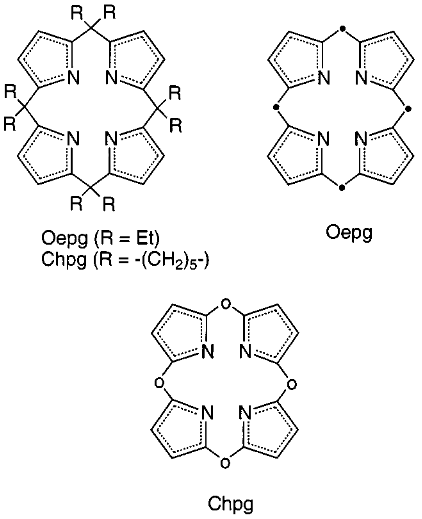
B. Macrocyclic Tetrapyrrolyl Complexes

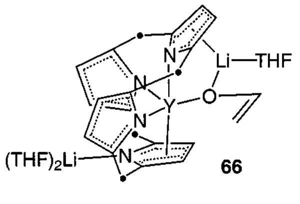
Cyclic calix[4]tetrapyrrolyl (also called porphynogen) macrocyclic ligands have been used in lanthanide chemistry. These ligands provide a rather rigid environment in which the lanthanide metal centre can use most of its coordination sites, often in an $\eta^5,\eta^1,\eta^5,\eta^1$-coordination mode with the pyrrolyl rings, one or two coordination sites on the metal centre then being left for chemical transformations. In addition, the very electron-rich environment (up to four negative charges on the tetrapyrrolide anion) enhances the reactivity of the metal centre towards the activation of small molecules, as reported hereafter. Two ligands have been used, mainly octaethylporphynogen (Oepg) as well as cyclohexylporphynogen (Chpg) (Scheme 1).



Scheme 1. For clarity, the following abbreviations are used in the subsequent schemes: • = $C(Et)_2$, o = C $[-(CH_2)_5-]$

The outcome of the reaction of $LnCl_3$ with porphynogen anions depends very much on the nature of the counterion; the reactions of the lithium salts are described first.

The reaction of $OepgLi_4$ with $YCl_3(THF)_{3.5}$ gave an enolate complex, $[Li(THF)_2(Oepg)Y(\mu\text{-}OCH{=}CH_2)Li(THF)]$ (**66**), in which the yttrium atom is $\eta^5,\eta^1,\eta^1,\eta^1$-bonded to the Oepg ligand. The enolate moiety probably arises from THF cleavage. Attempted substitution of this enolate with an alkyl or hydride group was unsuccessful and instead a lithium salt of the Oepg ligand, $[\{(Oepg)[Li(THF)]_4\}\{(THF)Li(OCH{=}CH_2)\}_2]$, was isolated[57].



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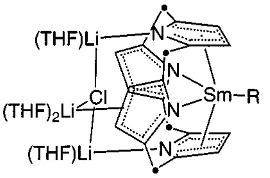
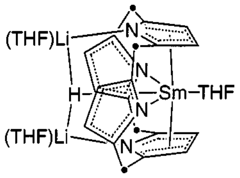
The reaction of $SmCl_3(THF)_3$ with $OepgLi_4$ or $ChpgLi_4$ gave $[(Oepg)ClSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ (**67**) and $[(Chpg)ClSm(\mu_3\text{-}Cl)Li_3(THF)_4]$, respectively. In this case, the Sm atom displays $\eta^5,\eta^1,\eta^5,\eta^1$-coordination with the pyrrolyl ligands, and the lithium atoms are also bonded to the pyrrolyl groups. These compounds have a very rich chemistry: The reaction of $[(Oepg)ClSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ with RLi gave the σ-bonded $[(Oepg)RSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ [R = Me, vinyl (**68**)]. Treatment of $[(Oepg)RSm(\mu_3\text{-}Me)Li_3(THF)_4]$ with H_2 or phenylsilane afforded an Sm^{III} hydride, $[(Oepg)(THF)Sm(\mu_3\text{-}H)Li_2(THF)_2]$ (**69**), which could also be conveniently obtained from $[(Oepg)RSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ by reaction with $LiAlH_4$. Compound **68** was thermally unstable and decomposed into an Sm^{II} complex, $[(Oepg)(THF)Sm(\mu_3\text{-}Cl)Li_3(THF)_4]$.[58]



R = Cl (**67**), CH=CH2 (**68**)



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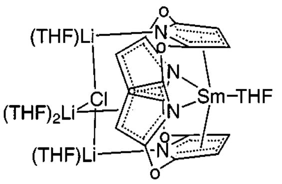

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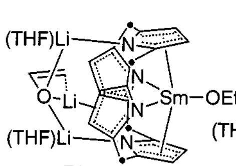
Similar μ_3-chloro$-Sm^{II}$ complexes are also available by lithium reduction of the appropriate chloro$-Sm^{III}$ complexes: Reaction of lithium with $[(Chpg)ClSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ under argon gave $[(Chpg)(THF)Sm(\mu_3\text{-}Cl)Li_3(THF)_4]$ (**70**) while reduction of $[(Oepg)ClSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ resulted in an μ_3-enolato$-Sm^{II}$ complex, $[(Oepg)(Et_2O)Sm(\mu_3\text{-}OCH{=}CH_2)Li_3(THF)_2]$ (**71**), in which the enolate moiety is again likely to arise from THF cleavage. This complex **71** reversibly added ethylene to give an Sm^{III} dimer, $[\{(Oepg)Sm(\mu_3\text{-}OCH{=}CH_2)Li_3(THF)_2\}_2(\mu\text{-}CH_2CH_2)]$ (**72**), in which the ethylene has been formally reduced to its dianion as suggested by the long C$-$C bond (1.49 Å).[59] The reaction of lithium with $[(Oepg)ClSm(\mu_3\text{-}Cl)Li_3(THF)_4]$ [formed in situ by reaction of $SmCl_3(THF)_3$ and $OepgLi_4$] under nitrogen resulted in nitrogen reduction and the formation of an Sm^{III} complex containing a tetralithium hydrazide, $[\{(Oepg)SmLi\ (THF)_2\}_2(N_2Li_4)]$ (**73**), presumably through a transient Sm^{II} species which is reoxidized to Sm^{III} by means of an electron transfer to N_2.[60]

A different series of complexes was obtained when the reaction stoichiometry of Sm and Oepg is 2:1. The reaction of 2 equivalents of $SmCl_3(THF)_3$ with one equivalent of $OepgLi_4$ gave the dinuclear $[(Oepg)\{Sm(\mu\text{-}Cl)_2Li(THF)_2\}_2]$ (**74**) in which both Sm atoms are $\eta^5,\eta^1,\eta^5,\eta^1$-coordinated to the Oepg ligand. Permethylation of this complex with MeLi afforded $[(Oepg)\{Sm(\mu\text{-}Me)_2Li(THF)_2\}_2]$ (**75**). Hydrogenolysis of **75** did not give the expected result (replacement of the two μ-Me ligands by two μ-H ligands) but instead yielded the above-mentioned monosamarium hydride complex **69**. This complex **69** was also obtained by reduction of **74** with phenylsilane, but in this case a bis(μ-enolate) intermediate, $[(Oepg)(THF)Sm(\mu_3\text{-}H)Li_2(\mu_3\text{-}OCH{=}CH_2)_2Li_2(THF)_2]$ (**76**), was isolated.[61]



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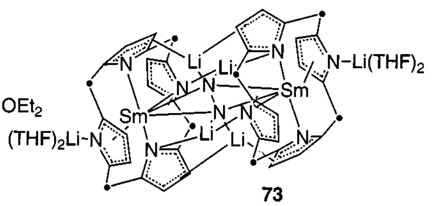

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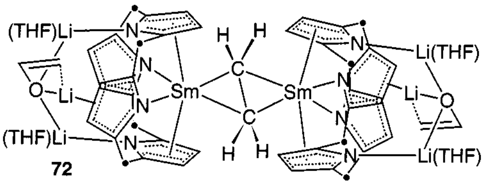

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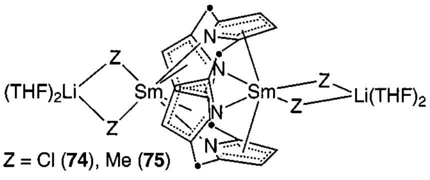
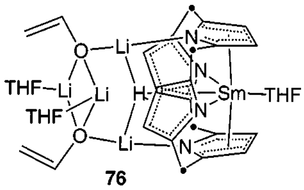


Z = Cl (**74**), Me (**75**)



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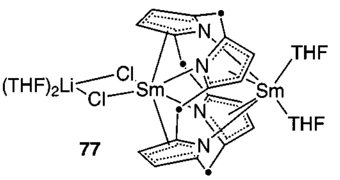
The reaction of **74** with $LiAlH_4$ did not give the expected dihydride either but instead reduction to Sm^{II} occurred. This reduction could be performed stepwise. Depending on the reaction conditions, a mixed-valent $Sm^{II,III}$ complex, $[(THF)_2Sm(Oepg)Sm(\mu\text{-}Cl)_2Li(THF)_2]$ (**77**), or a fully reduced Sm^{II} complex, $[(Oepg)Sm_2(THF)_4]$ (**78**), was obtained. This latter complex could also be made by lithium reduction of **74** or by the metathesis reaction of $OepgLi_4$ with $SmI_2(THF)_2$. The closely related $[(Oepg)Sm_2(Et_2O)_2]$ (**79**) could be prepared by the acid$-$base reaction of the Sm^{II} precursor, $[\{(TMS)_2N\}_2Sm(Tmeda)]$, with $OepgH_4$.[60b] All bimetallic Oepg$-$Sm complexes described above display a remarkably short Sm$-$Sm distance (3.30$-$3.40 Å), with the consequence that the magnetic moments of **78** and **79** (1.98 and 1.95 μ_B, respectively) are much lower than expected, presumably because of a magnetic interaction between the two Sm atoms.[61]

The reaction of the sodium salt of Oepg ($OepgNa_4$) with lanthanide halides provides an entry into yet another class of compounds. Here, the structure of the isolated products



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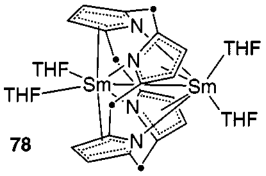

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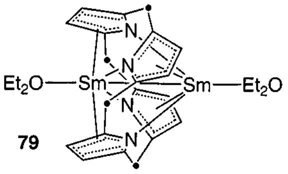

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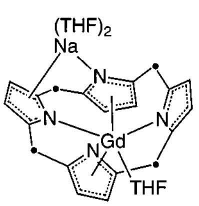
is very much dependent on the reaction conditions and in particular on the solvent used in the reaction and/or for recrystallisation. In all cases there are no anionic ligands other than the Oepg macrocycle bonded to the Ln metal centre (such as chloride or enolate as described above when $OepgLi_4$ was used as the precursor). In THF, the reaction of $OepgNa_4$ with $LnCl_3(THF)_n$ gave $[(Oepg)Ln(THF)Na(THF)_2]$ [Ln = Pr, Nd, Sm, Eu, Gd (**80**), Yb], in which the ligand is $\eta^5,\eta^1,\eta^5,\eta^1$-coordinated to the lanthanide metal centre and the sodium is η^3-ligated to one of the pyrrolyl rings and η^1-bonded to a nitrogen atom on another. By recrystallisation from DME, striking structural changes occur and $[\{(Oepg)_2Ln_2\}^{2-} \cdot 2\,\{Na(DME)_3\}^+]$ [Ln = Pr, Nd, Sm (**81**) Eu, Gd] were obtained. In these compounds, the macrocyclic ring bonded to the lanthanide centre has dimerised, with the formation of an Ln−C(pyrrole) σ-bond owing to C−H activation by the Ln metal centre. Further recrystallisation of these complexes in THF, THF/DME, or THF/dioxane mixtures only affects the coordination mode of the sodium atom and the $(Oepg)_2Ln_2$ dimeric structure in $[\{(Oepg)_2Ln_2\}\{Na(S)_2\}_2]$ (Ln = Pr, Nd, Sm, Gd; S = DME or THF) (**82**: Ln = Pr, S = DME) and in the polymeric $[(\{(Oepg)_2Ln_2\}\{Na(THF)\}_2\{\mu\text{-Dioxane}\})_n]$ (Ln = Nd, Gd) is left intact. Thus, it appears that the Oepg dimerisation by C−H activation is essentially irreversible.[62]



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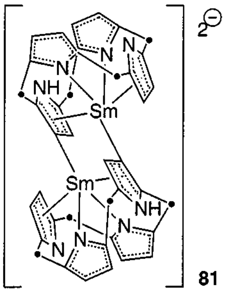

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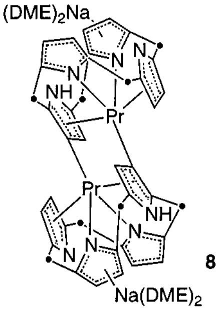

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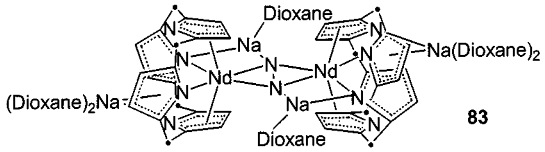
The reaction of $[(Oepg)Ln(THF)Na(THF)_2]$ with sodium naphthalenide in the presence of N_2 resulted in the reduction and formation of a diazenide dianion (N_2^{2-}) complexed to two OepgLn entities, $[\{[Na(THF)_2]_2(Oepg)Ln\}_2(\mu{:}\eta^2,\eta^2\text{-}N_2)]$ (Ln = Pr, Nd). Again, recrystallisation from donor solvents resulted in structural variations concerning the bonding properties of the sodium cation: In dioxane two sodium atoms are also bonded to the diazenide ligand in $[\{[Na(Dioxane)_2(Oepg)Nd(Dioxane)Na]_2(\mu{:}\eta^1 \mathit{Na},\eta^2 \mathit{Nd},\eta^1 \mathit{Na'},\eta^2 \mathit{Nd'}\text{-}N_2)]$ (**83**), while in DME only one sodium atom is bonded to the Oepg moiety in the anionic complex $[\{[Na(THF)_2(Oepg)Pr]_2(\mu{:}\eta^2,\eta^2\text{-}N_2)\}^{2-} \cdot 2\,\{Na(DME)_3\}^+]$ (**84**). Evidence for a diazenide is provided by the N=N bond length (1.24 Å).[63]



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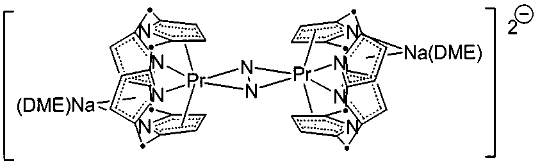

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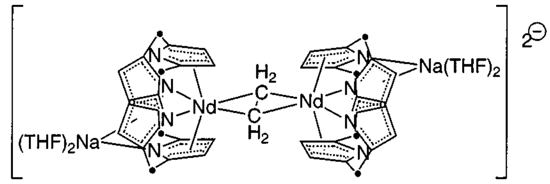
Similarly, reduction of $[(Oepg)Ln(THF)Na(THF)_2]$ (Ln = Pr, Nd) with sodium naphthalenide in the presence of ethylene yielded $[\{[Na(THF)_2(Oepg)Ln]_2(\mu{:}\eta^2,\eta^2\text{-}CH_2CH_2)\}^{2-} \cdot \{Na_2(THF)(18\text{-}C\text{-}6)_2(\mu\text{-Dioxane})\}^{2+}]$ [Ln = Pr, Nd (**85**)] in which the ethylene has been reduced to ($CH_2CH_2^{2-}$) as indicated by the C−C single-bond length of 1.49 Å. Interestingly, these compounds could also be obtained from the above-mentioned diazenide complexes **83** and **84** simply by reaction with ethylene in the presence of [18-C-6]. The behaviour of $[(Oepg)Ln(THF)Na(THF)_2]$ in the presence of sodium naphthalenide has been attributed to a reduction of these complexes to transient Pr^{II} and Nd^{II} species which are then able to activate small molecules such as N_2 or C_2H_4 by electron transfer.



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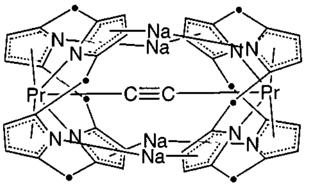

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When the $[(Oepg)Ln(THF)Na(THF)_2]$ (Ln = Pr, Nd)/sodium naphthalenide methodology was applied to acetylene, deprotonation occurred (not reduction) and the resulting acetylide led to the formation of $[\{(\mathrm{Oepg})\mathrm{LnNa}_2\}_2(\mu\text{-}\mathrm{C{\equiv}C})]$ (**86**) in which four unsolvated sodium atoms and the C≡C unit are inserted as "spacers" between the two OepgLn units.[64]

Conclusion

The use of heterocyclopentadienyl ligands in group-3 metal chemistry has led to the formation of compounds with several coordination modes. Some of them exhibit remarkable reactivity, for instance, in the activation of small molecules (N_2 and ethylene) and in achieving transient uncommon low-valent oxidation states [$\mathrm{Pr^{II}}$, $\mathrm{Nd^{II}}$]. From here, there are some obvious challenges that for some of them will, undoubtedly, be met in the future.

The relatively electron-poor π-phospholyl ligand might be used to stabilise uncommon lanthanide(II) oxidation states such as $\mathrm{Tm^{II}}$. There is also a clear synthetic challenge to include the phospholyl or other phosphorus-based ligands in the bridged or cavitand-like structures such as those used with the pyrrolyl ligand.

As far as nitrogen-based ligands are concerned, there still remains the objective of preparing a complex with an η^5-coordinated pyrazolyl ligand. The reactivity of the bridged or cavitand-like pyrrolyl complexes with other small molecules such as CO and CO_2 will certainly be investigated.

The actinide chemistry is relatively underrepresented, especially in the domain of the nitrogen-based ligands.

Finally, several reported complexes have great potential in catalytic applications.[65]

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