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Review

Molecular compounds of “new” divalent lanthanides

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Contents

Abstract

The data on synthesis, structure and reactivity of lanthanide compounds (except samarium, europium and ytterbium derivatives as well as insertion phases of LnX_2 type) containing a metal in subvalent state with a particular emphasis on divalent derivatives are collected and systematized. Most of the references considered concern diiodides of Nd(II), Dy(II) and Tm(II) and their reactions with various substrates although a number of Sc(II), La(II) and Ce(II) complexes and multiple attempts to synthesize other divalent compounds of rare earth metals are also described.

Keywords: Divalent lanthanides; Synthesis; Structure; Properties

1. Introduction

Derivatives of rare earth and other metals in unusual oxidation states have always drawn the attention of chemists not only as attractive objects for academic investigation but also as potentially useful substrates for applications. Progress in this area leads to the creation of new valuable materials, effective technologies and industrial processes. Investigation of divalent samarium iodide, SmI_2, described in 1977 by Kagan and co-workers as a specific single-electron reductant [1] but which then found broad application in organic and organometallic synthesis [2] is a nice example.

Sc, Y, La and the following 14 metals (the Ln symbol is used to describe all of these elements) exist in the stable oxidation state +3. Other valence states are known only for cerium (+4), samarium, europium and ytterbium (+2), for which numerous inorganic and organometallic compounds in tetravalent and divalent states, respectively, have been synthesized [3,4]. For all other Ln elements, a valence state other than +3 is atypical although in some cases solid state

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Abbreviations: DME, 1,2-dimethoxyethane; TMEDA, tetramethylethylenediamine; py, pyridine; bipy, 2,2-bipyridyl; Cp^R, η^5-$C_5H_3R_2$-1,3; η^5-C_4Me_4P, η^5-2,3,4,5-tetramethylphospholyl; Cp'', η^5-$C_5H_3(SiMe_3)_2$-1,3

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chemistry provides evidence for the existence of tetravalent compounds of La, Ce, Pr, Gd, Tb, Er [5]. Investigation of halide phases of composition LnX_2 (X = Cl, Br, I) prepared by extensive heating of trihalides LnX_3 with the appropriate metal at 800–1000 °C have shown that only Nd, Dy and Tm form true divalent salts [6] besides Sm, Eu and Yb. In the cases of Sc, La, Ce, Pr, Gd and Ho, the divalent state is unstable and these phases contain Ln^{3+} cations despite their composition LnX_2. In the crystals of these substances, layers with short metal–metal contacts are formed that provides them with metallic conductivity. Usually similar solids are depicted by the formula $(Ln^{3+})(e^-)(X^-)_2$ reflecting the existence of delocalized electrons [6]. The lanthanum monoiodide LaI is synthesized (similar to LaI_2) by heating LaI_3 with metallic lanthanum; judging by the data of X-ray analysis the metal is also in the trivalent state [7].

Comparing the stability of Ln^{2+} cations with the value of their electrode potentials E° (Ln^{3+}/Ln^{2+}), it is easy to note that the stability of the divalent state decreases when the reduction potential increases (V): Eu (−0.34) < Yb (−1.18) < Sm (−1.50) < Tm (−2.22) < Pm (−2.44) < Dy (−2.56) < Nd (−2.62) < Ho (−2.79) < Tb (−2.83) < Pr (−2.84) < Gd (−2.85) < Er (−2.87) < Ce (−2.92) < La (−3.1) [8]. In this series, the lanthanides beginning from holmium (as mentioned above) do not form low valency metal salts. However, this limitation does not apply to molecular organometallic compounds. So, aromatic ligands may stabilize the metal atom in unusual oxidation states due to donation of d and s electrons to π-orbitals of the ligand. This has resulted in a series of bis(arene) complexes containing the metal even in the quite unusual zerovalent state. The stability of such complexes greatly increases when arenes with the bulky *tert*-butyl substituents are used. The stability of such complexes $(1,3,5\text{-}t\text{-}Bu_3C_6H_3)_2Ln$ does not coincide with the Ln^{3+}/Ln^{2+} electrode potentials series adduced earlier. Thus, the derivatives of Sc, Y, Nd, Gd, Tb, Dy, Ho, Er, and Lu are quite stable in this case. Their La, Pr and Sm analogues are less stable; Ce, Eu, Tm, and Yb do not form π-arene complexes. It is proposed that, in this case, the difference in stability of the compounds is connected to the difference in ionic radii of the metals and the difference in promotion energy of the $f^n s^2 \rightarrow f^{n-1} d^1 s^2$ transitions because the $d^1 s^2$ lanthanide atom configuration is required to form a stable bis(arene) complex [9]. Heterocyclic ligands containing *tert*-butyl substituents also yield rare earth complexes in atypical low oxidation state. In particular, by co-condensation of metal vapor and substituted pyridine or phosphine the zerovalent complexes of scandium and holmium $(\eta\text{-}2,4,6\text{-}t\text{-}BuC_5H_2N)_2Sc$ [9a] and $(\eta\text{-}2,4,6\text{-}t\text{-}BuC_5H_2P)_2Ho$ were synthesized [10]. A triple decker complex of monovalent scandium $[\{(\eta^5\text{-}P_3C_2\text{-}t\text{-}Bu_2\text{-}3,5)Sc\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_3C_3\text{-}t\text{-}Bu_3\text{-}2,4,6)]$ was synthesized by the same method when 2,2-dimethylpropylidenphosphine was used as a ligand [11].

Evans has previously reviewed the topic of low valency lanthanide complexes [12–14]. Particular attention was paid to the compounds of samarium, europium and ytterbium as well as to the complexes of composition R_2Ln (R = C_4H_5, $Me_2C_4H_4$) of indefinite structure obtained in the specific conditions of cryogenic synthesis from the appropriate unsaturated hydrocarbon 2,4-dimethylbutadiene-1,3 or butene-2, 2,3-dimethylbutene-2 and lanthanide metal vapor. This review [14] also includes the first data on compounds of divalent thulium. All known complexes of subvalent rare earth metals are quoted in a very constrained form in the short 2002 review of Lappert and co-workers [15]. A brief paper about perspectives for the development of the chemistry of Nd(II), Dy(II) and Tm(II) was published recently by Izod [16].

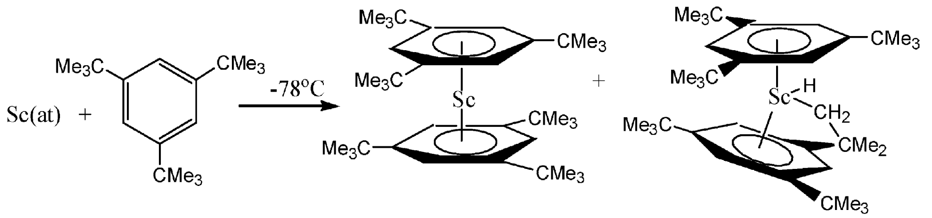
In this paper, compounds containing rare earth metals (except Sm, Eu and Yb) in formally divalent state are considered. This group of subvalent derivatives are the most promising not only in theory but also in applied aspects. The volume of current information especially on the triad of divalent of Nd, Dy and Tm iodides requires generalization and systematization. Complexes of zerovalent and monovalent lanthanides are mentioned only in summary form.

The synthetic methods, description of structure, main physical properties and reactivity of the indicated compounds are arranged in order of increasing atomic number of the metals. This leads to some inevitable repetition but it gives a more concise general scheme of the paper allowing for readers to orient easily in the text, and find needed sections.

2. Compounds of scandium

Scandium is unstable in its divalent state. Heating of halides ScX_3 with metallic scandium yields metal-like phases of composition close to ScX_2 but containing Sc(III). The direct reaction (burning of scandium shavings and iodine) useful for preparation of iodides of Nd(II), Dy(II), and Tm(II) [17] also leads, in the case of Sc, to a substance containing trivalent metal, judging by its properties (diamagnetism, insolubility in THF, low chemical activity) [18]. Similar results arise from the reactions of iodine with Y, La, Ce, Pr, Gd, Tb, Ho, Er, and Lu [18].

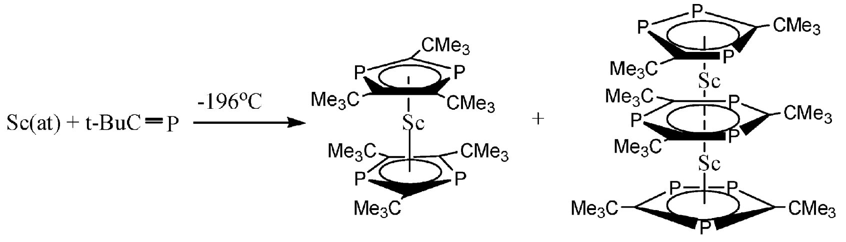
In contrast, for organic derivatives of scandium all three subvalent forms are known: 0, +1, and +2. All belong to the class of π-arene complexes and were mainly obtained by the co-condensation of Sc vapor with the appropriate organic compound. Reaction with 1,3,5-tri(*tert*-butyl)benzene (Eq. (1)) leads to formation of two complexes: zerovalent bis(arene) compound **1** and a product of its intramolecular transformation **2** containing divalent metal [19].



1 **2** (1)

An intractable mixture of the products **1** and **2** are formed as a red-violet crystalline substance. Upon heating of the material in vacuum, only the red bis(arene) component **1** is sublimed whereas the violet compound **2** decomposes. In toluene solution, **2** decomposes at 80 °C. Its structure has been established on the basis of EPR and UV-Vis spectroscopy data.

The second complex of divalent scandium was obtained by co-condensation of Sc vapor and *tert*-butylphosphalkyne (t-BuC≡P) (Eq. (2)) [20]. The reaction is accompanied by cyclization of phosphalkyne and, as for co-condensation with 1,3,5-t-$Bu_3C_6H_3$, affords two products. In this case, one contains Sc(II) and is an analogue of scandocene (**3**) while the second one (**4**) is a triple decker sandwich with formally monovalent metal.



3 **4** (2)

The complex **3** is isolated as a dark violet crystalline solid soluble in non-polar solvents and sublimable in vacuum at 220 °C. Its solutions in THF decompose very quickly. The magnetic moment of **3** ($1.70\mu_B$) corresponds to the presence of one unpaired d electron. The EPR spectrum shows splitting by ^{45}Sc nucleus at 295 K as a broadened singlet; however, upon decreasing the temperature to 120 K, superhyperfine structure appears reflecting the splitting by phosphorus nuclei. No X-ray analysis of **3** was provided in contrast to dark green product **4** for which a binuclear structure with a bridging six-membered cycle has been confirmed [11].

Continuing the investigations of the complexes with phosphacyclopentadienyl ligands, the same group of investigators established that reduction of the trivalent scandium compound $[Sc(\eta^5\text{-}P_3C_2\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}P_3C_2\text{-}t\text{-}Bu_2)]$ by one equivalent of KC_8 in toluene gives the dimeric complex **5** (Fig. 1) isolated from hexane in the form of dark green crystals [21]. The compound is quite stable thermally and can be sublimed in vacuum at 170–180 °C. X-ray structural analysis (Sc–P, P–P, and P–C distances) and quantum–chemical calculations correspond to a mixed-valence scheme Sc(III)/Sc(I) that is in agreement with the diamagnetism of the compound in the solid state. However, the solutions of **5** in benzene and toluene are paramagnetic and the value of $\mu_{\rm eff} = 1.73\mu_B$ per one Sc atom corresponds to a d^1 state. Interestingly, a toluene solution of **5**, in contrast to sandwich **3**, does not reveal an EPR signal, probably because of association of the monomeric form.

The unusual heterobimetallic compound **6** was isolated as blue-green crystals by extraction with toluene of the solid products of the reaction of the β-diketiminate complex $[Et_2N\,CH_2\,CH_2NC\,(Me)\,CHC\,(Me)\,NCH_2\,CH_2\,NEt_2]ScBr_2$ with two equivalents of allylmagnesium bromide [22]. The stoichiometry of the reaction, elemental and fragmental composition of **6** and its structure (resembling the structure of bent sandwich Cp_2ScBr, in which flat fragments NC(Me)CHC(Me)N play the role of Cp rings) led the authors to conclude that scandium exists in the +1 oxidation state. However, an alternative interpretation of its nature $[LMgBr]^-{}_2Sc^{3+}Br^-$ cannot be excluded.

Attempts to synthesize subvalent complexes of yttrium, except the above-mentioned bis(arene) complexes, have never been reported.

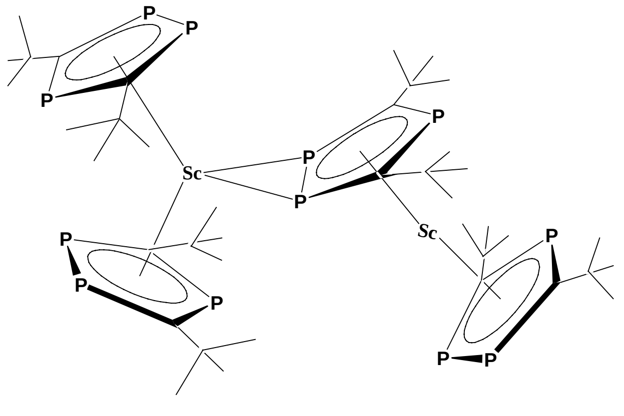
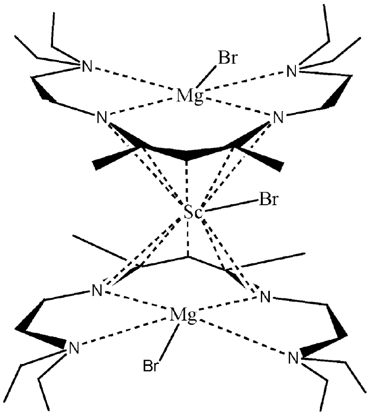


Fig. 1. Molecular scheme of **5**.



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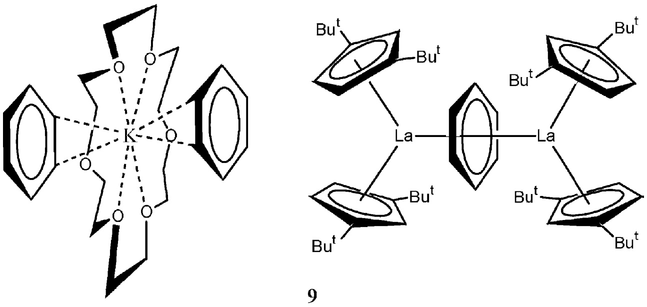
3. Compounds of lanthanum

For stabilization of low valence states of lanthanum, cerium and neodymium Lappert and co-workers have used cyclopentadienyl ligands with bulky *t*-Bu and $SiMe_3$ substituents. However, attempts to obtain desirable lanthanum compounds by reduction of $La[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_3$ or $\{La[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2$ by a potassium mirror or a mixture of KC_8/18-crown-6 in benzene led to formation of an *ate*-complex $[K(18\text{-crown-}6)]\{La[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(C_6H_6)\}$ containing trivalent lanthanum coordinated by the dianion of 1,4-cyclohexa-2,5-diene [23]. The reaction of $La[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_3$ with a potassium mirror in DME at room temperature also only yielded colorless compounds of La(III): $\{La[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}OMe)\}_2$ and polynuclear lanthanum methoxide of indefinite structure. However, in this case, at a temperature of −40 °C the authors observed the appearance, in the solution at an intermediate stage of the reaction, of dark blue color [24]. This blue solution is paramagnetic and its EPR spectrum revealed the presence of two well resolved octuplets from hyper fine interaction of an unpaired metal-centered electron with ^{139}La nuclei. Analysis of the spectrum and its comparison with the spectra of other paramagnetic lanthanum complexes containing radical anion ligand ($[La^{3+}@C_{82}{}^{3-}]$, $[LaI_2(bipy)_2(DME)]$, $[LaI_2(bipy)(DME)_2]$, $[LaI_2(bipy)_2(THF)_2]$) suggested that the observed EPR signals were due to complexes of divalent lanthanum **7** and **8** existing in temperature-dependent equilibrium (Eq. (3)).

$$\begin{aligned}&Cp''_3La \xrightarrow{K,DME,-40\,^{\circ}C} \underset{\mathbf{7}}{[K(DME)_x][Cp''_3La]}\\&\leftrightarrow \underset{\mathbf{8}}{Cp''_2La(DME)_y}\\&+Cp''K(DME)_n \xrightarrow[-Cp''K]{} [Cp'_2LaOMe]_2,\\&Cp''_2 = \pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3 \qquad (3)\end{aligned}$$

If the reaction is carried out in benzene the product is isolated as a dark green precipitate. The EPR spectra of the dark violet-blue solution formed in this case at the initial stages of the reaction displayed the presence of no less than four paramagnetic species of divalent lanthanum [25]. In an attempt to confirm the possibility of generation of Ln(II) compounds, electrochemical reduction of Cp''_3La was carried out in THF solution under comparable conditions. The reduction process of the complex is reversible with a Ln(III)/Ln(II) potential of −2.8 V [24].

The reduction potential of the *tert*-butyl analog $La[\pi\text{-}C_5H_3(t\text{-}Bu)_2\text{-}1,3]_3$ is a little more negative (−3.1 V) and the reduction products less stable. However, application of this ligand has allowed the isolation of the reduced product in the form of good crystals useful for X-ray analysis [26]. Upon treating $La[\pi\text{-}C_5H_3(t\text{-}Bu)_2\text{-}1,3]_3$ with excess potassium in DME at −40 °C, a violet-blue solution forms that indicates the formation of La(II) derivatives, and at room temperature quickly transforms into the colorless methoxide $\{La[\pi\text{-}C_5H_3(t\text{-}Bu)_2\text{-}1,3]_2((\mu\text{-}OMe)\}_2$. The same reaction in a benzene medium in the presence of crown ether at 20 °C is characterized by the appearance of dark red coloration, which gradually transforms into dark green. In a few days, dark green highly air- and light-sensitive crystals of compound **9** precipitate from solution. An X-ray analysis has shown that the product is an ionic complex containing in the anionic part two $La[\pi\text{-}C_5H_3(t\text{-}Bu)_2\text{-}1,3]_2$ fragments bonded by bridging ligand $\eta^6\text{-}C_6H_6$. The flat shape of the ligand and the equal C–C bond lengths (1.42(1)–1.45(1) Å [15]) led the authors to consider it as benzenide anion but the compound as a whole is a complex of divalent lanthanum [26]. Supporting this conclusion are the somewhat elongated La–C(Cp) distances (average 2.97(1) Å; cf. 2.90(1) Å for above-mentioned trivalent complex $[K(18\text{-crown-}6)]\{La[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(C_6H_6)\}$ [23]) and the existence of an EPR signal in the reaction mixture.



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4. Compounds of cerium and praseodymium

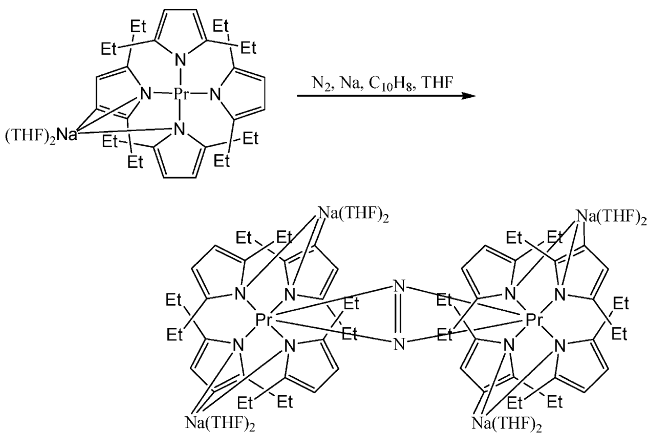
Cerium was the first of the "trivalent" lanthanides for which complexes containing the metal in the +2 oxidation state were sought. A green solid product was obtained by reaction of the cyclooctatetraenyl derivative $(C_8H_8)_2Ce$ with an excess of potassium metal at 30 °C in DME [27]. Elemental composition and IR spectra corresponded to the formulae $[(C_8H_8)_2Ce][K(DME)]_2$. On the basis of these data, cerium was concluded to reside in the divalent state. However, the high stability of this compound at room temperature contradicts such a conclusion since practically all divalent lanthanide molecular compounds (except Sm, Eu, Yb, and Tm) obtained subsequently, have low stability.

Thus, reduction of the cerium and praseodymium complexes $Ln[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_3$ and $\{Ln[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2$ by two equivalent of potassium in benzene in the presence of 18-crown-6 at room temperature does not afford Ln(II) derivatives but leads to complexes of Ln(III) with 1,4-cyclohexa-2,5-dienyl dianion: $[K(18\text{-crown-}6)]\{Ln[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(C_6H_6)\}$ [23,25].

The products of $Ce[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_3$ and $Ce[\pi\text{-}C_5H_3(t\text{-}Bu)_2\text{-}1,3]_3$ reduction by lithium in DME are the methoxides $[Cp^{\#}{}_2Ce(OMe)]_2$, forming (as the authors believe) as a result of splitting of solvent by divalent intermediates (Eq. (4)) [28].

$$Cp^{\#}_3Ce + Li \xrightarrow{DME} [Li(DME)_n][CeCp^{\#}] \xrightarrow[-Cp^{\#}Li(DME)_n]{} [Cp^{\#}_2Ce] \rightarrow [Cp^{\#}_2Ce(\mu\text{-}OMe)]_2 \qquad (4)$$

The octaethylporphyrinogen complex of praseodymium $\{[\eta^5:\eta^1:\eta^5:\eta^1\text{-}Et_8(C_4H_2N)_3(C_4HN)]Pr(THF)\}Na(THF)_2$ does not yield Pr(II) compounds when reacted with sodium in the presence of naphthalene in a nitrogen atmosphere, but forms a product containing the dianion $N_2{}^{2-}$: $\{Et_8(C_4H_2N)_2(C_4HN)_2)Pr(THF)][Na(THF)_2]_2\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (Eq. (5)) [29].



(5)

Reduction of nitrogen can be considered as indirect proof of formation in this reaction of an extremely reactive species of divalent praseodymium. However, investigation of similar processes with other lanthanides adduced below provided a different interpretation of these transformations.

5. Compounds of neodymium

Based on E° values among the cations Eu^{2+} Sm^{2+}, Yb^{2+}, Dy^{2+}, Tm^{2+}, and Nd^{2+}, the last is the strongest reductant. In the late 1970s, a communication concerning the synthesis of the molecular chloride $NdCl_2(THF)_2$ by the reaction of $NdCl_3$ with a deficiency of lithium naphthalenide in THF was published [30]. However, later the divalent state of neodymium in this compound was questioned [31] as were analogous complexes obtained using this salt as a starting reagent [32–34].

Reduction of the tricyclopentadienyl complexes, $(Cp^R)_3Nd$, containing the bulky Cp ring substituents R ($SiMe_3$, $CH(SiMe_3)_2$, t-Bu) by potassium in THF led to formation of dark brown solutions, which at room temperature gradually decomposed affording the metal and the initial $(Cp^R)_3Nd$ [34]. Application of DME, TMEDA, 18-crown-6 or $[NBu_4][BF_4]$ for stabilization of possible intermediate Nd(II) compounds was unsuccessful.

An attempt to obtain a bis(phospholyl) complex of divalent neodymium $(\eta^5\text{-}C_4Me_4P)_2Nd$ by the reduction of the σ-alkyl derivative $(\eta^5\text{-}C_4Me_4P)_2NdCH(SiMe_3)_2$ with hydrogen also failed [35]. Unlike the samarium analogue, which gave the expected $(\eta^5\text{-}C_4Me_4P)_2Sm$, reaction with the neodymium compound led to the hydride $(\eta^5\text{-}C_4Me_4P)_2NdH$.

There is no definite evidence for the formation of Nd(II) intermediates in the reduction of the porphyrinogen complex $\{[Et_8(C_4H_2N)_3(C_4HN)]Nd(THF)\}Na(THF)_2$ by sodium naphthalenide under a nitrogen atmosphere [29].

Indirect indications of the formation of very active intermediate complexes of divalent neodymium in the reactions of $Nd[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_3$ with lithium and potassium include the formation of methoxides $\{Nd[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}OMe)\}_2$ or $\{Nd[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}OMe)_2Li(DME)\}$ [28]. It is suggested that neodymocene $Nd[\pi\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2$ generated at an initial stage, splits the solvent to give ethylene and Nd–OMe groups. Also unsuccessful were attempts to reduce (by potassium in THF medium at room temperature) the complexes $\{Nd[\pi\text{-}C_5H_4CH(SiMe_3)_2](\mu\text{-}Cl)\}_2$ and $\{Nd[\pi\text{-}C_5H_3(SiMe_2\text{-}t\text{-}Bu)_2\text{-}1,3]_2(\mu\text{-}Cl)\}_2$ [36]. In both cases a slow (during 2 days) formation of brown solutions containing, as the authors believe, divalent neodymium derivatives resulted. From the solutions a black precipitate, presumably neodymium metal gradually deposited. The second product in both reactions was the respective neodymium tricyclopentadienide.

The first confirmed molecular compounds of divalent neodymium $NdI_2(THF)_5$ and $NdI_2(DME)_3$ were obtained by crystallization of NdI_2 from the THF and DME solutions, respectively [17,37] although spectroscopic study of these solutions was carried out earlier [38]. The diiodides used for these studies were synthesized by the direct method, i.e. by the reaction of the appropriate metal with iodine [17,39,40]. The complexes were isolated as dark vi-

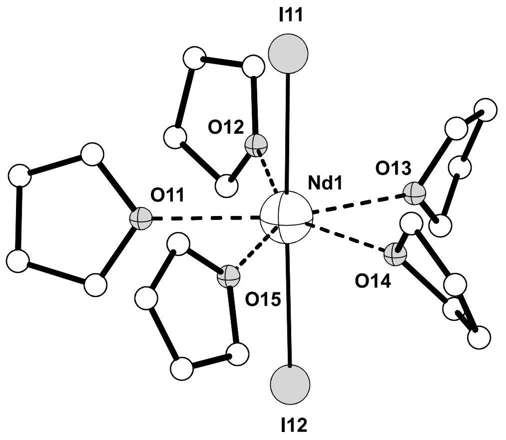


Fig. 2. Molecular structure of $NdI_2(THF)_5$.

olet crystals that decompose upon fast heating in a capillary at 50 °C. The decoloration at room temperature became noticeable in 3 h. The solutions decompose much quicker. Divalent neodymium is confirmed by magnetic measurements ($\mu_{eff} = 2.7–2.8\mu_B$) [17] and X-ray structural analysis of $NdI_2(THF)_5$. The molecular complex, similar to the previously obtained samarium iodides $SmI_2(THF)_5$ and $SmI_2(DME)_2(THF)$ [41], has a pentagonal bipyramidal structure with iodine atoms in axial positions (Fig. 2) [42].The Nd–I and Nd–O bond lengths coincide with respective distances in samarium analogues after accounting for the differences in ionic radii of Nd(II) and Sm(II). Interestingly, the average Nd–I distance 3.276 Å in $NdI_2(THF)_5$ is significantly longer than that in the molecule NdI_2 (2.973 Å) determined by electron diffraction in the gas phase [43]. In the trivalent neodymium complexes $(\eta^5\text{-}C_5Me_5)NdI_2(py)_3{\cdot}C_7H_8$ and $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4SiMe_3)NdI(py)$ the Nd–I bond lengths were found to be 3.1603(5) and 3.0664(4) Å, respectively [44].

Investigation of the behavior of $NdI_2(THF)_5$ in THF solution revealed that the addition of even a minor amount of aromatic compounds (PhH, PhMe, *t*-BuPh, Ph-Ph, $PhCH{=}CH_2$, Ph_2Hg, Ph_4Sn) causes a rapid change of color of the reaction solution from violet to brown and the formation of a precipitate of $NdI_3(THF)_3$, the molar yield of which corresponds to half of the amount of initial diiodide [45]. It was established by indirect methods that the brown substance formed in these conditions is a mixture of monoiodide derivatives $LnIRR'(THF)_x$ where R and R′ are the fragments of split THF including hydrogen. Analogous transformations occur in DME solutions. To explain this effect of addition of aromatic species, a scheme involving the existence of LnI_2 in solution in equilibrium with its ionic form $\{[LnI_3]^-[LnI]^+\}$ has been proposed [45]. Similar ionic diversity $\{[LnX_4]^-[LnX_2]^+\}$ is well known for halides of trivalent rare earth metals [46]. It is suggested that aromatic compounds promote the electron transfer from anion to cation leading to formation of the neutral iodides NdI_3 and NdI (Eq. (6)). The latter contains monovalent metal and consequently possesses extremely high reductive power. It attacks the solvent not only at the most reactive C–O bond but it also splits the C–H and C–C groups to give a mixture of σ-complexes of LnIRR′ type. The aromatic substrate itself is changed only to a minor degree.

$$2\,LnI_2 \leftrightarrow [LnI_3]^-[LnI]^+ \rightarrow LnI_3 + LnI \qquad (6)$$

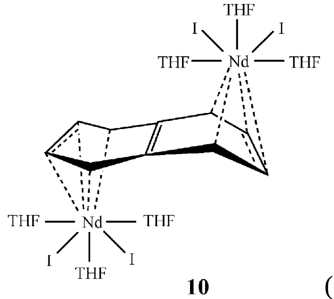
Such an approach explains another unusual property of NdI_2: change in reactivity with phenol in THF when cooling down to −90 to −100 °C. While at about 0 °C, the ordinary displacement of the OH group hydrogen atom takes place with formation of the expected monophenoxide $PhONdI_2(THF)_4$ an yield of which reaches 76% (Eq. (7a)), at −100 °C the main products become the diphenoxide $(PhO)_2NdI(THF)_3$ (46%) and $NdI_3(THF)_3$ (37%) whereas $PhONdI_2(THF)_4$ is isolated in only 11% yield (Eq. (7b)) [45].

$$NdI_2 + PhOH \xrightarrow{THF} \begin{cases} \xrightarrow{0\ -\ -5^{\circ}C} PhONdI_2(THF)_4 & (7a) \\ \xrightarrow{-90\ -\ -100^{\circ}C} (PhO)_2NdI(THF)_3 + PhONdI_2(THF)_4 + NdI_3(THF)_3 & (7b) \end{cases}$$

Evidently, at low temperature the reactivity of the OH groups greatly decreases and the “normal” reaction direction significantly slows down while the reactivity of the aromatic Ph group in promoting the disproportionation of NdI_2 does not change. As a result, NdI_3 and the extremely reactive monoiodide NdI form, and the latter is oxidized by phenol to give the diphenoxide $(PhO)_2NdI(THF)_3$. In agreement with this explanation *t*-BuOH, which does not contain an aromatic functional group, reacts with NdI_2 through its hydroxyl group in a temperature independent reaction [45].

Interaction of NdI_2 with polycyclic aromatic compounds such as naphthalene and anthracene proceeds otherwise. Their oxidation potential is high enough to provide “normal” single-electron processes. The complexes $[NdI_2(THF)_3]_2(C_{10}H_8)$ (**10**) (Eq. (8)) and $[NdI_2(THF)_3]_2(C_{14}H_{10})$, formed in high yield, contain the arene dianion [47].

$$NdI_2 + C_{10}H_8 \xrightarrow{THF}$$



10 (8)

The X-ray analysis of these products was not carried out but the similarity of the spectroscopic data, color and solubility with the structurally characterized lanthanum complexes [48], as well elemental analysis, suggest for them this reverse sandwich structure.

NdI_2 in THF reacts readily with alkyl(aryl) halides [49] in a similar fashion to the alkali metals. The main product with PhX is benzene, most of which (30–67%) is formed directly in the reaction while 10–17% of it is isolated after hydrolysis of a reaction mixture. That some benzene requires hydrolysis for isolation is an indirect indication of the amount of phenylneodymium complex produced in the processes. The coupling product Ph–Ph was found only in trace amounts. In contrast, interaction of NdI_2 with benzyl chloride gives both the expected compound PhMe and $PhCH_2CH_2Ph$ in approximately equal quantities (47 and 51%, respectively) (Eq. (9)).

$$NdI_2 + RX \xrightarrow{THF, 20\,^{\circ}C} RH + R\text{–}R,$$

$$R = Ph,\ X = Cl, Br, I;\ R = PhCH_2,\ X = Cl \qquad (9)$$

The source of hydrogen in these processes is probably THF.

Application of NdI_2 in the coupling reactions of alkylhalides RX (R = *n*-Bu, *s*-Bu, *t*-Bu, $PhCH_2CH_2$) with ketones or aldehydes has shown that this salt can be successfully used in organic synthesis [50]. In all the cases, except *t*-BuCl, the respective alcohols were obtained in 80–100% yield.

The high reductive ability of NdI_2 leads to the synthesis of cyclopentadienyl complexes $CpNdI_2$ by direct reaction of the salt with cyclopentadiene; this readily proceeds at room temperature (Eq. (10)) [51].

$$NdI_2 + CpH \xrightarrow[-H_2]{THF} CpNdI_2(THF)_3 \qquad (10)$$

On the basis of this reaction, a new convenient one-pot method for the preparation of vanadocene has been reported. The approach consists of the simultaneous interaction of VCl_3, NdI_2 and cyclopentadiene in THF medium (Eq. (11)) [52].

$$NdI_2 + VCl_3 + CpH \xrightarrow[-H_2, -NdI_2Cl]{THF} Cp_2V \qquad (11)$$

The first stage of the process (interaction of NdI_2 with CpH) proceeds at room temperature and the second one (reaction of the $CpNdI_2$ formed, with VCl_3) at 60–65 °C. The yield of vanadocene reaches 60%. The reaction involves the partial reduction of VCl_3 to VCl_2. It is suggested that the method can also be used for preparation of metallocenes of other metals.

In the late 1980s, it was established that organolanthanide compounds in the presence of lithium or sodium naphthalenide can reduce dinitrogen at ambient conditions [53]. It was suggested that highly reactive subvalent intermediates are responsible for the reduction of N_2; however, the attempts to isolate these compounds or their complexes with nitrogen failed. Recently similar complexes were obtained by Evans and co-workers when they used compounds of samarium, thulium, dysprosium and neodymium. In particular, a phenoxide of Nd(III) containing the dianion $[N_2]^{2-}$ has been synthesized in 30% yield by the extended reaction of a solution of NdI_2 and KOC_6H_3-*t*-Bu_2-2,6 in THF at −35 °C in an N_2 atmosphere [54]. The product (Fig. 3) contains the characteristic flat Nd_2N_2 fragment similar to the Sm_2N_2 fragment in the previously obtained $[(C_5Me_5)_2Sm]_2N_2$ [55] and analogous Ln_2N_2 structures in the dysprosium and thulium complexes quoted below. In a similar fashion to the praseodymium analogue, the porphyrinogen complex of Nd(III) $\{[\eta^5{:}\eta^1{:}\eta^5{:}\eta^1\text{-}Et_8(C_4H_2N)_3(C_4HN)]Nd(THF)\}$ $Na(THF)_2$ adds nitrogen under ambient conditions to give a binuclear complex containing the same central Nd_2N_2 fragment with the bridging dianion $(N{=}N)^{2-}$ that was established by X-ray diffraction [29]. The reduction of nitrogen, in this case, likely proceeds through low valence neodymium intermediates.

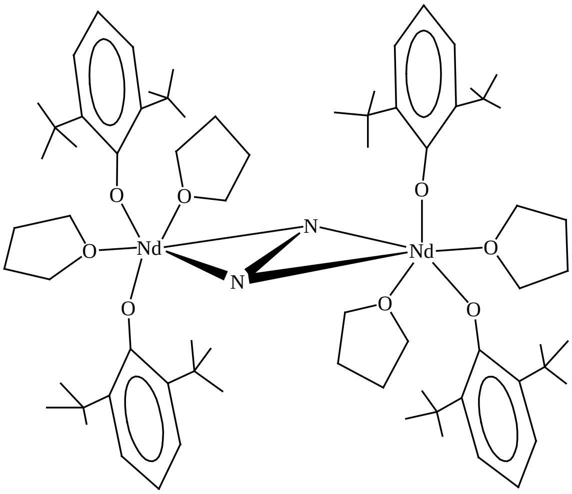


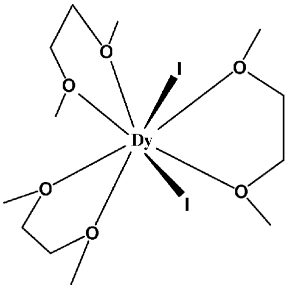
Fig. 3. Molecular scheme of $[(2,6\text{-}{}^tBu_2C_6H_3O)Nd(THF)_2]_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}N_2)$.

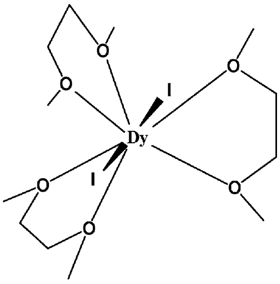
Despite the high reduction potential of NdI_2, the complete splitting of the N=N bond in its reaction with azobenzene does not occur, in contrast to the previously observed reactions of PhNNPh with naphthalene complexes of ytterbium and samarium [56]. The product $[NdI(THF)_2]_2(N_2Ph_2)_2$ generated in these conditions was characterized by elemental analysis, IR and UV-Vis spectroscopy [39]. These data revealed that the structure of the complex is similar to that of the dysprosium analogue considered further, which has been characterized structurally.

6. Compounds of dysprosium

The only currently known molecular compounds of divalent dysprosium remain the tetrahydrofuran and dimethoxyethane complexes of the diiodide: $DyI_2(THF)_5$

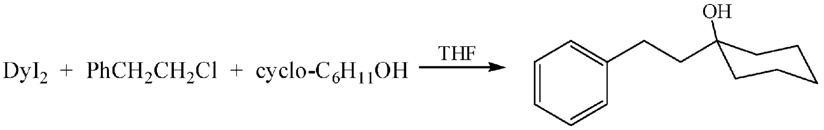
and $DyI_2(DME)_3$. Like the related neodymium compounds, these products were obtained in 1999 by removal of solvent at low temperature from a solution of DyI_2 in THF or DME [17,37]. Holding the green crystals of $DyI_2(THF)_5$ in dynamic vacuum at −30 °C for 1–2 h leads to loss of two THF molecules and formation of a violet powder of composition $DyI_2(THF)_3$. Dysprosium diiodides are somewhat more stable than their neodymium analogues. Decoloration of the crystals of these compounds at room temperature in the dark occurs in 4–5 days, but in solution decomposition is complete in 2–3 h. The X-ray analysis of $DyI_2(DME)_3$ was reported by Evans et al. [57] and revealing two independent isomeric molecules: with linear and bent I–Dy–I groups.





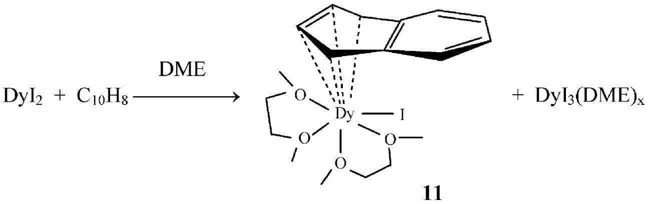
In both molecules, all three DME ligands are coordinated to the metal atom in an η^2-fashion. The Dy–I distances in $DyI_2(DME)_3$ are 3.2628(3) and 3.2371(3) Å which are noticeably longer than the Dy–I bond length (3.1382(4) Å) in the only structurally characterized iodine complex of trivalent dysprosium $(C_{10}H_8)DyI(DME)_2$ [57].

Investigation of the chemical properties of dysprosium diiodides showed that it is a more powerful reductant than SmI_2 and even more so than TmI_2 but a little weaker than NdI_2. Condensation of ketones with alkylchlorides in the presence of DyI_2 proceeds at −45 °C and gives the respective alcohol in 88% yield (Eq. (12)) [57].



(12)

In contrast to NdI_2, which in reaction with naphthalene gives the binuclear complex **10**, dysprosium diiodide reacting with $C_{10}H_8$ in a DME medium affords along with the triiodide $DyI_3(DME)_x$ the mononuclear compound **11** also containing the naphthalene dianion (Eq. (13)) [57].



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(13)

Formation of these products indicates that the reaction is accompanied by disproportionation, which can be realized through alternative mechanisms: (1) after formation of the primary complex $[I_2Dy(DME)_x]_2C_{10}H_8$, which is similar to the neodymium product; or (2) DyI_2 can form DyI_3 and DyI according to the previously noted scheme. In the last case the complex $C_{10}H_8DyI(DME)_2$ can be a result of oxidation of the monovalent species DyI by naphthalene. Taking into account the very mild reaction (−20 °C) conditions the first variant seems less plausible. In contrast, disproportionation of DyI_2 is quite possible, which is confirmed by transformations observed in solutions of DyI_2 in THF or DME when benzene or its derivatives are added. Similar to the solutions of NdI_2 such additives cause a quick color change of the mixture to brown and formation of a precipitate of DyI_3 [45]. However, in contrast to NdI_2, dysprosium iodide affords only the monophenoxide $PhODyI_2(THF)_4$ upon reaction with phenol, independent of the reaction temperature (0, −90 °C) [45].

No differences have been found in reactions with cyclopentadiene between neodymium and dysprosium iodides (Eq. (14)) [51].

$$DyI_2 + CpH \xrightarrow[-H_2]{THF} CpDyI_2(THF)_3 \qquad (14)$$

But in the one-pot synthesis of vanadocene, DyI_2 gives a higher yield of the desired product (68%) (Eq. (15)) [52].

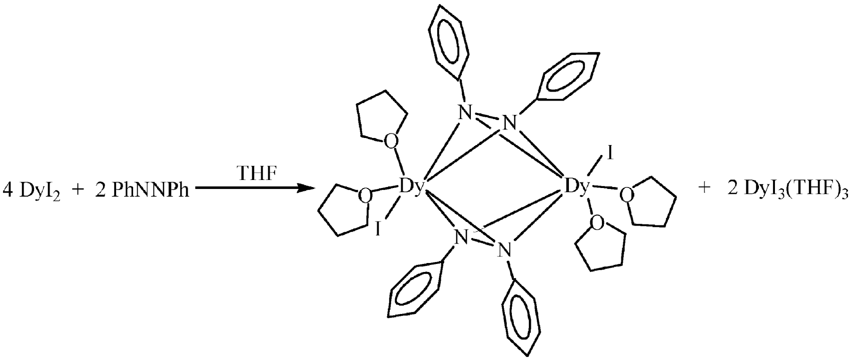
$$DyI_2 + VCl_3 + CpH \xrightarrow[-H_2,-DyI_2Cl]{THF} Cp_2V \qquad (15)$$

The differences are more strongly evident in the synthesis of Cp_2Co: from DyI_2, $CoCl_2$ and cyclopentadiene, cobaltocene was isolated in 38% yield whereas NdI_2 under the same conditions gives only traces amount of the product [52].

In the synthesis of vanadocene and cobaltocene, described earlier, NdI_2 and DyI_2 play a pseudo-alkali metal role; however, we have established that DyI_2 can be used as self-sufficient new synthons in the preparation of π-arene complexes of d-transition metals. In the synthesis of bis(arene) complexes, Fisher's method, i.e. heating of a mixture of Al powder, $AlCl_3$ and a metal halide in appropriate aromatic solvent is usually used [58]. The reaction of dysprosium diiodides with VCl_4 in benzene at 85 °C does not give the desirable $(C_6H_6)_2V$ but results in the reduction of vanadium chloride to VCl_3. However, when Cp_2V was used instead of vanadium chloride the reaction led to formation of brown solution from which, after removal of benzene and sublimation of the residue, bis(benzene) vanadium was obtained in 15% yield [59]. Despite the low yield of the desired product, this reaction is very important because it has shown that the reactions of LnI_2 can be successfully carried out not only in solvating ethereal solvents but also in non-polar media.

It was found that DyI_2 in DME solution adds to the triple bond of diphenylacetylene to give a product of indefinite structure, which after hydrolysis yields *cis*-stilbene [57].

The double N=N bond in azobenzene also is reduced by dysprosium diiodides but is limited to two electron reduction (Eq. (16)) [39]. X-ray structural analysis has shown that product **12**, isolated as light yellow crystals, is isostructural with the Tm analogue, i.e. in the molecule of the complex, two $DyI(THF)_2$ fragments are bonded by bridging N_2Ph_2 ligands in such a way that each nitrogen atom coordinates both metal atoms.



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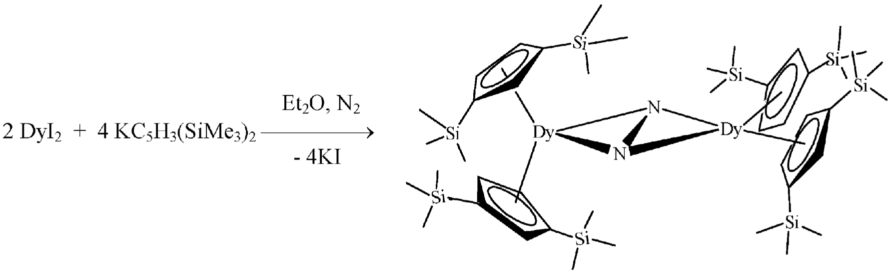
(16)

When the reaction is carried out in sunlight a solution of intense green color is formed. In a few hours the color changes to red-brown, characteristic of the final product $[DyI(THF)_2]_2(N_2Ph_2)_2$. The authors suggest that the green color is determined by generation of intermediate, unstable, electron transfer complexes of $[DyI_2(THF)_x(PhN{=}NPh)]$ type.

The methathesis reaction of DyI_2 with two equivalents of $NaN(SiMe_3)_2$ in THF in an atmosphere of nitrogen at −78 °C leads to formation of the nitrogen containing complex $\{[(Me_3Si)_2N]_2Dy(THF)\}_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}N_2)$ isolated as orange crystals [54]. A reduced form of nitrogen and the trivalent state of dysprosium is confirmed by X-ray analysis, which revealed that the molecule contains the same flat Ln_2N_2 fragment found before in other nitrogen-lanthanide complexes.

The nitrogen complex of Dy(III) (**13**) is obtained by interaction of the sterically crowded cyclopentadienyl anion with dysprosium diiodide in a nitrogen atmosphere (Eq. (17)) [60]. In this case the reaction was carried out in ether at −15 °C.



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(17)

The authors believe that an intermediate complex of divalent dysprosium is responsible for nitrogen reduction.

Besides THF and DME, dysprosium diiodide dissolves in acetonitrile but dissolution in this case is accompanied by disproportionation of the salt and its interaction with the solvent leading to formation of C–C bonds [61]. The products with reduced iodine content, $DyIRR'$, are isolated as intractable yellow solids, the IR spectrum of which display the presence of C≡N, C=N, C–N and N–H groups. The triiodide formed was isolated in two forms: as $DyI_3(MeCN)_4$ and a new type of compound $[\{(HN{=}CMe)_2MeCNH_2\}Dy(MeCN)_6]I_3$ (**14**), in which the metal atom is coordinated not only to six molecules of acetonitrile but also to a new tridentate ligand—2,4-diimino-3-methyl-3-aminopentane (Fig. 4).Iodine anions in the crystal of **14** are separated from the Dy^{3+} cation and from each other at distances which exclude direct interaction. Hydrogen atoms were not located, but the presence of C=N–H and $C{-}NH_2$ groups in the compound is surely confirmed by IR spectroscopy data. It is suggested that highly reactive DyI species reduce acetonitrile to give a mixture of organometallic and organic compounds including the bis(imine)amine system, which then coordinates to the Dy^{3+} cation in the triiodide.

Benzonitrile, which unlike acetonitrile does not contain acidic C–H groups also readily oxidizes dysprosium diiodide but the only definite product isolated from the reaction mixture was the triiodide $DyI_3(PhCN)_4$ (Eq. (18)) [62]. After separation of this complex and removal of PhCN all other products remain as an intractable mixture of yellow solids. Its hydrolysis and subsequent

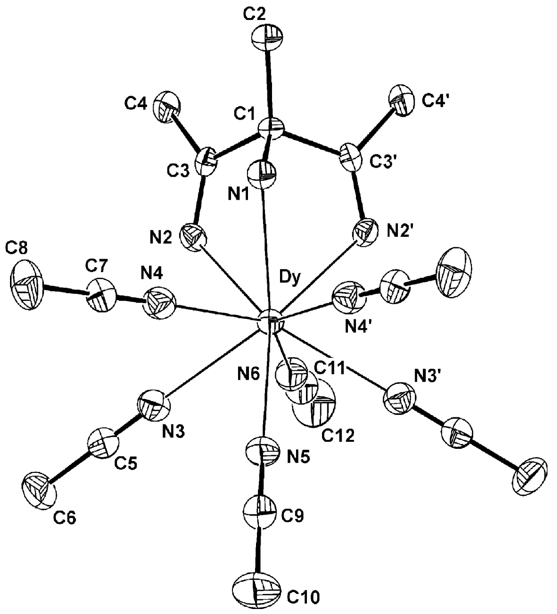
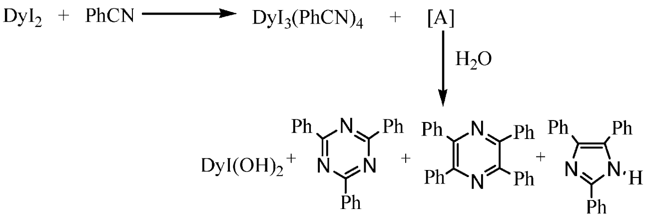


Fig. 4. Cation structure in the complex **13**.

crystallization from various solvents yielded a set of nitrogen compounds among which 2,4,6-triphenyl-1,3,5-triazine, 2,3,5,6-tetraphenyl-1,4-pyrazine and 2,4,5-triphenylimidazole were identified.



(18)

Note that NdI_2 reacts with PhCN in a similar way, but because of superior solubility of neodymium compounds the triiodide formed have been isolated only after replacing PhCN in the complex with THF. The yields of triazine, pyrazine and imidazole were comparable [62].

7. Compounds of thulium

Among “new” divalent lanthanides the thulium compounds are the most studied. This is explained first of all by the relatively positive (in comparison to Dy(II) and Nd(II)) potential of Tm(II) (E° Tm^{3+}/Tm^{2+} -2.22 V [8]) suggesting greater stability of its divalent derivatives.

The first molecular complex of divalent thulium $TmI_2(DME)_3$ was obtained by refluxing a mixture of shavings of thulium metal and TmI_3 in DME (Eq. (19)) [63].

$$TmI_3 + Tm \xrightarrow{\text{DME},60\,^\circ\text{C}} TmI_2(DME)_3 \tag{19}$$

The product is isolated as emerald-green crystals in good yield by removal of solvent in vacuum. X-ray analysis revealed that, similar to the samarium analogue $SmI_2(THF)_5$ [41], the molecule has a pentagonal bipyramidal structure with iodine atoms in axial positions and oxygen atoms in the equatorial plane (Fig. 5).The compound has rare coordination for DME complexes: two molecules of the ligand are chelating but the third one is monodentate. The Tm–I (3.141(2) and 3.186(2) Å) contacts in this product are about 0.15 Å longer than those in the Tm(III) complexes reflecting the difference of ionic radii of Tm^{2+} and Tm^{3+}. Thus, in the phenoxide $PhOTmI_2(DME)_2$ the respective distances are 3.0021(9) and 3.0236(10) Å [64]. In vacuum or inert atmosphere the compound very slowly decomposes at room temperature probably to give $MeOTmI_2$ type products. Under sunlight the decomposition accelerates. The divalent state of the metal in the complex is confirmed by the UV-Vis spectrum, which coincides with the previously obtained spectrum of a TmI_2 solution in THF [38] and also by the magnetic moment $\mu_{\text{eff}} = 4.53\mu_B$ agreeing with that calculated for the electron configuration $4f^{13}$ and coinciding with the moments found for isoelectronic compounds of Yb^{3+} [65].

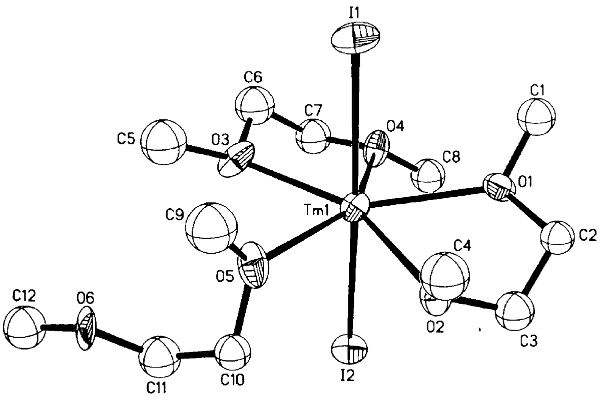


Fig. 5. Molecular structure of $TmI_2(DME)_3$.

When the same reaction was carried out in THF the complexes $TmI_2(THF)_5$ [37,66], $TmI_2(THF)_3$ [54], and

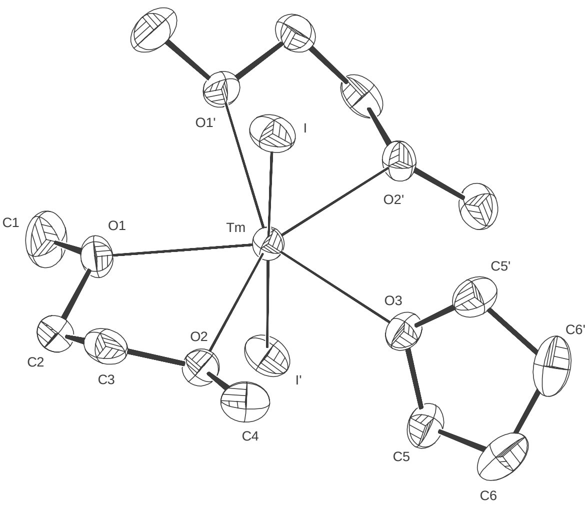


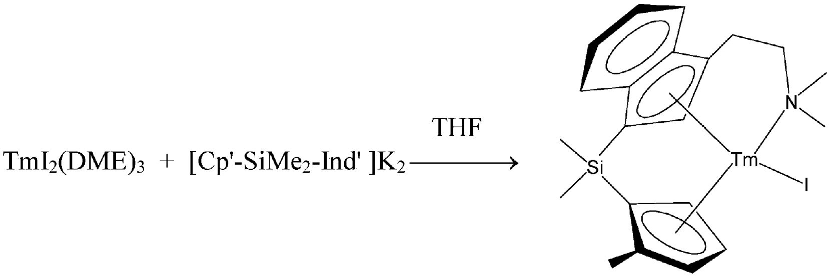
Fig. 6. Molecular structure of $TmI_2(THF)(DME)_2$.

$TmI_2(THF)_2$ [66] were obtained. The number of molecules of coordinated solvent in these complexes is determined by the conditions of drying. Often the diiodides $TmI_2(THF)_x$ obtained in situ are used in the reactions. Dissolution of TmI_2 in the THF/DME mixture and subsequent crystallization from the same mixture afforded the ligand-mixed complex $TmI_2(THF)(DME)_2$, which has been characterized structurally (Fig. 6) [42].Note that the method of preparation of the same complexes, described above, by burning the Ln/I_2 mixture and subsequent dissolution of the salt in THF or DME, is more convenient and fast [17].

A magnesium trimethylsilyl-substituted cyclopentadienyl compound gave the cyclopentadienyl-halide complex of Tm(III) [66] in a similar reaction carried out under comparable conditions (Eq. (22)).

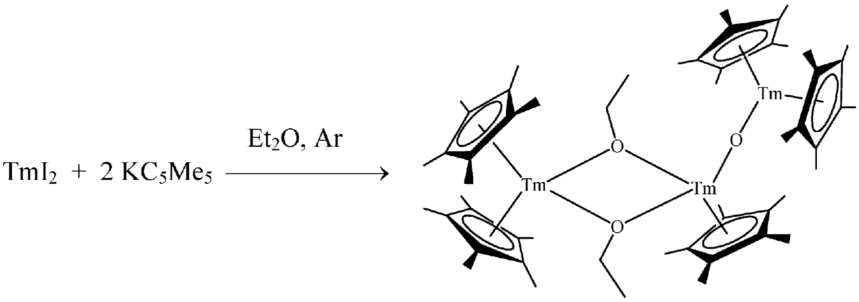
$$2TmI_2(THF)_2 + 4[1,3\text{-}(Me_3Si)_2C_5H_3]MgCl \xrightarrow{THF} \{[1,3\text{-}(Me_3Si)_2C_5H_3]_2TmCl\}_2 \quad (22)$$

Interaction of thulium diiodide with the potassium derivative of an amine-functionalized indenyl ligand led to the formation of the ansa-complex (**16**) but one iodine atom remained affixed to the metal atom (Eq. (23)) [68].



16 (23)

Just after the synthesis of $TmI_2(DME)_3$ and $TmI_2(THF)_2$ attempts to prepare organic derivatives of divalent thulium from these diiodides were undertaken by various investigators. In practically all cases they used the same approach: metathesis reactions of thulium diiodide with alkali metal derivatives containing sterically crowded ligands for enhancing the kinetic stability of expected products. However, all led to the formation of compounds of trivalent thulium. Thus, the reaction of $TmI_2(THF)_3$ with KC_5Me_5 in diethyl ether is accompanied by cleavage of the C–O bonds of the solvent [60]. When non-solvated TmI_2 is used and the reaction is conducted in an argon atmosphere the purple color which appeared in solution in the first minutes quickly transforms into yellow-orange and only an ethoxide of Tm(III) (**15**) is isolated as the final product (Eq. (20)) [67].



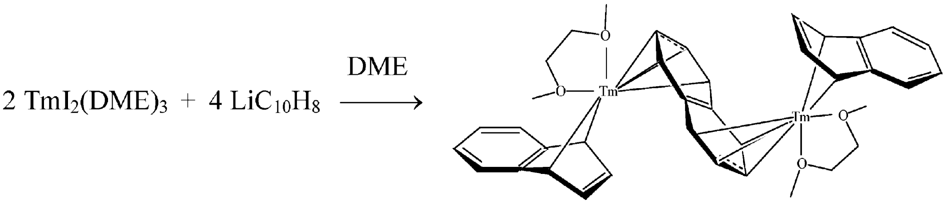
15 (20)

In THF the metathesis is accompanied by disproportionation to give two products of trivalent thulium (Eq. (21)) [66].

$$TmI_2(THF)_2 + 2KC_5Me_5 \xrightarrow{THE} (C_5Me_5)_2TmI(THF) + TmI_3(THF)_3 \quad (21)$$

The generation of an amide of divalent thulium $[(Me_3Si)_2N]_2Tm(THF)_x$ is supposed in the reaction of $TmI_2(THF)_3$ with two equivalents of $Na[N(SiMe_3)_2]$ [54]. However, only a very reactive violet substance was isolated from the dark green-brown solution, and this was not identified.

Reactions of thulium diiodide with such strong reductants as lithium naphthalenide and lithium anthracenide, which could lead to stabilization of Tm^{2+} by an aromatic dianion, are also accompanied by transfer of thulium to the trivalent state. In the first case the product was the triple decker binuclear complex with a bridging naphthalene dianion $[(\eta^2\text{-}C_{10}H_8)Tm(DME)]_2(\mu_2\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)$ (**17**) (Eq. (24)) [69], but in the second case the ligand-mixed iodine-arene product with the anthracene dianion $(\eta^2\text{-}C_{14}H_{10})TmI(DME)_2$ (**18**) was isolated (Eq. (25)) [70].



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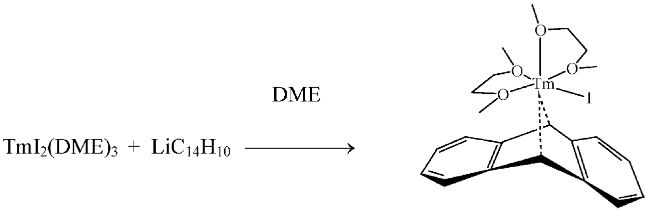
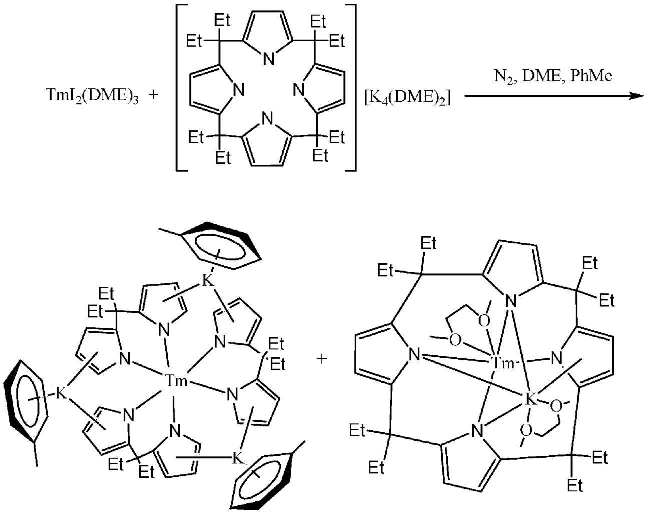


18

(25)

The magnetic moments of both products (6.59μ_B and 6.5μ_B, respectively) is noticeably lower than that value 7.1–7.5μ_B normally observed for compounds of trivalent thulium [65]. One possible reason probably could be an admixture of a low spin monovalent or a divalent oxidation state of the metal as a result of the reversible transition: $[Tm^{3+}]_2[arene^{2-}] \leftrightarrow [Tm^{2+}]_2[arene^0]$ or $[Tm^{3+}][Arene^{2-}] \leftrightarrow [Tm^{+}][Arene^0]$.

Treatment of $TmI_2(DME)_3$ with the porphyrinogen tetraanion in DME in a nitrogen atmosphere, which also targeted the synthesis of new divalent thulium compounds, actually gave the new lanthanide compounds **19** and **20** but containing formally trivalent metal (Eq. (26)) [71].



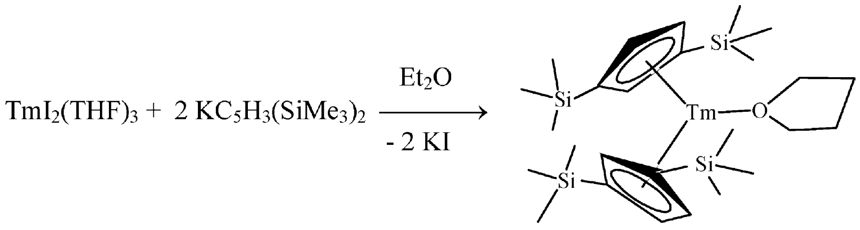
19 **20**

(26)

In these reactions, the rarely observed cleavage of the calixarene ligand is observed. Note the formation of product **19**, which contains three separate ansa-dianions $Et_2C(C_4H_3N)_2$.

Attempts to prepare Tm(II) compounds using an alternative pathway, reducing trivalent thulium derivatives by alkali metals, was also unsuccessful. Thus, treatment of $PhOTmI_2(DME)_2$ or t-$BuOTmI_2(THF)_3$ with sodium in THF yielded the already known diiodide $TmI_2(THF)_5$ [64] instead of the expected complexes $ROTmI(THF)_x$. Monoiodide compounds $(RO)_2TmI(THF)_2$ as well as triphenoxides $(PhO)_3Tm$ and (2,4,6-t-$Bu_3C_6H_2O)_3Tm$ are not reduced by sodium even upon heating at 70 °C. In the reaction of the cyclopentadienyl complex $(C_5Me_5)_2TmI$ with an excess of sodium in DME, the appearance of a green color in solution, characteristic of a compound of divalent thulium, was observed but the color quickly transformed into light brown [67]. A polynuclear Tm(III) complex with fragments of cleaved solvent $(DME)_2NaCp^*TmCp^*(OMe)_2NaCp^*(OMe)_2TmCp^*$ was isolated from the solution. The transient appearance of a green color in the solution was also noted in the reaction of $(C_5H_4CH_2CH_2NMe_2)_2TmI$ with excess sodium in diethyl ether [67]. The presence of cyclopentadienyl rings containing donating NMe_2 groups coordinating to the Tm atom (that was confirmed by the X-ray analysis data) did not provide enough stability to generate a complex of Tm(II). When another cyclopentadienyl-iodide compound containing the bulky $SiMe_2$-t-Bu substituents on the Cp rings, $\{[C_3H_3(SiMe_2\text{-}t\text{-}Bu)_2]_2TmI\}_2$, was reduced by potassium in THF, the solution acquired a brown color but then quickly decomposed to give a black precipitate presenting, as supposed by the author, thulium metal [36]. The same result was obtained in the reaction of potassium with tricyclopentadienyl complexes $(Cp^R)_3Tm$ (R = $SiMe_3$, $CH(SiMe_3)_2$, t-Bu, substituents on Cp ring) [34].

The first organometallic Tm(II) compound was isolated and characterized by Evans et al. [60]. They found that the reaction of $TmI_2(THF)_3$ with bis(trimethylsilylcyclopentadienyl) potassium in diethyl ether or THF gives a dark green solution from which, after removal of insoluble product and solvent, a violet powder of $[(Me_3Si)_2C_5H_3]_2Tm(THF)$ (**21**) is isolated (Eq. (27)). The composition and divalent state of metal in the product were confirmed by elemental analysis, IR data, NMR spectroscopy, magnetic measurements ($\mu_{eff} = 4.6\mu_B$) and structural investigations.

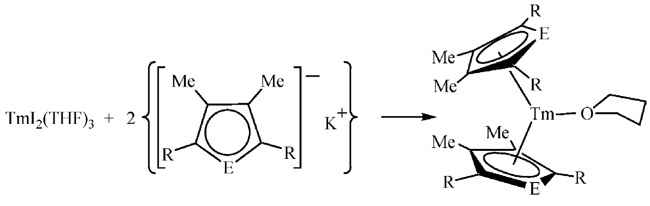


21 (27)

The Tm–Cp″(centroid) distance in **21** (2.394 Å) is very close to that of the Yb analogue $Cp''_2Yb(THF)$ (2.39 Å) [72] but noticeably longer than the same distance in the trivalent complex $[Cp''TmCl]_2$ (2.315(3) Å) [66].

The violet solution of the complex in ether at room temperature is stable for a few hours, whereas the dark green solution in THF decomposed over 30 min. Nothing is reported about the stability of the complex in the solid state.

The same approach i.e. application of sterically crowded ligands with lowered π-donating ability for stabilization of divalent thulium has been used in preparation of phospholyl (**22** and **24**) and arsolyl (**23**) complexes (Eq. (28)) [73].



22, 23, 24

R = $SiMe_3$; E = P (**22**), As (**23**); R = t-Bu; E = P (**24**)

(28)

The synthesis was carried out in ether at room temperature and afforded dark green solutions, the stability of which turned out to be somewhat greater than that of solutions of the complex with $C_5H_3(SiMe_3)_2$ ligands. The green crystals were isolated by crystallization from hexane in 50–70% yield. In the solid state the compounds are quite stable at −30 °C but slowly decompose at 25 °C. Magnetic moments of all three complexes ($4.7\mu_B$) correspond to divalent thulium. X-ray analyses performed on **23** and **24** revealed somewhat elongated (in comparison with the $C_5H_3(SiMe_3)_2$ analogue) Tm–C and Tm–O distances that testify to greater steric loading of the former. On the whole, the molecular geometry of **23** and **24** is similar to that of **21** but the Tm–C and Tm–O contacts in phospholyl and arsolyl derivatives are a little longer: Tm–C distances are reported from 2.759(4) to 2.824(5) Å for **23** and **24**, but from 2.651 to 2.711 Å for **21**; Tm–O 2.410(4) Å (**23**), 2.455(2) Å (**24**) and 2.365(5) Å (**21**).

A special group of molecular compounds of Tm(II) are represented by the endohedral metallofullerenes $Tm@C_{82}$. Three isomers of such complexes differing by symmetry group have been isolated by means of liquid chromatography from a mixture of metallofullerenes obtained by burning a carbon rod, doped with the thulium salt, in a voltaic arc [74]. Investigation of these products by UV-Vis, ^{13}C NMR, EPR spectroscopy and electrochemistry allowed the authors to conclude the encapsulated metal was in a divalent oxidation state. Conclusive proof of this was obtained by means of high-energy spectroscopy [75].

Table 1 lists all currently known molecular compounds of Nd(II), Dy(II), and Tm(II). The number of compounds obtained reflects enhanced stability of Tm(II) derivatives compared with Nd and Dy analogues.

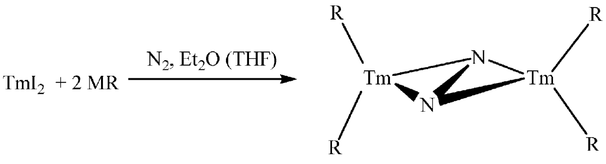
As could be expected from a comparison of the electrode potentials of Sm(II), Tm(II), Dy(II), and Nd(II), compounds of divalent thulium are more powerful reductants than samarium derivatives but generally weaker reductants than neodymium and dysprosium analogues.

The organic complexes of Tm(II) are noticeably more active than solvated and solvent free diiodide TmI_2. Thus, the latter does not react with nitrogen under ambient conditions whereas its reactions with $Na[N(SiMe_3)_3]_2$, KC_5Me_5, $KC_5H_4SiMe_3$, and $KC_5H_4(SiMe_3)_2$, in which

Table 1
Molecular compounds of divalent neodymium, dysprosium and thulium

Compound	Characteristics
$NdI_2(THF)_5$	Synthesis, IR, UV-Vis, μ_{eff} [17]; structure [42]
$NdI_2(DME)_3$	Synthesis, IR, UV-Vis, μ_{eff} [17]
$DyI_2(THF)_5$	Synthesis, IR, UV-Vis [17]
$DyI_2(THF)_3$	Synthesis, IR [17]
$DyI_2(DME)_3$	Synthesis, IR, UV-Vis [17]; structure [56]
$TmI_2(THF)_2$	Synthesis [66]
$TmI_2(THF)_3$	Synthesis [54]
$TmI_2(THF)_5$	Synthesis [37,66]
$TmI_2(THF)(DME)_2$	Synthesis, structure [42]
$TmI_2(DME)_3$	Synthesis, IR, UV-Vis, μ_{eff}, structure [63]
$[(Me_3Si)_2C_5H_3]_2Tm(THF)$	Synthesis, ^1H NMR, μ_{eff}, structure [60]
$[Me_2(Me_3Si)_2C_4P]_2Tm(THF)$	Synthesis, ^1H NMR, μ_{eff} [73]
$[Me_2(Me_3Si)_2C_4As]_2Tm(THF)$	Synthesis, ^1H NMR, μ_{eff} [73]
$[Me_2(t\text{-}Bu)_2C_4P]_2Tm(THF)$	Synthesis, ^1H NMR, μ_{eff}, structure [73]
$Tm@C_{82}$	Synthesis, high-energy spectroscopy [74,75]

the formation of the corresponding divalent intermediates $[(Me_3Si)_2N]_2Tm(THF)_x$, $(C_5Me_5)_2Tm(THF)_x$, $\{[C_5H_3(SiMe_3)_2]_2Tm(THF)_x$ and $\{[C_5H_4(SiMe_3)]_2Tm(THF)_x$ are proposed, when conducted in an N_2 atmosphere give complexes containing reduced nitrogen: $\{[(Me_3Si)_2N]_2Tm(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ [53], $[(C_5Me_5)_2Tm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, $\{[C_5H_4(SiMe_3)]_2Tm(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, and $\{[C_5H_3(SiMe_3)_2]_2Tm\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (Eq. (29)) [67]. X-ray diffraction analysis has shown that all these compounds have the characteristic flat Ln_2N_2 fragment mentioned previously for the neodymium and dysprosium complexes. In all cases the distances between nitrogen atoms, 1.236(8)–1.264(4) Å, correspond to a N=N bond length.



M = Na, K; R = $N(SiMe_3)_2$; $\eta^5\text{–}C_5Me_5$; $\eta^5\text{–}C_5H_4(SiMe_3)$; $\eta^5\text{–}C_5H_3(SiMe_3)_2$

(29)

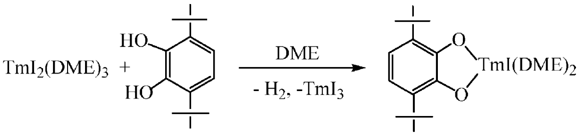
Quite recent data on the preparation and X-ray analysis of similar nitrogen complexes of yttrium, holmium and lutetium [76], for which the divalent state seems doubtful, as well as the data, quoted above, on the Pr_2N_2 compound, give a basis for supposing about another scheme for dinitrogen reduction occurs in these systems.

The diiodide $TmI_2(DME)_3$ is inert towards C–H and N–H groups of alkyls, aryls and amines but reacts with cyclopentadiene upon heating in THF solution [51]. The reaction is accompanied by partial disproportionation of the initially generated product $CpTmI_2(THF)_3$, which leads to formation of a mixture of mono- and dicyclopentadienyl derivatives (Eq. (30)).

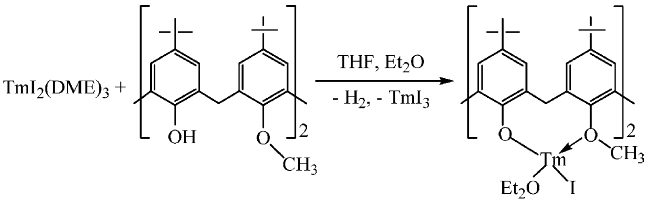
$$TmI_2 + CpH \xrightarrow[-H_2]{THF, 60\,^\circ C} CpTmI_2(THF)_3 + TmI_3(THF)_3 + Cp_2TmI(THF)_2 \qquad (30)$$

The OH group hydrogen atom in alcohols (but not in the sterically crowded 2,4,6-t-$Bu_3C_6H_2OH$) is easily displaced by thulium diiodide at room temperature (Eq. (31)) [64,77].

$$TmI_2(DME)_3 + ROH \xrightarrow[-H_2]{THF(DME)} ROTmI_2(L)_x,$$
$$R = t\text{-Bu, Ph};\ L = THF\ (x = 3), DME\ (x = 2) \qquad (31)$$



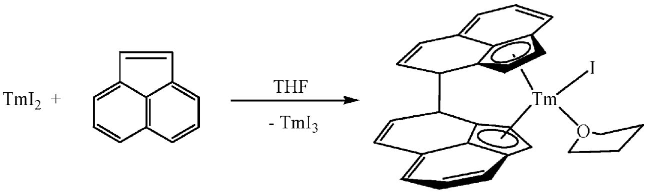
(32)



(33)

In the reactions with 3,6-di-*tert*-butylpyrocatechol (Eq. (32)) and 5,11,17,23-tetra-*tert*-butyl–25,27-dihydroxy-26,28-dimethoxycalix[4]arene (Eq. (33)) the diiodides of $I_2TmOC_6H_2(t\text{-Bu})_2OTmI_2$ and (MeOcalix[4]arene-O)$_2$-$(TmI_2)_2$ are initially formed, which then quickly disproportionate to give the final products. One of the main reasons facilitating redistribution of the substituents at the metal atoms is probably the bidentate nature of the aryloxy ligands because formation of chelating systems is thermodynamically preferable.

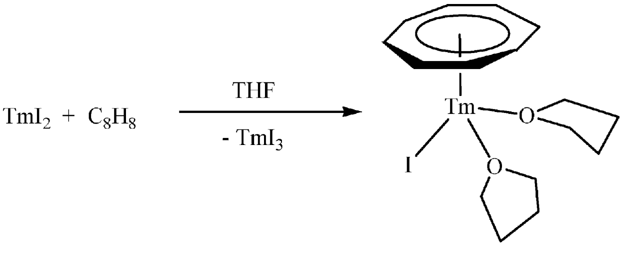
Unlike the diiodides of neodymium and dysprosium, TmI_2 does not react with benzene, naphthalene and anthracene but acenaphthylene, having a higher electron affinity, readily oxidizes thulium to the trivalent state. The reaction is accompanied by formation of C–C bonds that lead to generation of the ansa-rac-complex **25** (Eq. (34)) [70].



25

(34)

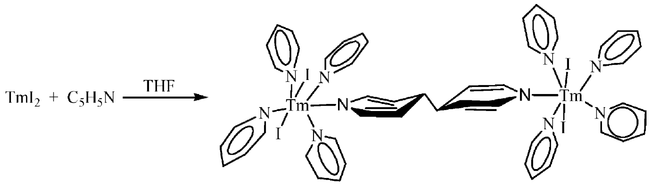
In the first minutes after mixing of the reagents, the solution acquires a dark violet color, which quickly transforms to light brown with formation of a precipitate. Apparently at an initial stage the deeply colored anion-radical $[(C_{12}H_8)^-(TmI_2)^+]$ is formed, which then quickly disproportionates to give TmI_3 and complex **25**, which is isolated in high yield. In contrast, in the reaction with cyclooctatetraene (Eq. (35)), thulium triiodide and the monoiodide coordinated by the $C_8H_8{}^{2-}$ dianion (**26**) are formed at once [71].



26

(35)

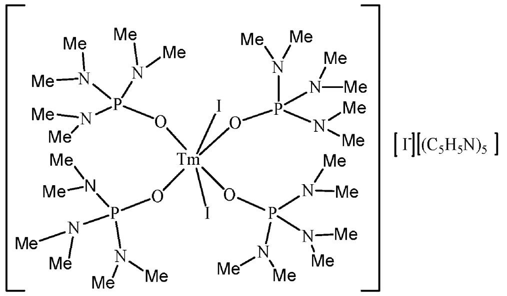
The rare example of C–C bond formation and reduction of pyridine is observed in the reaction 36 [78]:



(36)

In this case, disproportionation does not occur despite the appearance of the bidentate bipyridine ligand in the reaction mixture. 4,4′-Arrangement of nitrogen atoms in the latter excludes the possibility of their coordination to the same Tm atom, i.e. organization of the energetically beneficial (L–L)TmI structure observed in the 2,2′-bipyridine complexes [79]. Note, that in DME solution, the reaction also proceeds with oxidation of the metal to Tm(III) but identification of the products failed.

The reductive properties of thulium diiodide are demonstrated clearly in reactions with compounds containing C=O and P=O groups. Thus, the dissolution of $TmI_2(DME)_3$ in hexamethylphosphoramide and subsequent crystallization of the products from pyridine allowed isolation and structural characterization of complexes of Tm(III) **27** and **28** with P–O–Tm groups differentiated from each other by the locations of the iodine anion and pyridine ligand [80].



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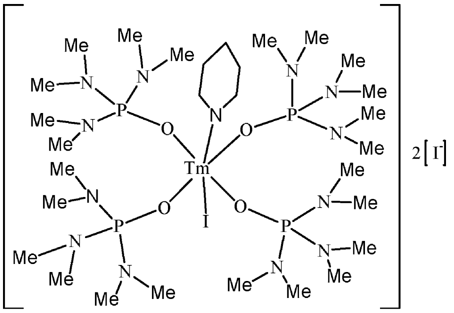
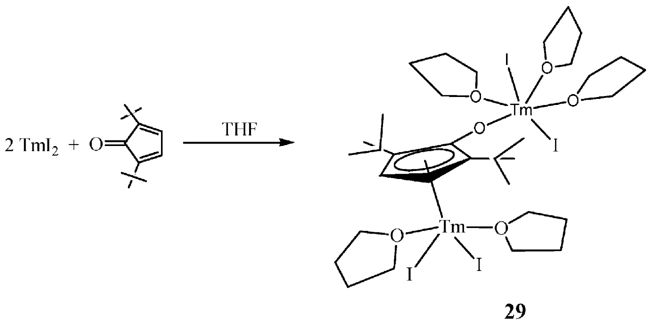


28

Interaction of $TmI_2(DME)_3$ with 3,6-di-*tert*-butylbenzoquinone-1,2 leads to the iodine-catecholate complex 3,6-*t*-$Bu_2C_6H_2O_2TmI(DME)$ quoted above in the reaction with 3,6-di-*tert*-butylpyrocatechol [64].

The reaction of thulium diiodide with 2,5-di-*tert*-butylcyclopentadieneone (Eq. (37)) is more complicated. In this case with the reagent ratio 2:1, two electron reduction of the ketone leads to a binuclear complex **29**, in which a $TmI_2(THF)_3$ fragment is σ-bonded with the oxygen of the apparent alcohol group, but the second Tm is η^5-bonded to the cyclopentadienyl ring [78].

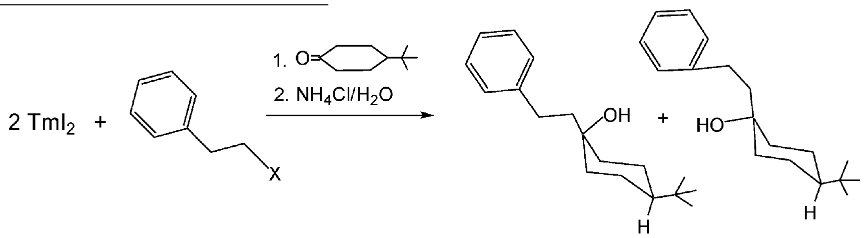


29

(37)

Product **29** is isolated as orange crystals in 76% yield.

Evans and Allen have established that TmI_2 can be successfully used in the cross-coupling reactions of alkylhalides and ketones (Eq. (38)) [81].



(38)

Comparison of the reaction conditions and the product yields revealed that the efficiency of the thulium salt in this synthesis is higher than that of SmI_2 normally applied in similar processes [82] but lower than that of dysprosium analog.

In contrast to SmI_2, which dissolves in acetonitrile but is not oxidized by it [38a,83], TmI_2 like DyI_2 reacts with this substrate easily and gives the same set of products (with appropriate metal) in comparable yield (Eq. (39)) [61].

$$TmI_2 + MeCN \rightarrow \underset{\textbf{30}}{[\{(HN{=}CMe)_2MeCNH_2\}Tm(MeCN)_6]I_3}$$
$$+ TmI_3(MeCN)_8 + [TmI(R, R')] \quad (39)$$

According to the X-ray analysis the bis(imine)amine complex **30** has the same structure as the dysprosium compound **14** after accounting for the difference in ionic radii of Tm(III) and Dy(III). The reaction of thulium iodide with benzonitrile also resembles the transformations observed for NdI_2 and DyI_2 [62]. However, in this case, the yields of triazine and pyrazine are lower whereas the yield of imidazole is higher than for the first two salts.

The thulium diiodide manifested low activity towards compounds with a C=C bond. It feebly catalyzes styrene polymerization and is thoroughly inert towards propylene [84].

8. Conclusion

As seen from the above material the chemistry of divalent lanthanides is not restricted by the compounds of traditional Sm, Eu and Yb but includes other rare earth metals. Convenient methods for the preparation of the diiodides of Nd, Dy and Tm are known. These are useful starting reagents for various organic and organometallic synthesis, and are commercially available materials. Investigation of the properties of these substances is still in the initial stages but already one can affirm that these compounds posses a number of peculiar properties, which make them attractive as objects for theoretical investigation and as the perspective synthons in diverse processes of practical chemistry. The most important characteristic of these “new” divalent lanthanides is their strong reductant capability, which under some conditions exceeds the power of alkali metals. Their solubility in organic solvents and ability to coordinate many ligands, give them a series of advantages compared to Li, Na and K in the application as reductants for various organic and organometallic substrates. Another advantage of the LnI_2 diiodides (Nd, Dy, Tm) is that they are non-hazardous. This property (allowing for minor difference in price between Nd, Dy and Li, Na, K) allows in particular NdI_2 and DyI_2 to be recommended as convenient and effective drying reagents for organic solvents such as THF, DME, ether, benzene, etc. A test study has shown the water content in THF (initial value was 0.225% after distillation over NaOH) in 30 min after treatment with sodium sand, sodium benzoketyl, $LiAlH_4$, and NdI_2 are relatively 0.074, 0.029, 0.020 and <0.013% [85]. Juxtaposing the reactivity of the diiodides of neodymium, dysprosium and thulium with that of the broadly applied SmI_2, one can with certainty predict intense development of the chemistry of these salts and their organic derivatives.

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