

## Yttrium 1994

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### 1. Introduction

This review covers the coordination chemistry of yttrium, published in 1994, and follows the format of the 1993 survey [1]. The literature has been searched using *Current Contents* and the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2]. This review is not fully comprehensive but does provide a significant coverage of papers published.

Organometallic complexes have generally been excluded, although several organo-metallic species which also contain ligands of interest to the coordination chemist are described. An article which considers trends in metallo-organic chemistry of scandium, yttrium and the lanthanoids has appeared [3], and the effective use of  $[\text{Cp}_2\text{YCl}]$  and yttrium(III) chloride as catalysts for the regioselective acylative cleavage of epoxides has been reported [4]. Fullerene derivatives continue to fascinate, and the endohedral derivative Y at  $\text{C}_{82}$  has been isolated and characterized [5,6].

#### 1.1. Separation and extraction

The cations  $\text{Y}^{3+}$  and  $\text{Sr}^{2+}$  can be separated by column chromatography with condensation polymers containing crown ether carboxylic acid monomer sub-units as the stationary phase. The resin can be regenerated and their effective pH ranges and metal loading capacities have been determined. The loading capacity is influenced by structural characteristics of the crown ether [7].

The efficiency with which *N*-(2,2-dimethylvaleryl)-*N*-phenylhydroxylamine HL can chelate to and extract yttrium(III) has been investigated. The distribution of the metal ions between aqueous and tetrachloromethane phases has been determined for varying pH and concentration of HL. The extracted species is the complex  $[Y(L)_3(HL)]$  and the selectivity shown by the ligand in extracting Y(III) from lanthanoid(III) mixtures was shown to be excellent [8]. Saitoh *et al* have also studied the extracting potentials of *N*-alkylcarbonyl-*N*-phenylhydroxylamines [9].

## 1.2. Yttrium(III)

### 1.2.1. Complexes with oxygen-donor ligands

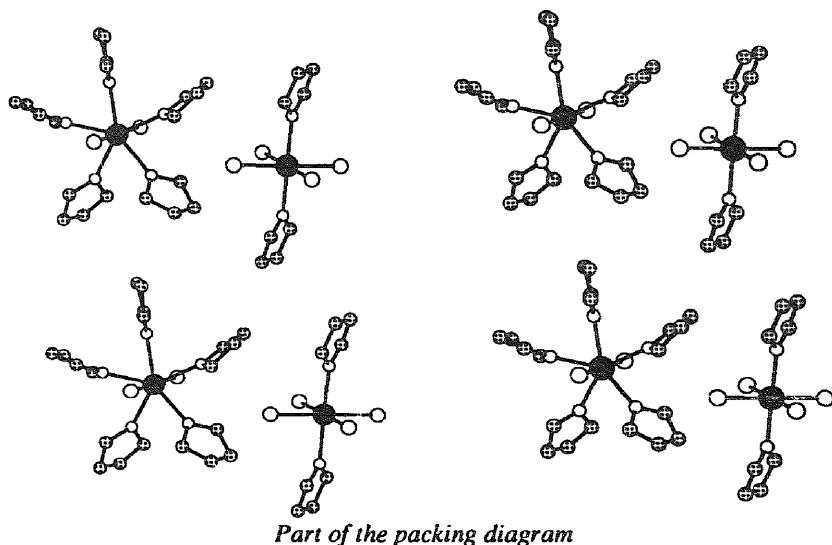
Thermal decomposition of  $Y(OAc)_3 \cdot 4H_2O$ ,  $Y(NO_3)_3 \cdot 5H_2O$  and  $Y_2(ox)_3 \cdot 8H_2O$  (100–700°C) produces  $Y_2O_3$  and the processes have been investigated by using TGA and DTA techniques. The intermediate and final products of the degradations have been characterized by IR spectroscopy and X-ray diffraction methods. Decomposition of  $Y(NO_3)_3 \cdot 5H_2O$  is complete at 450°C, whilst higher temperatures (650°C) are needed for the oxalate and acetate salts [10]. An experimental investigation of the solid-liquid equilibrium of  $H_2O$ - $Y(NO_3)_3$  has been complemented by model studies. One result shows that yttrium nitrate is dissociated in aqueous solution and the Y(III) centre forms tetra-, octa- and dodecahydrates [11].

A convenient method of preparing  $YCl_3 \cdot 3.5thf$  has been described. It involves the reaction of yttrium with  $Me_3SiCl$  and anhydrous MeOH in thf at room temperature for 10 h, and the yield is quantitative [12]. Recrystallization of  $YCl_3 \cdot 3.5thf$  from thf leads to the isolation of the salt  $[trans-YCl_2(thf)_5][trans-YCl_4(thf)_2]$  (1); the solid state lattice contains separated pentagonal bipyramidal cations and octahedral anions. If  $YCl_3 \cdot 3.5thf$  was recrystallized from dichloromethane, a polymer of formula  $[YCl_3 \cdot 2thf]_\infty$  (2) resulted. Structural characterization shows the presence of 7-coordinate yttrium(III) centres with Y–Y distances of 442.2(1) and 443.6(1) pm. Compounds (1) and (2) are active catalysts for the polymerization of ethene [13]. The reaction of  $YCl_3$ , sodium and cyclopentadiene (1:1:5) in thf has yielded the monomeric complex  $[CpYCl_2(thf)_3]$  which has been structurally characterized [14].

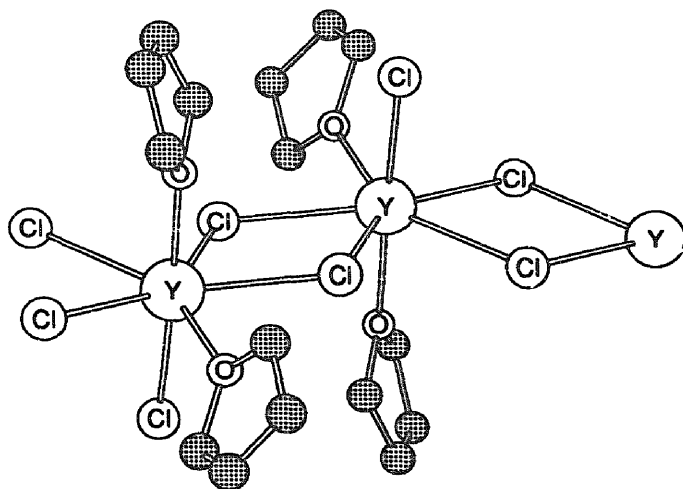
Yttrium(III) triiide has been shown to be an efficient catalyst for the addition of lithium enolates to 1,2-epoxides and the reaction gives a method of preparing  $\gamma$ -hydroxyketones [15].

A variety of yttrium(III) aqua complexes was reported in 1994. The crystal structure of  $[Y(NO_3)_3(H_2O)_3] \cdot 18\text{-crown-6}$ , [(3)], 18-crown-6, has been determined. The crown ether is uncoordinated and the yttrium centre is in a 9-coordinate environment [16]. Yttrium(III) picrate crystallizes from water as the hydrate  $[Y(pic)(H_2O)_7][pic]_2 \cdot 4.5H_2O$ . The cation contains an 8-coordinate metal centre as shown in structure (4). The nature of this complex and of the isomorphous dysprosium(III), erbium(III) and lutetium(III) complexes contrasts with that of the La(III) and earlier 4f-block picrates in which two pic<sup>−</sup> anions are coordinated to each metal centre [17].

The structure of  $[Y_2(HL)_6(H_2O)_4] \cdot 4H_2O$  ( $H_2L$ =salicylic acid) has been deter-

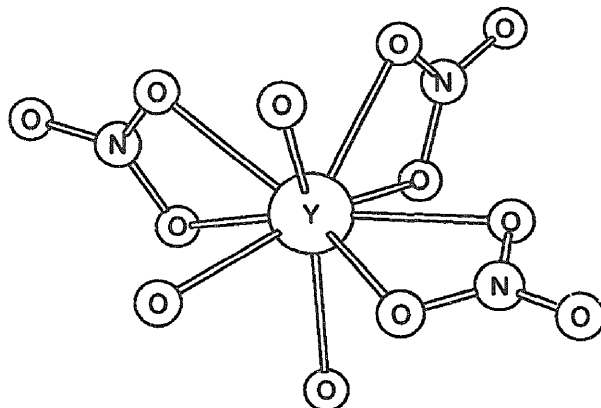


(1)



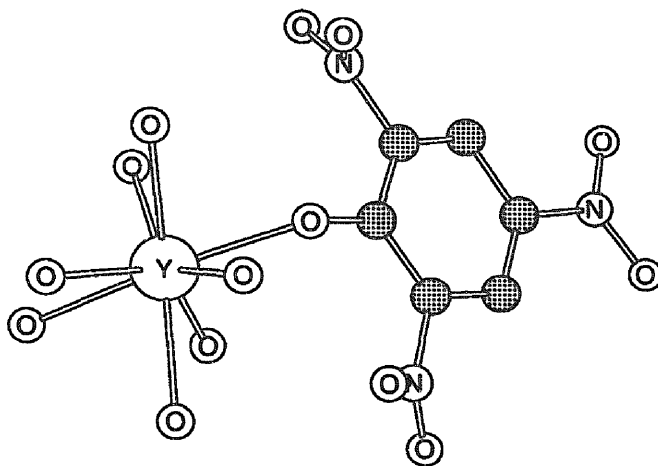
(2)

mined by X-ray diffraction methods. The  $Y_2$ -core is supported by four bridging carboxylate ligands, and each yttrium(III) centre is also bound to a terminal carboxylate and two aqua ligands [18].



*Hydrogen atoms are omitted*

(3)

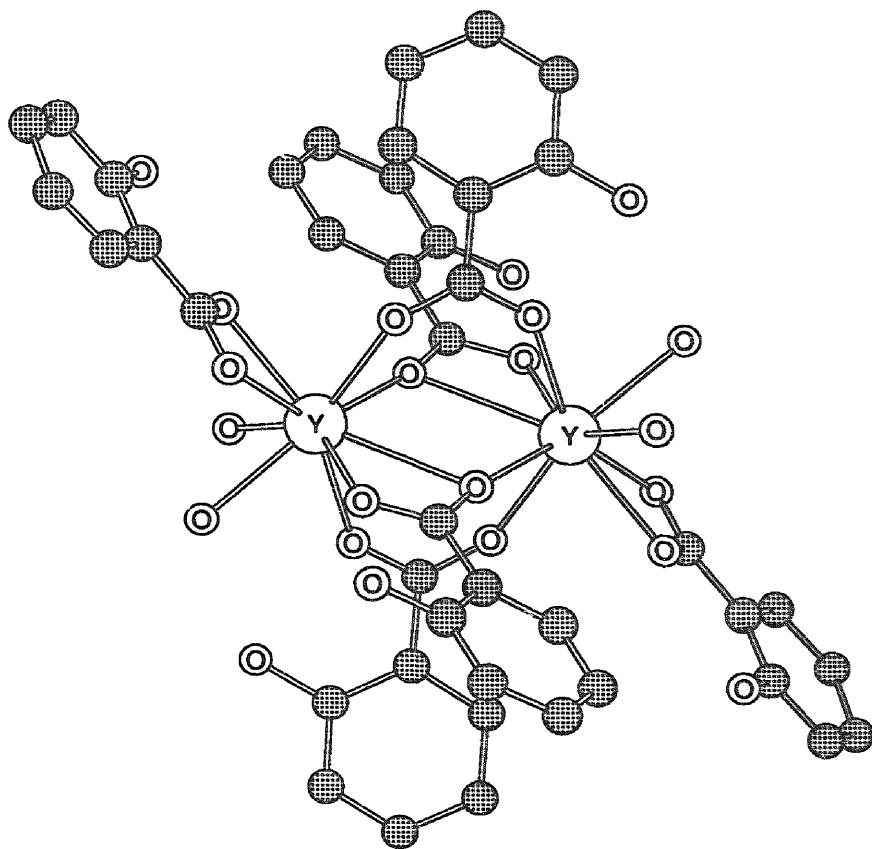


*Hydrogen atoms are omitted*

(4)

Carboxylate complexes are also represented by  $[YL_3 \cdot 2H_2O]$  which crystallizes as a tetrahydrate. Structure (6) shows part of the centrosymmetric polymeric structure which has been determined by an X-ray diffraction study. The Y-Y distances are 494.5(2) and 495.0(2) pm and the coordination environment at each yttrium(III) is distorted dodecahedral with Y-O bond distances in the range 225.2–247.3(2) pm [19].

Several papers concern  $\beta$ -diketonate complexes of yttrium(III). The direct synthe-

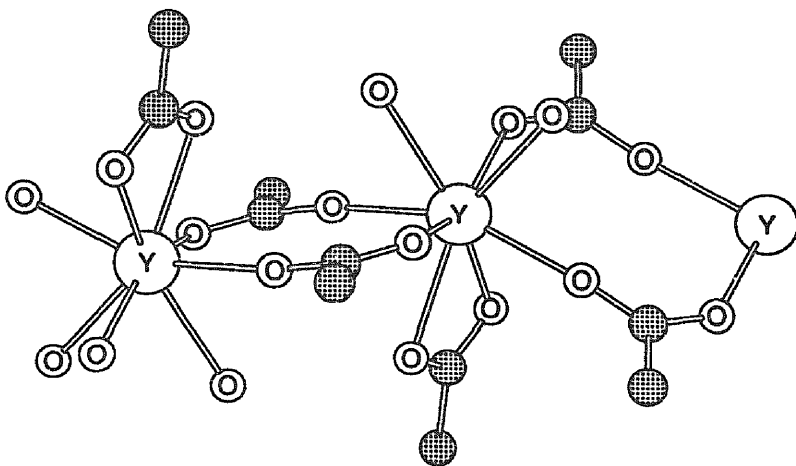


*Hydrogen atoms are omitted*

(5)

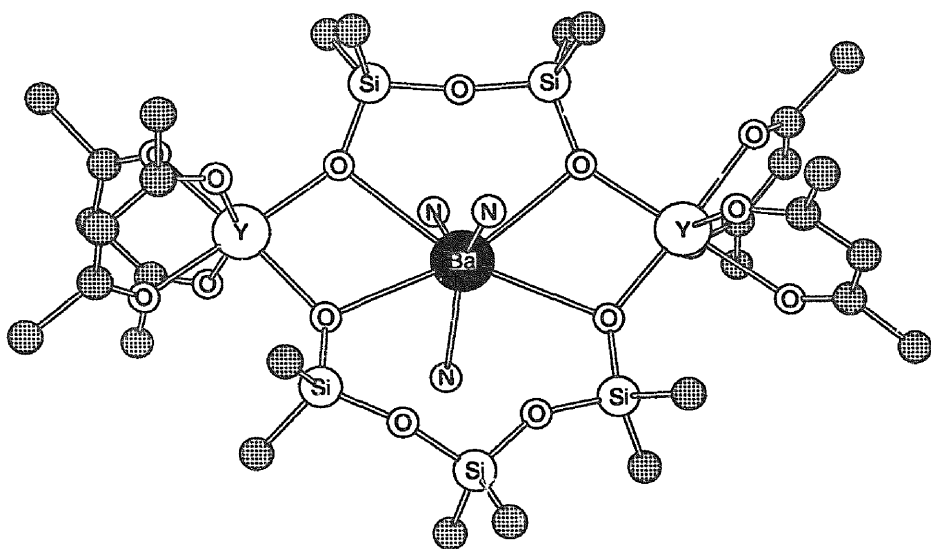
ses of yttrium(III) acac complexes in organic systems have been described [20]. The reactions of  $\text{Y}(\text{OH})_3$  with HL ( $\text{HL} = \text{C}_6\text{F}_{11}\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CF}_3$  or  $\text{C}_6\text{F}_{11}\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{C}_3\text{F}_7$ ) produce the complexes  $[\text{YL}_3]$  isolated as dihydrates which have been characterized by IR and NMR spectroscopies and by DTA and TGA methods. Both complexes evaporate with decomposition [21]. Evaporation studies have also been carried out for  $[\text{YL}_3]$  where  $\text{HL} = \text{'BuC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{C' Bu}$  [22]. The conjugate base of  $\text{'BuC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{C' Bu}$  (HL) chelates to yttrium(III) in the trinuclear complex  $[(\text{L}_2\text{Y})_2\text{Ba}(\text{py})_3(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{O})\text{-}(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})]$  (7), the structure of which has been determined. Each yttrium centre is 6-coordinate [23].

When  $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$  is treated with tris(*tert*-butyl)methanol (HL), no reaction takes place, but when the steric bulk of the ligands is reduced and the precursor is



Only the ipso C atoms of the 3,5-(NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups are shown

(6)

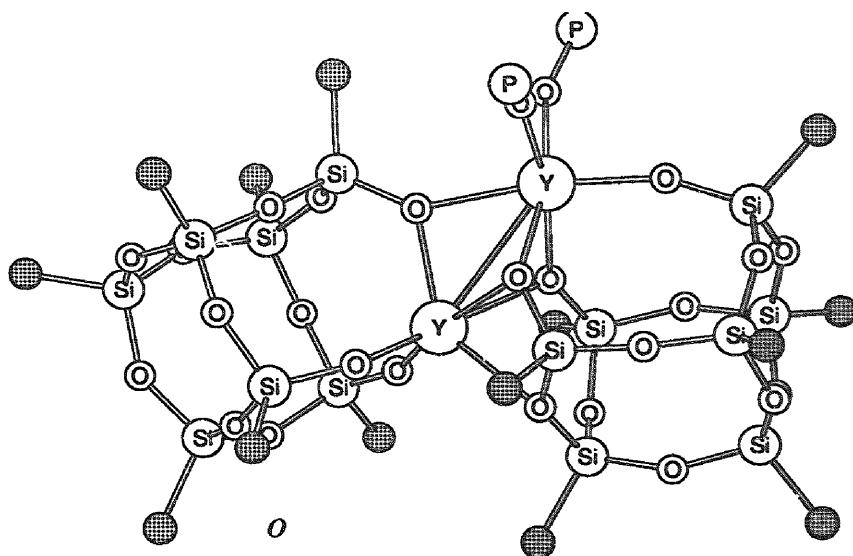
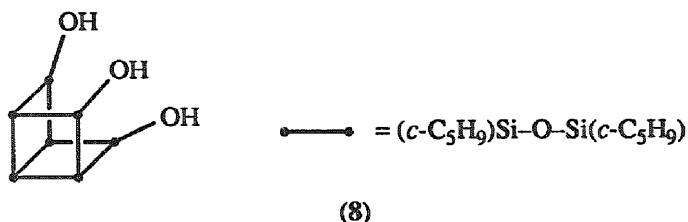


Methyl groups are omitted from the β-diketonate ligands,  
and only the N-donors atoms of the three py ligands are shown.

(7)

[Y{N(SiMe<sub>2</sub>H)<sub>2</sub>}]<sub>3</sub> · 2thf (see section 1.2.3), ligand substitution occurs. The product is [YL<sub>3</sub>(thf)] and has been characterized by IR and <sup>1</sup>H, <sup>13</sup>C and <sup>89</sup>Y NMR spectroscopies [24]. Herrmann *et al* have also been interested in the design of models for

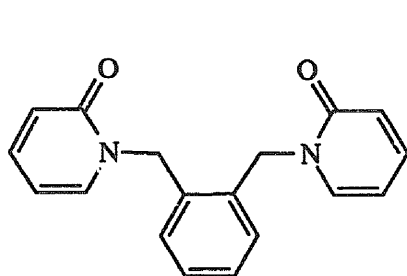
heterogeneous silica-supported metal catalysts and have investigated the reaction of ligand (8),  $H_3L$ , with  $[Y\{N(SiMe_3)_2\}_3]$  in thf. The complexes  $[YL(thf)]_n$  ( $n=1$  or 2) have been isolated and characterized by spectroscopic and mass spectrometric methods. It is proposed that the  $L^{3-}$  ligand coordinates through the three oxygen donor atoms. Crystals could not be grown, but when triphenylphosphine oxide is present, crystals of a dinuclear complex (9) were obtained. Oxygen atoms which are terminally attached to one cage are involved in bridging interactions between the two metal atoms, and an oxygen atom from one of the  $Si_7O_9$ -cages coordinates to one yttrium(III) centre [25].



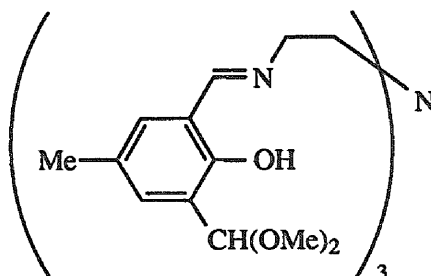
Only one C atom of each cyclopentyl ring and only the  
P=O groups of the  $Ph_3PO$  ligands are shown  
(9)

The preparation of compound (10), L, has been reported. The ligand reacts with yttrium(III) nitrate in acetonitrile to give the dinuclear complex  $[Y_2L_3(NO_3)_6] \cdot 3MeCN$ , one of a range of metal complexes to be prepared and characterized by Goodgame *et al.* The single crystal structure of

$[\text{Y}_2\text{L}_3(\text{NO}_3)_6] \cdot 3\text{MeCN}$  reveals that one bridging ligand supports the yttrium(III) centres at a non-bonded separation; each metal atom is 9-coordinate and coordinated to six oxygen donor atoms from three nitrate ions and three pyridone oxygens from one bridging and one chelating ligand L [26]. The syntheses of (11) and two related ligands have been described. Compound (11) reacts with hydrated yttrium(III) perchlorate in MeOH, and after recrystallization from MeCN/Et<sub>2</sub>O the complex  $[\text{YL}][\text{ClO}_4]_3 \cdot 3\text{MeCN}$  has been isolated. Structural characterization of this product confirms that the ligand coordinates only through the oxygen donor atoms, providing a 9-coordinate coordination sphere for the metal centre [27].



(10)



(11)

The zwitter-ionic complex  $[\text{Y}\{\text{OSi}^i\text{Bu}_2\{(\text{CH}_2)_3\text{NMe}_2\}\}_3\{\text{OSi}^i\text{Bu}_2\{(\text{CH}_2)_3\text{NMe}_2\text{H}\}\}]$  in which the yttrium(III) centre is coordinated by four oxygen donor atoms is described in section 1.2.5 [28].

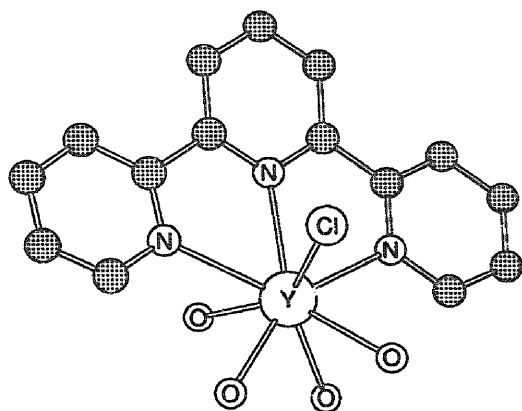
### 1.2.2. Complexes with sulfur or selenium-donor ligands

The reactions of  $[(^i\text{BuC}_5\text{H}_4)_2\text{Y}(\mu\text{-Me})_2\text{Y}(^i\text{BuC}_5\text{H}_4)_2]$  with  $\text{R}_2\text{E}_2$  ( $\text{E}=\text{S}$ ,  $\text{R}=\text{Ph}$ ,  $^n\text{Bu}$ ,  $^i\text{Bu}$  or benzyl;  $\text{E}=\text{Se}$ ,  $\text{R}=\text{Ph}$ ) have resulted in the formation of the dinuclear complexes  $[(^i\text{BuC}_5\text{H}_4)_2\text{Y}(\mu\text{-ER})_2\text{Y}(^i\text{BuC}_5\text{H}_4)_2]$ , characterized by elemental analyses and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies. The complex  $[(^i\text{BuC}_5\text{H}_4)_2\text{Y}(\mu\text{-SePh})_2\text{Y}(^i\text{BuC}_5\text{H}_4)_2]$  has been the subject of a crystallographic study; the  $\text{Y}_2$ -core (472.9 pm) is bridged by the two selenide ligands and the phenyl rings lie on opposite sides of the planar  $\text{Y}_2\text{Se}_2$  framework. The Y-Se distances are 291.5(1) pm and the Y-Se-Y angles are  $108.5(3)^\circ$  [29].

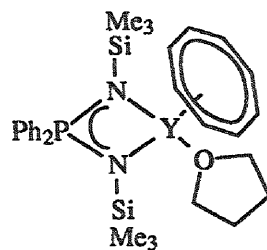
### 1.2.3. Complexes with nitrogen-donor ligands

Treatment of yttrium(III) chloride with three equivalents of  $\text{Li}[\text{N}(\text{SiMe}_2\text{H})_2]$  in thf results in the formation of  $[\text{Y}\{\text{N}(\text{SiMe}_2\text{H})_2\}_3] \cdot 2\text{thf}$  (see section 1.2.1). A structural study has shown that the yttrium(III) centre is in a trigonal bipyramidal environment with the thf ligands mutually *trans* [24].

As part of an investigation of a range of lanthanoid complexes of the type  $[\text{Ln}(\text{tpy})\text{Cl}_3] \cdot x\text{H}_2\text{O}$ , the yttrium(III) member of this family has been prepared and characterized. It crystallizes from water as  $[\text{Y}(\text{tpy})\text{Cl}(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and the results of an X-ray diffraction study confirm that the cation (12) possesses an 8-coordinate metal centre [30].



Hydrogen atoms are omitted  
(12)



(13)

The dimer  $[\{Y(\eta^8\text{-C}_8\text{H}_8)(\text{thf})\}_2(\mu\text{-O}_3\text{SCF}_3)_2]$  has proved to be a valuable starting material for the synthesis of a range of complexes containing nitrogen-donor ligands. For example, it reacts with  $\text{K}[\text{HBpz}_3]$  to yield  $[(\eta^8\text{-C}_8\text{H}_8)\text{Y}\{\text{HBpz}_3\}]$ , and with  $\text{Li}[\text{Ph}_2\text{P}(\text{NSiMe}_3)_2]$  to give  $[(\eta^8\text{-C}_8\text{H}_8)\text{Y}(\text{thf})\{\text{Ph}_2\text{P}(\text{NSiMe}_3)_2\}]$  (13). Products have been characterized by IR and multinuclear NMR spectroscopies, elemental analysis and mass spectrometry [31]. Yttrium(III) chloride reacts with  $\text{Li}[\text{N}^i\text{Pr}_2]$  in thf to yield the complex  $[\text{Y}(\text{N}^i\text{Pr}_2)_3] \cdot \text{thf}$  and further treatment with  $\text{Li}[\text{N}^i\text{Pr}_2]$  produces  $[\text{Li}(\text{thf})\text{Y}(\text{N}^i\text{Pr}_2)_4]$ . These products have been formulated on the basis of elemental analyses and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, and although an X-ray diffraction study of  $[\text{Li}(\text{thf})\text{Y}(\text{N}^i\text{Pr}_2)_4]$  has confirmed its composition, severe disorder problems were encountered. In the proposed structure, the lithium and yttrium metal centres are bridged by two amido ligands and the remaining two  $[\text{N}^i\text{Pr}_2]^-$  ligands occupy terminal sites on the yttrium atom which is tetrahedral. The thf molecule is bound to the alkali metal centre [32].

#### 1.2.4. Complexes with phosphorus-donor ligands

The reaction between  $[\text{Y}(\text{O}_3\text{SCF}_3)_3]$  and four equivalents of  $\text{Li}[\text{C}(\text{PMe}_2)_2\text{SiMe}_3]$  in thf leads to the formation of the complex  $[\text{Y}\{\text{C}(\text{PMe}_2)_2\text{SiMe}_3\}_4\text{Li}]$  for which the  $^{31}\text{P}$  NMR spectrum shows  $^{89}\text{Y}$ - $^{31}\text{P}$  spin-spin coupling of 57.9 Hz suggesting direct Y-P bonding interactions. Variable temperature NMR spectroscopic data are consistent with the magnetic equivalence of the phosphorus centres, possibly resulting from a fluxional process in solution. The crystal structure of a related La(III) complex has revealed an 8-coordinate metal centre in an  $\text{LaP}_8$ -coordination sphere [33].

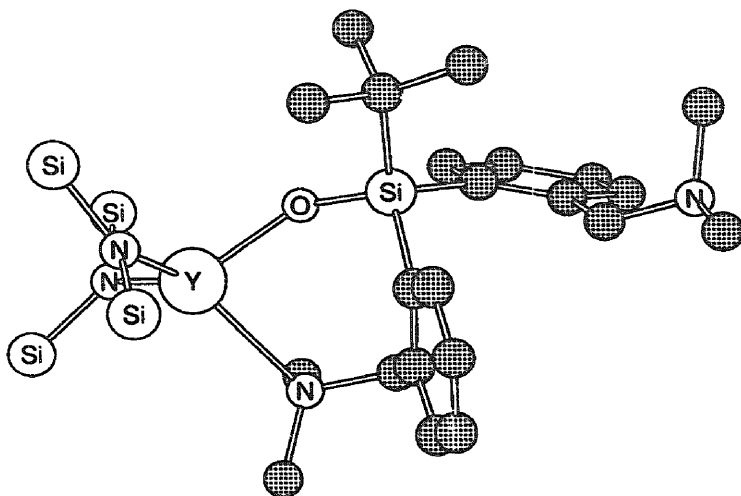
#### 1.2.5. Complexes with oxygen and nitrogen-donor ligands

The syntheses of the ligands  $\text{HOSi}^i\text{Bu}_{3-n}\{(\text{CH}_2)_3\text{NMe}_2\}_n$  ( $n=1$  or  $2$ ) have been achieved in two-step reactions. When these silanols (HL) react with

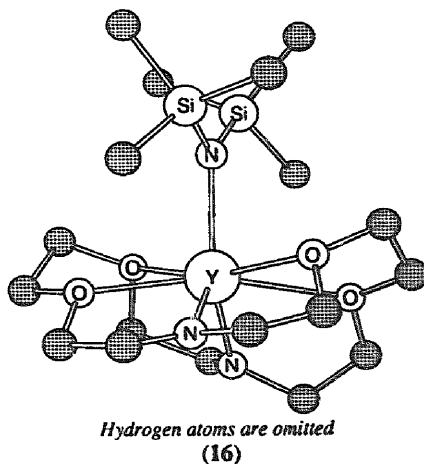
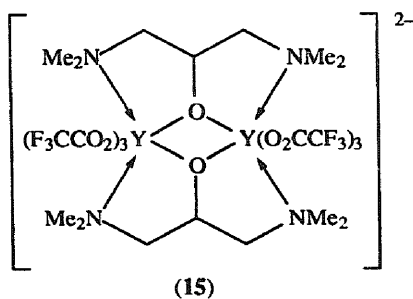
$[Y\{N(SiMe_3)_2\}_3]$ , the products are the complexes  $[YL_3]$ . The complex  $[Y\{OSi^tBu_2\{(CH_2)_3NMe_2\}\}_3]$  sublimes without chemical change at  $115^\circ\text{C}$  and  $10^{-4}$  torr, and crystallographic data for this compound reveal a trigonal bipyramidal structure in which the equatorial sites contain oxygen donor atoms, whilst the axial sites are occupied by two nitrogen atoms; the third  $NMe_2$ -unit is pendant. In solution, the complex is fluxional on the NMR spectroscopic timescale from room temperature to  $-80^\circ\text{C}$  and it is proposed that exchange occurs between the pendant and coordinated  $NMe_2$  groups. When  $[Y\{N(SiMe_3)_2\}_3]$  was treated with four equivalents of  $HOSi^tBu_2\{(CH_2)_3NMe_2\}$ , a zwitter-ionic complex  $[Y\{OSi^tBu_2\{(CH_2)_3NMe_2\}\}_3\{OSi^tBu_2\{(CH_2)_3NMe_2H\}\}]$  resulted. A crystallographic study of the yttrium(III) analogue of the yttrium(III) complex has shown that the metal centre is tetrahedrally sited, bound by the four oxygen donor atoms. In toluene solution, the yttrium(III) complex  $[Y\{OSi^tBu_2\{(CH_2)_3NMe_2\}\}_3\{OSi^tBu_2\{(CH_2)_3NMe_2H\}\}]$  is in equilibrium with  $[Y\{OSi^tBu_2\{(CH_2)_3NMe_2\}\}_3]$  and  $HOSi^tBu_2\{(CH_2)_3NMe_2\}$ , and  $^1\text{H}$  NMR spectroscopic data have been used to determine values of  $\Delta H^\circ = 40 \pm 4 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 124 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$  for this process. The complex  $[Y\{OSi^tBu_2\{(CH_2)_3NMe_2\}\}_3\{OSi^tBu_2\{(CH_2)_3NMe_2H\}\}]$  reacts with  $LiCH_2SiMe_3$  to yield  $Li[Y\{OSi^tBu_2\{(CH_2)_3NMe_2\}\}_4]$  [28]. The preparation of  $HOSi^tBu_2(2\text{-}C_6H_4CH_2NMe_2)_2$  has also been described. This ligand reacts with  $[Y\{N(SiMe_3)_2\}_3]$  to give the complex  $[Y\{OSi^tBu(2\text{-}C_6H_4CH_2NMe_2)_2\}\{N(SiMe_3)_2\}_2]$  (14) for which crystallographic data have confirmed that the conjugate base of the silanol acts as an *O,N*-chelate. Compound (14) reacts with  $2,6\text{-}^tBu_2C_6H_3OH$  with the formation of the complex  $[Y\{OSi^tBu(2\text{-}C_6H_4CH_2NMe_2)_2\}\{OC_6H_3Bu_2\text{-}2,6\}\}_2]$ . The new compounds have been characterized in solution by NMR spectroscopy and both exhibit fluxional behaviour [34].

With the aim of producing a precursor system to the superconductor  $YBa_2Cu_3O_{7-x}$ , Wang *et al* have studied the reaction between  $[Cu_2(OAc)_4(H_2O)_2]$ ,  $[Ba(OAc)_2]$ ,  $[Y(OAc)_3(H_2O)_4]$ , acetic acid and 1,3-bis(dimethylamino)propan-2-ol (HL). The resulting powder had an onset superconducting temperature of 92 K. As part of this investigation, the salt  $[Cu_3L_3(O_2CCF_3)_2][YL_2(O_2CCF_3)_6]$  was isolated and characterized by thermal and magnetic measurements and X-ray crystallography. The diyttrium unit in the anion (15) is supported by bridging L<sup>−</sup> ligands giving a Y–Y distance of 374.8(5) pm. When heated under dioxygen,  $[Cu_3L_3(O_2CCF_3)_2][YL_2(O_2CCF_3)_6]$  decomposes to metal oxides [35]. The same *N,O,O'*-bonding mode is observed when  $Na[2,6\text{-(}CH_2NMe_2)_2\text{-}4\text{-}MeC_6H_2O]$  reacts with yttrium(III) chloride in thf. The product is  $[YL_3 \cdot NaCl]$  and a crystallographic study of the lutetium analogue has confirmed three bridging ligands supporting a Lu–Na (or by analogy, a Y–Na) framework with the chloro ligand terminally attached to the Lu (or Y) atom. The complex  $[YL_3 \cdot NaCl]$  has been studied in solution by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies. It has been suggested that it is possible that these complexes might be useful for the selective complexation and activation of Lewis bases [36].

The crown ether 4,13-diaza-18-crown-6 ( $H_2L$ ) reacts with  $[Y\{N(SiMe_3)_2\}_3]$  to yield  $[YL\{N(SiMe_3)_2\}]$  (16). The yttrium(III) centre is 7-coordinate (confirmed by the results of an X-ray diffraction study) and pertinent bond distances are



Only the Si atoms of the SiMe<sub>3</sub> groups are shown; H atoms are omitted  
(14)

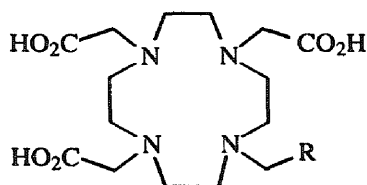


Y-N(amide) = 233.9, Y-N(macrocyclic) = 228.3 (av), Y-O (range) = 245.7–259.1 pm [37].

The reaction between yttrium(III) perchlorate, lanthanum(III) perchlorate and  $\alpha$ -alanine (ratio 1:1:4) in aqueous solution at pH 3 results in the formation of a heterometallic complex formulated as  $\text{LaY}_5(\text{ala})_{12}(\text{ClO}_4)_{18} \cdot 15\text{H}_2\text{O}$ . Similar reactions involving  $\text{Nd}(\text{ClO}_4)_3$  or  $\text{Er}(\text{ClO}_4)_3$  yield  $\text{Nd}_2\text{Y}_5(\text{ala})_{14}(\text{ClO}_4)_{21} \cdot 25\text{H}_2\text{O}$  and  $\text{ErY}(\text{ala})_4(\text{ClO}_4)_6 \cdot 8\text{H}_2\text{O}$ , respectively. The complexes have been characterized by

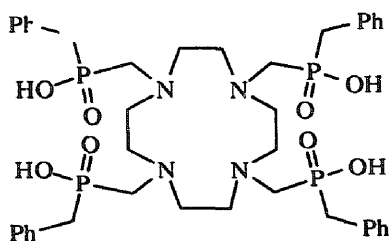
infrared spectroscopy and an X-ray diffraction study has been carried out on  $\text{ErY(ala)}_4(\text{ClO}_4)_6 \cdot 8\text{H}_2\text{O}$ . The erbium and yttrium atoms are disordered over two sites with equal occupancies [38].

Complex formation of the conjugates bases of ligands (17)–(19) with yttrium(III) has been investigated, and the protonation constants for the carboxylates and the stability constants of the complexes have been determined by potentiometric and spectrophotometric techniques. The thermodynamic stability of the yttrium(III) complexes follows the sequence (with respect to the ligand) of  $(19) > (18) > (17) > \text{edtaH}_4$ . The complex  $[\text{YL}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  where  $\text{H}_3\text{L} = (18)$  has been structurally characterized. The yttrium(III) centre is 9-coordinate with  $\text{L}^{3-}$  providing an  $N, N', N'', N''', O, O', O'', O'''$ -donor set [39]. Related ligands are (20)–(22) and their syntheses have been reported. By using ligand displacement reactions as the synthetic methodology, the kinetics of the complex formation between ligands (20)–(22) and yttrium(III) have been studied. All the reactions were pseudo-first order. Ligand (20) forms an yttrium(III) complex approximately twice as fast as the non-pendant reference ligand (22), although the rates for ligands (21) and (22) were approximately equal [40]. A low temperature (115 K) structural analysis of the compound  $\text{Na}[\text{YL}(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  in which  $\text{H}_4\text{L} = (19)$  has been reported. The metal centre is in a monocapped square antiprismatic environment; important bond distances are  $\text{Y-O}(\text{water}) = 242.4(2)$ ,  $\text{Y-O}(\text{macrocycle}) = 231.9\text{--}233.0(2)$ ,  $\text{Y-N} = 262.8\text{--}266.6(2)$  pm [41]. Ligand (23),  $\text{H}_4\text{L}$ , features four pendant phosphinic acid functionalities and forms kinetically stable 8-coordinate complexes with lanthanoid metal ions; yttrium(III) is included in the study. It was found that single diastereomers were preferentially formed. The crystal structure of  $[\text{H}_3\text{O}][\text{YL}]$  has been determined and the manner in which ligand  $\text{L}^{4-}$  (like the pendant ligand described above) can wrap around the metal ion is displayed in the structure of the anion  $[\text{YL}]^-$  (24) [42].

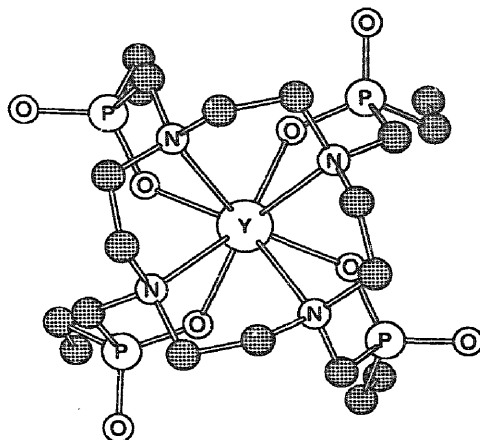


- (17)  $\text{R} = \text{H}$   
 (18)  $\text{R} = \text{CH}_2\text{CH}(\text{OH})\text{Me}$   
 (19)  $\text{R} = \text{CH}_2\text{CO}_2\text{H}$   
 (20)  $\text{R} = \text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{--}4$   
 (21)  $\text{R} = \text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{--}$   
 (22)  $\text{R} = \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{--}4$

The macrocycle (25) forms a dinuclear complex with yttrium(III) in aqueous solution, and the identity of the complex has been confirmed by single crystal X-ray crystallography. The two metal centres lie between the two macrocycles such that one carbonyl group and one carboxylate from one ligand and one carbonyl functionality and two carboxylates from the second ligand bond to each yttrium(III) centre. A water molecule completes a 6-coordinate, all oxygen donor primary coordination sphere although there are additional, weak interactions involving three nitrogen donors (per metal) giving what is described by the authors as a tricapped trigonal prismatic geometry overall [43]. Ligand (26)  $\text{H}_3\text{L}$  complexes with yttrium(III) in aqueous solution to give as the isolated species  $[\text{YL}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ . An X-ray diffrac-

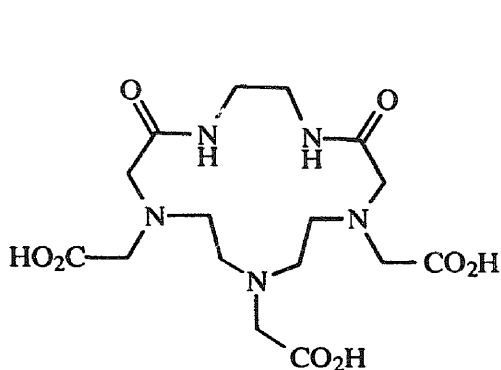


(23)

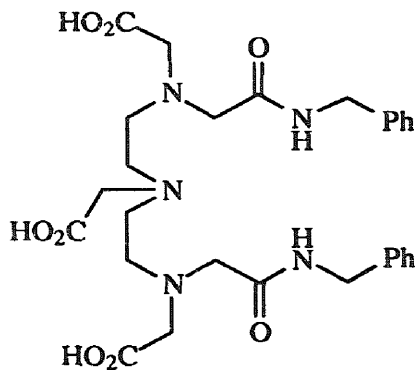


Only the ipso-C atoms of the phenyl rings are shown (24)

tion study revealed that in the solid state the Y(III) centre is in a monocapped square antiprismatic environment, with  $L^3$  coordinating through the two amido oxygen atoms, the three carboxylate groups and three nitrogen donor atoms [41].



(25)



(26)

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