Coordination Chemistry Reviews, 124 (1993) 41–49

2. Scandium

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CONTENTS

INTRODUCTION

This chapter surveys the coordination chemistry of scandium reported during 1990. The format is similar to that used in the last review covering scandium which appeared in *Coordination Chemistry Reviews* [1]. The literature has been surveyed by use of *Chemical Abstracts* (volumes 112, 113 and 114) and *Current Contents*, as well as independent searches of major journals. I should like to acknowledge the Cambridge Crystallographic Data Base for allowing access to crystallographic coordinates for structures **(1)**, **(2)**, **(4)**, **(6)**, **(7)** and **(8)**; hydrogen atoms have been omitted for clarity.

The organometallic chemistry of scandium (defined as compounds with Sc-C bonds only) has not been included here; a review covering the 1990 literature for organometallic compounds has appeared elsewhere [2]. Two other reviews which will be of interest are by Komissarova (a review of the behaviour of scandium in exchange and sorption processes; 173 references) [3] and by Kilbourn (extractive metallurgy) [4].

2.1 SCANDIUM (III)

2.1.1 Complexes with nitrogen ligands

The reaction of Cp^*_2ScMe with an equivalent of anhydrous hydrazine gives the complex $Cp^*_2ScN(H)NH_2$ which is an unusual example of an unsubstituted hydrazido(1–) ligand.

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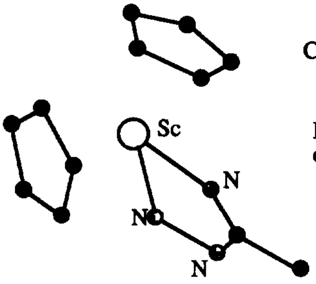
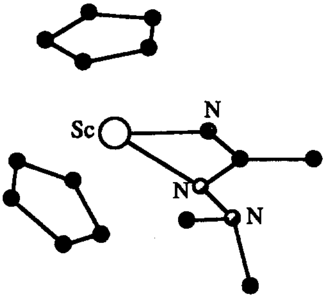
$Cp^*_2ScN(H)NH_2$ reacts with acetonitrile to give compound **(1)**. The results of labelling experiments using $^{15}NCMe$ are consistent with a mechanism which involves the insertion of the acetonitrile molecule into an Sc-N bond of $Cp^*_2ScN(H)NH_2$ followed by tautomerisation. The structure of **(1)** has been confirmed crystallographically; the ScN_3C-ring is planar and important parameters are Sc-N = 2.277 (4) and 2.155 (4) Å, N-N = 1.494 (5) Å and ∠NScN = 72.4 (1)°. The substituted compounds $Cp^*_2ScN(H)NMe_2$ and $Cp^*_2ScN(H)C(Me)NNMe_2$, **(2)**, have also been prepared and **(2)** has been structurally characterised. Pertinent geometrical parameters in **(2)** are Sc-N = 2.264 (4) and 2.161 (4) Å, N-N = 1.439 (6) Å and ∠NScN = 59.8 (2)° [4].



$Cp^*_2ScNHC(Me)NNH_2$

Methyl substituents are omitted from the Cp* rings

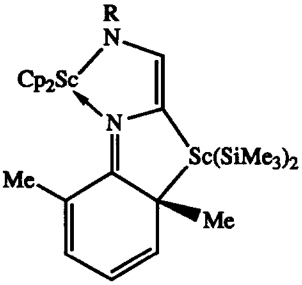
(1)



Methyl substituents are omitted from the Cp* rings

(2)

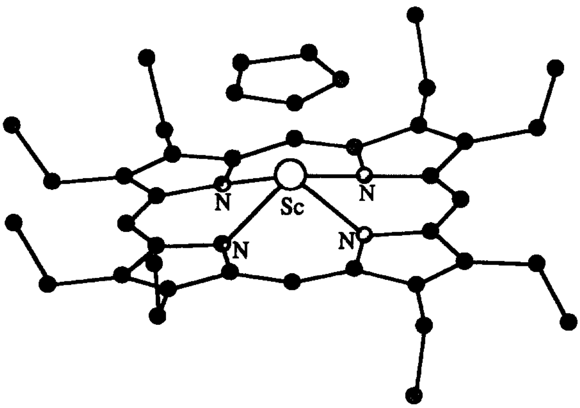
The reaction of $Cp_2Sc\{Si(SiMe_3)_3\}(thf)$ with one equivalent of $CN\text{-}C_6H_3\text{-}2,6\text{-}Me_2$ (CNR) leads to $Cp_2Sc\{\eta^2\text{-}C(NR)Si(SiMe_3)_3\}$. Treatment of this complex with a further equivalent of NCR leads to complex **(3)**; **(3)** may be obtained directly from $Cp_2Sc\{Si(SiMe_3)_3\}(thf)$ by reaction with two equivalents of NCR. Complex **(3)** has been structurally characterised. The chelate ring originates from two isocyanide groups. The two Sc-N bonds are of lengths 2.133 (7) and 2.324 (8) Å, the longer of the two being the dative bond; C-N bond distances in the chelate ring are 1.416 (9) and 1.413 (12) Å and pertinent angles are ∠NScN = 76.6 (3)°, ∠ScNC = 110.5 (5) and 105.3 (5)° [6]. Reactions of $Cp_2Sc\{Si(SiMe_3)_3\}(thf)$ are discussed further in Section 2.1.3.



R = 2,6-Me_2-C_6H_3

(3)

The reaction of $[Li(thf)_4][LiOEP]$ (H_2OEP = octaethylporphyrin) with $ScCl_3(thf)_3$ produces red crystals of Sc(OEP)Cl in ≈90% yield. The complex is air-stable in the solid state but moisture sensitive when in solution. Sc(OEP)Cl represents a precursor to a range of derivatives. Two examples are the reactions of Sc(OEP)Cl with MR (M = Li, R = $CH\{SiMe_3\}_2$ or $N\{SiMe_3\}_2$; M = K, R = $OSiMe_3$) to give Sc(OEP)R or with LiCp to give Sc(OEP)(η^5-Cp), (4). The latter complex has been characterised by single-crystal X-ray diffraction. The scandium atom lies 0.80 Å above the plane containing the four nitrogen donors of the porphyrin ligand; the average Sc-N distance is 2.190 (3) Å. For the cyclopentadienyl ring, the distance from its centroid to the scandium atom is 2.196 Å and ∠Cp(centroid)-Sc-Cp(centroid) = 111.3° [7].

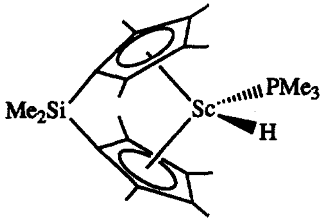


(4)

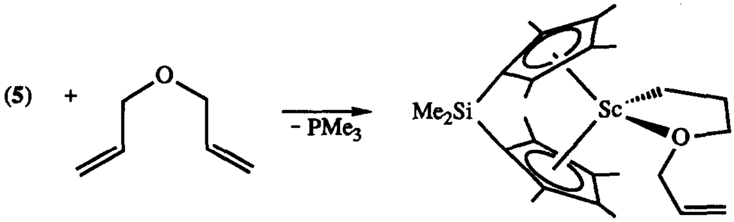
2.1.2 Complexes with phosphorus donor ligands

A review of complexes with neutral phosphorus ligands which includes a section on complexes of scandium and yttrium has appeared [8].

The complex $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}Sc(PMe_3)H$, (5), catalyses the cyclisation of α,ω-diolefins [9]. For example, the hydrocyclisation of 1,5-hexadiene to methylcyclopentane is a clean transformation [9,10]. $^2H\{^1H\}$ NMR spectroscopy has been used to probe the mechanism of the catalytic process, in particular with respect to α-agostic assistance; *trans,trans-1,6-d_2*-1,5-hexadiene yields a mixture of *cis*- and *trans-d_2*-methylcyclopentane [10]. The oxophilicity of the scandium atom in (5) is apparent in the reaction represented in Scheme I. The product is very stable and does not undergo β-elimination and cyclisation [10].

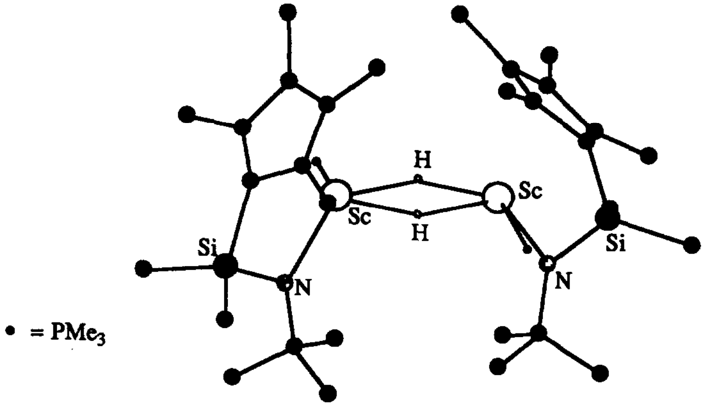


(5)



Scheme I

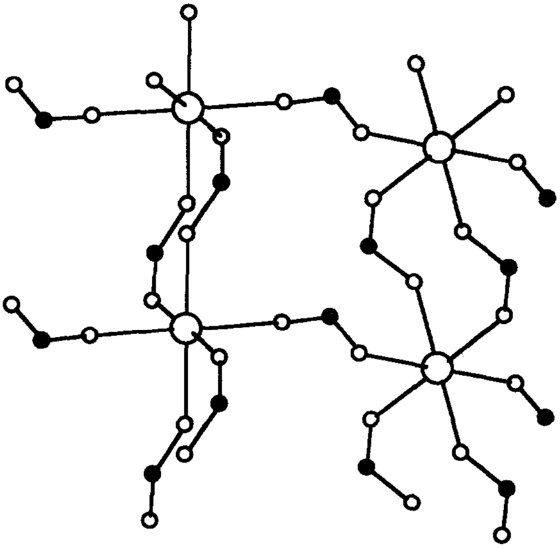
Complex (6) is related to (5) but exhibits a dimeric structure with two bridging hydride ligands. (6) is synthesised from $\{(\eta^5\text{-}C_5Me_4)SiMe_2NCMe_3\}ScCl$ and has been fully characterised crystallographically. The complex is of particular significance because it is a single component α-olefin polymerisation catalyst, catalysing the polymerisation of propene, but-1-ene and pent-1-ene with greater than 99% head-to-tail coupling producing linear, atactic products [11].



(6)

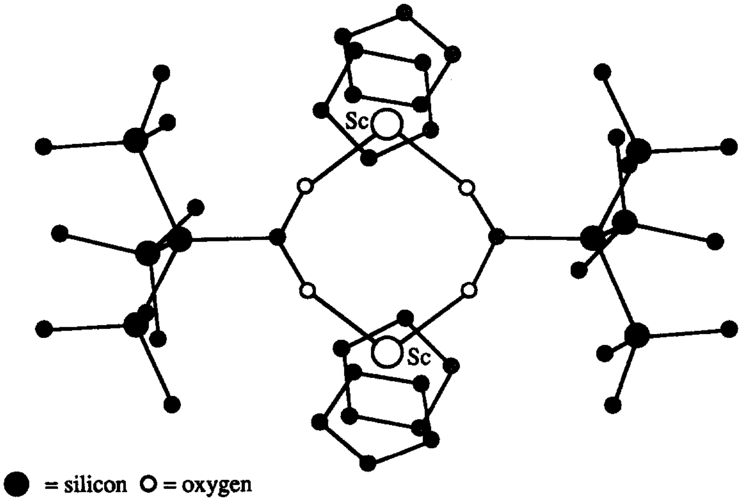
2.1.3 Complexes with oxygen donor ligands

Several carboxylate complexes of scandium(III) were reported in 1990. The structure [12] of catena-{*tris*-μ-formato-*O,O′*}scandium, (7), has been redetermined [13]. *Tris*(dibenzoylmethanato-*O,O′*)scandium crystallises in both monoclinic and triclinic forms; structural details of both forms have been reported [14].



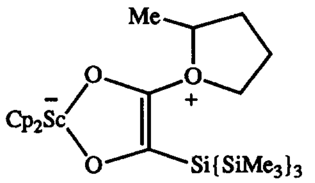
Section of the lattice of (7)

The compound $Cp_2Sc(thf)\{SiR_3\}$ (R_3 = $\{SiMe_3\}_3$ or $^iBuPh_2$) may be prepared from $[Cp_2ScCl]_2$. Yellow $Cp_2Sc(thf)\{SiR_3\}$ reacts rapidly with CO_2 (1 atm) in diethyl ether or benzene to give $\{Cp_2Sc\}_2\{\mu\text{-}O_2CSiR_3\}_2$. The carboxylate-bridged complexes have been characterised by infrared, ^1H and ^{13}C NMR spectroscopy. Crystallographic data for $\{Cp_2Sc\}_2\{\mu\text{-}O_2CSi\{SiMe_3\}_3\}_2$, (**8**), confirm the dimeric nature of the complex and the presence of two carboxylate bridges supporting the Sc_2-framework [15].

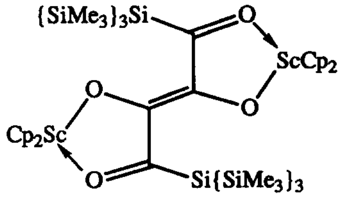


(**8**)

The reaction of $Cp_2Sc\{Si(SiMe_3)_3\}(thf)$ with CN-2,6-Me_2-C_6H_3 was described in Section 2.1.1. $Cp_2Sc\{Si(SiMe_3)_3\}(thf)$ also reacts with carbon monoxide (50 psi) in C_4H_7MeO (methyl substituted thf) to give (**9**). This species in stable in solution but attempts to isolate it have not been successful. Instead complex (**10**) is favoured as the isolated product. The direct synthesis of (**10**) is achieved if $Cp_2Sc\{Si(SiMe_3)_3\}(thf)$ is treated with CO in non-polar solvents [6].



(**9**)



(**10**)

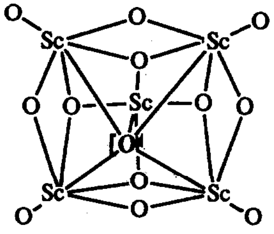
The electronic structures of scandium acetylacetonate and acetylacetoneiminate complexes have been examined. For the photoelectron spectra obtained, band assignments have been made. A comparison of the results for complexes containing the $[MeC(O)CHC(O)Me]^-$ and $[MeC(O)CHC(NH)Me]^-$ ligands indicates that substitution of NH for O in the ligand increases the population of the atomic orbitals on scandium as well as the covalent contribution to the Sc-ligand bonds [16]. The results of gas phase XPS studies on ScL_3 for HL = $^tBuC(O)CH_2C(O)^tBu$ have been reported along with studies on related yttrium and lanthanide complexes. Spectral assignments have been made [17].

The interaction of $Sc(acac)_3$ with molecular iodine has been examined by use of electronic, vibrational and NMR spectroscopy. Other related metal complexes have also been studied. A high degree of charge transfer between $Sc(acac)_3$ and I_2 is observed and this is attributed to intermolecular interactions which involve two $[ScO_2C_3]$-chelate rings simultaneously transferring charge to an I_2 molecule [18].

Structural data for trivalent metal trifluoroacetylacetonates including the scandium(III) *tris*-chelate have been reported [19].

Interest in scandium alkoxide and aryloxide complexes continues. A chapter in *Inorganic Synthesis* [20] has been devoted to synthetic routes to scandium, yttrium and various lanthanide compounds and includes two methods of preparing $Sc(OAr)_3$. The first route involves the reaction of $ScCl_3$ with $[Li(\mu\text{-}OAr)(OEt_2)]_2$ in refluxing thf (OAr = $O\text{-}C_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}R$; R = Me, ^tBu). In the second method, $Sc\{N(SiMe_3)_2\}_3$ is treated with three equivalents of ArOH. The aryloxides are very sensitive to air and moisture, but in an inert atmosphere they are thermally stable and sublime at around 250°C at a pressure of 10^{-3} torr. $Sc(O\text{-}C_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)_3$ is a white solid, with a melting point of 150-152°C; it is soluble in hydrocarbon solvents and cryoscopic data show that it is monomeric. The trigonal planar geometry around the scandium(III) centre in $Sc(O\text{-}C_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)_3$ has previously been confirmed crystallographically [21]. $Sc(O\text{-}C_6H_2\text{-}2,4,6\text{-}^tBu_3)_3$ is also an air and moisture sensitive white solid (m. pt. = 140-142°C) [20].

Attempts have been made to prepare $Sc(O^iPr)_3$. However, the reaction of anhydrous $ScCl_3$ with NaO^iPr in isopropanol yields, after recrystallisation, $Sc_5(O^iPr)_5(\mu_5\text{-}O)(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4$, (**11**). The same product is obtained from the reaction of $Sc\{N(SiMe_3)_2\}_3$ with isopropanol in benzene/pentane under reflux. Analogous products $M_5(O)(O^iPr)_{13}$ have been obtained for M = Y, In and Yb and structural data are available for M = In and Y (see the following Chapter of this volume) [22].



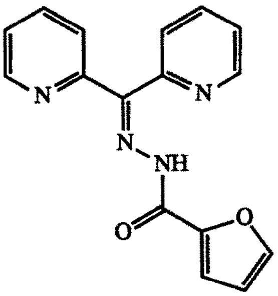
[O] = μ_5-O
Each remaining O atom
is bonded to an ^{i}Pr group

(**11**)

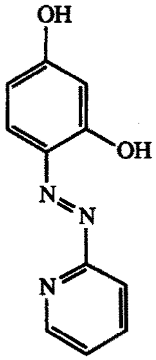
2.1.4 *Complexes with nitrogen-oxygen mixed donor ligands*

A comparative study of acetylacetonate and acetylacetoneiminate complexes of scandium(III) has already been mentioned in Section 2.1.3 [16].

A study of the complexation of di-2-pyridylketone-2-furoylhydrazone, **(12)**, with scandium(III) ions in aqueous ethanol provides a fluorometric method for the determination of trace amounts of the metal. The fluorescent scandium(III) complex which forms exhibits an emission maximum at 492 nm (pH = 6.5-7.5) [23]. The electronic structures of the ligand 3-(2'-pyridylazo)dihydroxypyridine and of the complex formed with scandium(III) ions have been investigated theoretically (MO-LCAO approach). The results have been compared with those obtained for those obtained previously for 4-(2-pyridylazo)resorcinol, **(13)** [24].



(12)



(13)

2.2 *SCANDIUM (II)*

The synthesis, structure and properties of the layered metallic scandium iodide $Sc_{0.93}I_2$ have been reported. The compound is prepared by the reaction of gaseous or liquid ScI_3 with an excess of elemental scandium at 550-870°C. The stoichiometry of the product has been confirmed, in part by powder and single-crystal X-ray diffraction methods. The powder pattern indicates a cadmium diiodide-type lattice with vacancies in the metal sites; Sc-I = 2.934 (1) Å. The molar susceptibility is small; a value of 334×10^{-6} emu mol^{-1} has been determined at room temperature with changes to 504×10^{-6} emu mol^{-1} and 465×10^{-6} emu mol^{-1} at 118 K and 77 K respectively. The ^{45}Sc NMR spectrum of the iodide shows no variation over the range 150 to 77 K. Comparisons are made between $Sc_{0.93}I_2$ and LaI_2 and CeI_2 [25].

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