

## 2. Scandium

Catherine E. Housecroft

### CONTENTS

|   |    |
|---|----|
| INTRODUCTION .....  | 41 |
| 2.1 SCANDIUM (III) .....                                      | 41 |
| 2.1.1 Complexes with nitrogen donor ligands .....             | 41 |
| 2.1.2 Complexes with phosphorus donor ligands .....           | 44 |
| 2.1.3 Complexes with oxygen donor ligands .....               | 45 |
| 2.1.4 Complexes with nitrogen-oxygen mixed donor ligands..... | 48 |
| 2.2 SCANDIUM (II) .....                                       | 48 |
| REFERENCES .....  | 49 |

### 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.

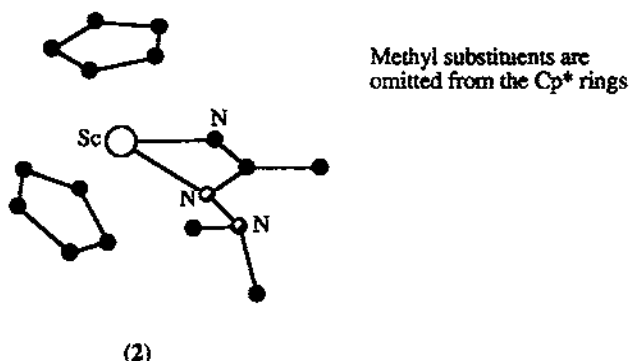
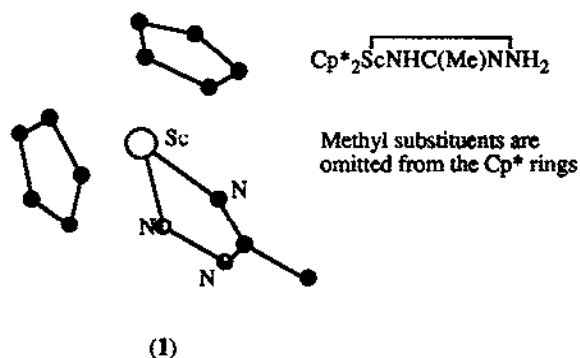
The organometallic chemistry of scandium (defined as compounds with Sc-C bonds only) has not been included here; a review covering the 1990 literature for organometallic compounds has appeared elsewhere [2]. Two other reviews which will be of interest are by Komissarova (a review of the behaviour of 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

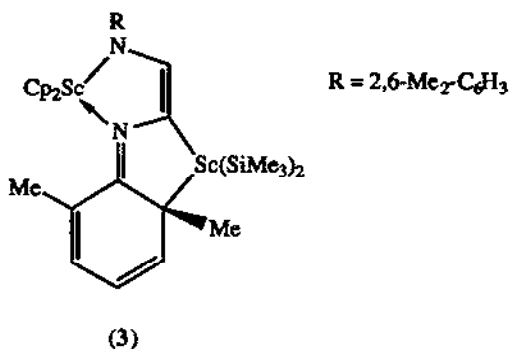
The reaction of  $\text{Cp}^*_2\text{ScMe}$  with an equivalent of anhydrous hydrazine gives the complex  $\text{Cp}^*_2\text{ScN(H)NH}_2$  which is an unusual example of an unsubstituted hydrazido(1–) ligand.

$\text{Cp}^*_2\text{ScN(H)NH}_2$  reacts with acetonitrile to give compound (1). The results of labelling experiments using  $^{15}\text{NCMe}$  are consistent with a mechanism which involves the insertion of the acetonitrile molecule into an Sc-N bond of  $\text{Cp}^*_2\text{ScN(H)NH}_2$  followed by tautomerisation. The structure of (1) has been confirmed crystallographically; the  $\text{ScN}_3\text{C}$ -ring is planar and important parameters are  $\text{Sc-N} = 2.277$  (4) and  $2.155$  (4) Å,  $\text{N-N} = 1.494$  (5) Å and  $\angle\text{NScN} = 72.4$  (1)°. The substituted compounds  $\text{Cp}^*_2\text{ScN(H)NMe}_2$  and  $\text{Cp}^*_2\text{ScN(H)C(Me)NNMe}_2$ , (2), have also been prepared and (2) has been structurally characterised. Pertinent geometrical parameters in (2) are  $\text{Sc-N} = 2.264$  (4) and  $2.161$  (4) Å,  $\text{N-N} = 1.439$  (6) Å and  $\angle\text{NScN} = 59.8$  (2)° [4].

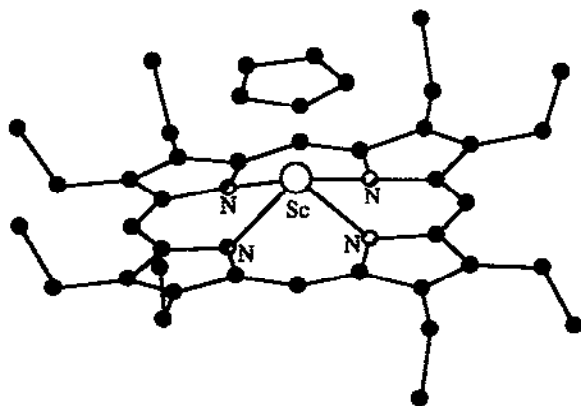


The reaction of  $\text{Cp}_2\text{Sc}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})$  with one equivalent of  $\text{CN-C}_6\text{H}_3\text{-2,6-Me}_2$  (CNR) leads to  $\text{Cp}_2\text{Sc}\{\eta^2\text{-C}(\text{NR})\text{Si}(\text{SiMe}_3)_3\}$ . Treatment of this complex with a further equivalent of NCR leads to complex (3); (3) may be obtained directly from  $\text{Cp}_2\text{Sc}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})$  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  $\angle \text{NScN} = 76.6 (3)^\circ$ ,  $\angle \text{ScNC} = 110.5 (5)$  and  $105.3 (5)^\circ$  [6]. Reactions of  $\text{Cp}_2\text{Sc}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})$  are discussed further in Section 2.1.3.



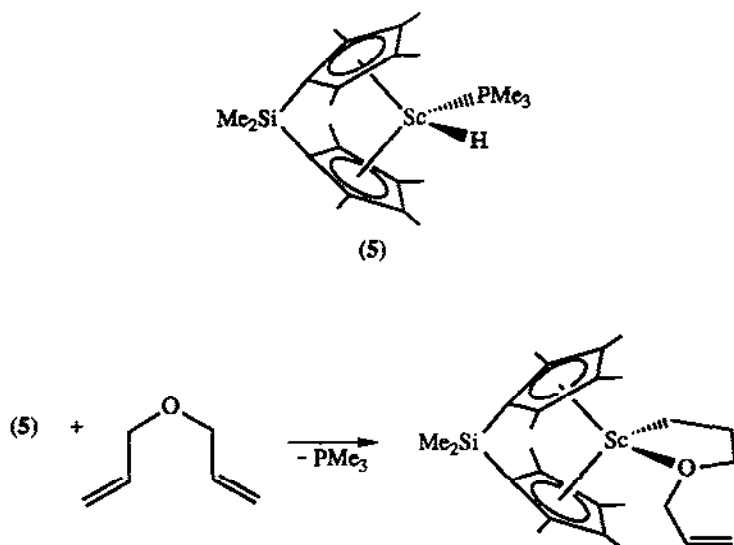
The reaction of  $[\text{Li}(\text{thf})_4][\text{LiOEP}]$  ( $\text{H}_2\text{OEP}$  = octaethylporphyrin) with  $\text{ScCl}_3(\text{thf})_3$  produces red crystals of  $\text{Sc}(\text{OEP})\text{Cl}$  in  $\sim 90\%$  yield. The complex is air-stable in the solid state but moisture sensitive when in solution.  $\text{Sc}(\text{OEP})\text{Cl}$  represents a precursor to a range of derivatives. Two examples are the reactions of  $\text{Sc}(\text{OEP})\text{Cl}$  with  $\text{MR}$  ( $\text{M} = \text{Li}$ ,  $\text{R} = \text{CH}\{\text{SiMe}_3\}_2$  or  $\text{N}\{\text{SiMe}_3\}_2$ ;  $\text{M} = \text{K}$ ,  $\text{R} = \text{OSiMe}_3$ ) to give  $\text{Sc}(\text{OEP})\text{R}$  or with  $\text{LiCp}$  to give  $\text{Sc}(\text{OEP})(\eta^5\text{-Cp})$ , (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  $\angle \text{Cp}(\text{centroid})\text{-Sc-Cp}(\text{centroid}) = 111.3^\circ$  [7].



### 2.1.2 Complexes with phosphorus donor ligands

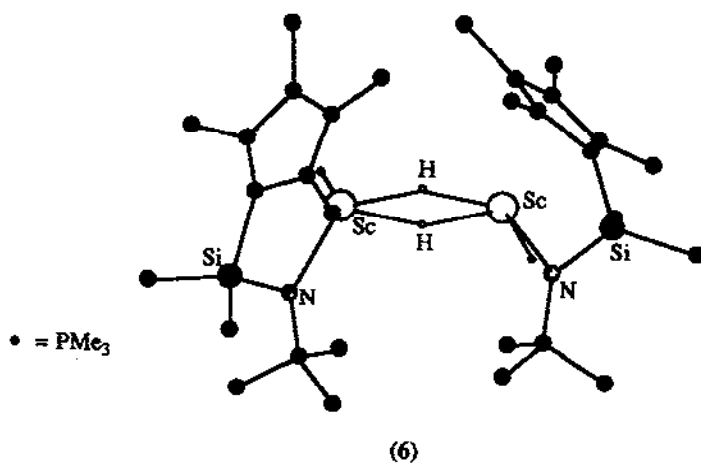
A review of complexes with neutral phosphorus ligands which includes a section on complexes of scandium and yttrium has appeared [8].

The complex  $\{(\eta^5\text{-C}_5\text{Me}_4)_2\text{SiMe}_2\}\text{Sc}(\text{PMe}_3)\text{H}$ , (5), catalyses the cyclisation of  $\alpha,\omega$ -diolefins [9]. For example, the hydrocyclisation of 1,5-hexadiene to methylcyclopentane is a clean transformation [9,10].  $^2\text{H}\{^1\text{H}\}$  NMR spectroscopy has been used to probe the mechanism of the catalytic process, in particular with respect to  $\alpha$ -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  $\beta$ -elimination and cyclisation [10].



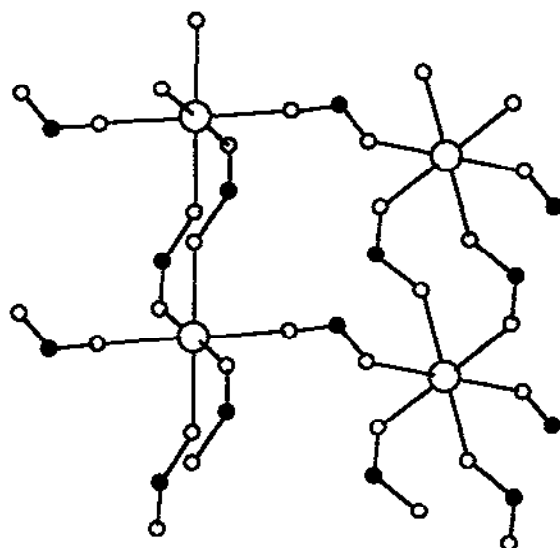
Scheme I

Complex (6) is related to (5) but exhibits a dimeric structure with two bridging hydride ligands. (6) is synthesised from  $\{(\eta^5\text{-C}_5\text{Me}_4)_2\text{SiMe}_2\text{NCMe}_3\}\text{ScCl}$  and has been fully characterised crystallographically. The complex is of particular significance because it is a single component  $\alpha$ -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].



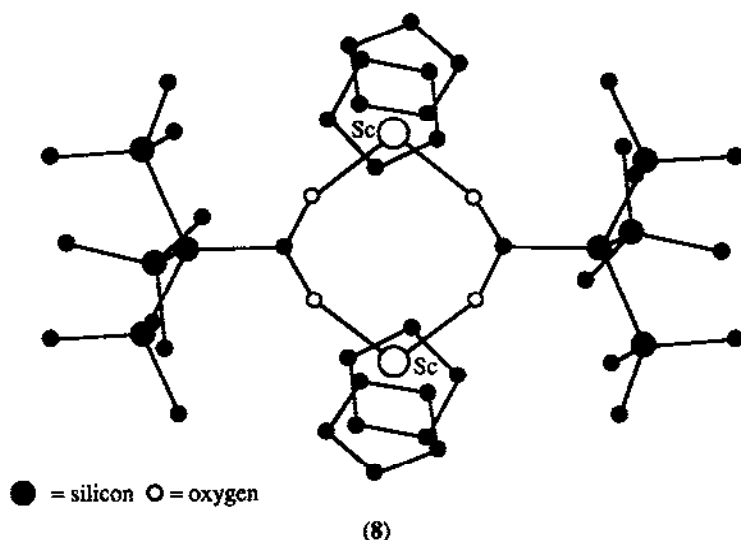
### 2.1.3 Complexes with oxygen donor ligands

Several carboxylate complexes of scandium(III) were reported in 1990. The structure [12] of catena- $\{tris\text{-}\mu\text{-formato-}O,O'\}$ 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].

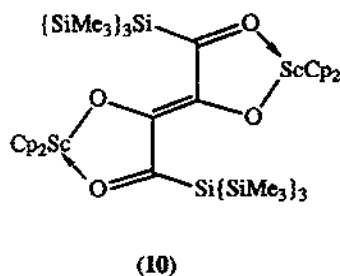
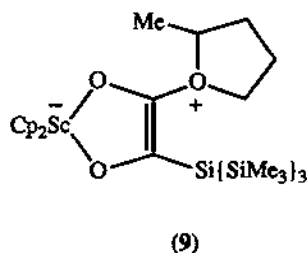


Section of the lattice of (7)

The compound  $\text{Cp}_2\text{Sc}(\text{thf})(\text{SiR}_3)$  ( $\text{R}_3 = \{\text{SiMe}_3\}_3$  or  $i\text{BuPh}_2$ ) may be prepared from  $\{\text{Cp}_2\text{ScCl}\}_2$ . Yellow  $\text{Cp}_2\text{Sc}(\text{thf})(\text{SiR}_3)$  reacts rapidly with  $\text{CO}_2$  (1 atm) in diethyl ether or benzene to give  $\{\text{Cp}_2\text{Sc}\}_2\{\mu\text{-O}_2\text{CSiR}_3\}_2$ . The carboxylate-bridged complexes have been characterised by infrared,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Crystallographic data for  $\{\text{Cp}_2\text{Sc}\}_2\{\mu\text{-O}_2\text{CSi}(\text{SiMe}_3)_3\}_2$ , (8), confirm the dimeric nature of the complex and the presence of two carboxylate bridges supporting the  $\text{Sc}_2$ -framework [15].



The reaction of  $\text{Cp}_2\text{Sc}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})$  with CN-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> was described in Section 2.1.1.  $\text{Cp}_2\text{Sc}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})$  also reacts with carbon monoxide (50 psi) in  $\text{C}_4\text{H}_7\text{MeO}$  (methyl substituted thf) to give (9). This species is 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  $\text{Cp}_2\text{Sc}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})$  is treated with CO in non-polar solvents [6].



The electronic structures of scandium acetylacetonate and acetylacetoniminato complexes have been examined. For the photoelectron spectra obtained, band assignments have been made. A

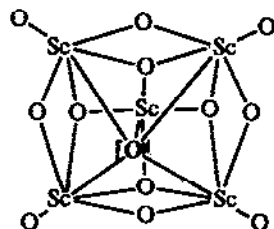
comparison of the results for complexes containing the  $[\text{MeC}(\text{O})\text{CHC}(\text{O})\text{Me}]^-$  and  $[\text{MeC}(\text{O})\text{CHC}(\text{NH})\text{Me}]^-$  ligands indicates that substitution of NH for O in the ligand increases the population of the atomic orbitals on scandium as well as the covalent contribution to the Sc-ligand bonds [16]. The results of gas phase XPS studies on  $\text{ScL}_3$  for  $\text{HL} = {}^t\text{BuC}(\text{O})\text{CH}_2\text{C}(\text{O}){}^t\text{Bu}$  have been reported along with studies on related yttrium and lanthanide complexes. Spectral assignments have been made [17].

The interaction of  $\text{Sc}(\text{acac})_3$  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  $\text{Sc}(\text{acac})_3$  and  $\text{I}_2$  is observed and this is attributed to intermolecular interactions which involve two  $[\text{ScO}_2\text{C}_3]$ -chelate rings simultaneously transferring charge to an  $\text{I}_2$  molecule [18].

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

Interest in scandium alkoxide and aryloxy 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  $\text{Sc}(\text{OAr})_3$ . The first route involves the reaction of  $\text{ScCl}_3$  with  $[\text{Li}(\mu\text{-OAr})(\text{OEt})_2]_2$  in refluxing thf ( $\text{OAr} = \text{O-C}_6\text{H}_2\text{-2,6-}^t\text{Bu}_2\text{-4-R}$ ;  $\text{R} = \text{Me}, {}^t\text{Bu}$ ). In the second method,  $\text{Sc}[\text{N}(\text{SiMe}_3)_2]_3$  is treated with three equivalents of  $\text{ArOH}$ . The aryloxides are very sensitive to air and moisture, but in an inert atmosphere they are thermally stable and sublime at around  $250^\circ\text{C}$  at a pressure of  $10^{-3}$  torr.  $\text{Sc}(\text{O-C}_6\text{H}_2\text{-2,6-}^t\text{Bu}_2\text{-4-Me})_3$  is a white solid, with a melting point of  $150\text{--}152^\circ\text{C}$ ; it is soluble in hydrocarbon solvents and cryoscopic data show that it is monomeric. The trigonal planar geometry around the scandium(III) centre in  $\text{Sc}(\text{O-C}_6\text{H}_2\text{-2,6-}^t\text{Bu}_2\text{-4-Me})_3$  has previously been confirmed crystallographically [21].  $\text{Sc}(\text{O-C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3)_3$  is also an air and moisture sensitive white solid (m. pt. =  $140\text{--}142^\circ\text{C}$ ) [20].

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



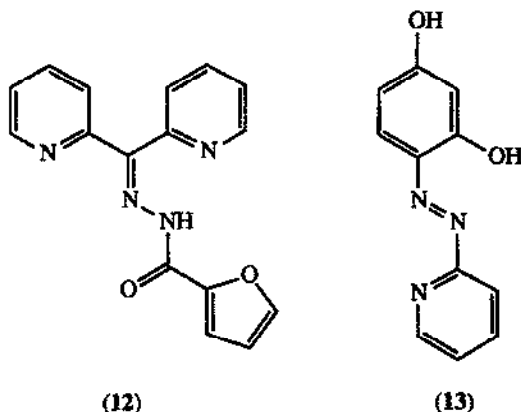
(11)

$[\text{O}] = \mu_5\text{-O}$   
Each remaining O atom  
is bonded to an  ${}^i\text{Pr}$  group

### 2.1.4 Complexes with nitrogen-oxygen mixed donor ligands

A comparative study of acetylacetonate and acetylacetonimine 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].



## 2.2 SCANDIUM (III)

The synthesis, structure and properties of the layered metallic scandium iodide  $\text{Sc}_{0.93}\text{I}_2$  have been reported. The compound is prepared by the reaction of gaseous or liquid  $\text{ScI}_3$  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;  $\text{Sc-I} = 2.934 (1) \text{ \AA}$ . The molar susceptibility is small; a value of  $334 \times 10^{-6} \text{ emu mol}^{-1}$  has been determined at room temperature with changes to  $504 \times 10^{-6} \text{ emu mol}^{-1}$  and  $465 \times 10^{-6} \text{ emu mol}^{-1}$  at 118 K and 77 K respectively. The  $^{45}\text{Sc}$  NMR spectrum of the iodide shows no variation over the range 150 to 77 K. Comparisons are made between  $\text{Sc}_{0.93}\text{I}_2$  and  $\text{LaI}_2$  and  $\text{CeI}_2$  [25].



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