

SCANDIUM

*Compounds, Productions
and Applications*



Viktor A. Greene
Editor

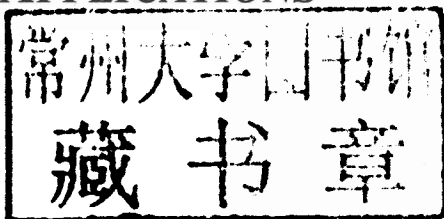
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CHEMICAL ENGINEERING METHODS AND TECHNOLOGY

SCANDIUM

COMPOUNDS, PRODUCTIONS AND APPLICATIONS



VIKTOR A. GREENE
EDITOR



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PREFACE

Scandium is a chemical element with symbol Sc and atomic number 21. A silvery-white metallic transition metal, it has historically been sometimes classified as a rare earth element. This book presents topical research material in the study of scandium, including the application of chiral scandium complexes in asymmetric catalysis; application of scandium oxide in dispenser thermionic cathodes; comparison of mechanisms of scandium recovery by phosphorous-containing inorganic and organic adsorbents; clinical use of scandium enriched power laser in sleep surgery; the physiology of scandium in relation to strain improvement and novel antibiotic discovery; and scandium aluminum nitride nanowires.

Chapter 1 - Catalytic asymmetric reaction is an important subject in modern organic chemistry. The development of high efficient and environmental friendly catalysts is an important effort in the study of asymmetric catalysis to construct potentially useful chiral molecules. Scandium complex has shown extraordinary high catalytic activity in many organic reactions which may be attributed to its small ionic radii compared with other rare-earth metal complexes. Another characteristic feature of Sc(III) complex is that it's stable and reusable as Lewis acid catalyst which is different from traditional Lewis acids such as AlCl_3 , TiCl_4 , $\text{Ti}(\text{OiPr})_4$ etc. The combination of magnetic properties with a chiral ligand resulted in the novel applications in asymmetric catalysis with high ee's and convenient experimental conditions. Many kinds of chiral ligands, such as bipyridine, bis(oxazolinyl)pyridine compound, *N,N'*-dioxide compound etc., have been evaluated based on their scandium complexes in asymmetric reactions. In this chapter, useful asymmetric transformations employing chiral scandium complex as Lewis-acid catalysts are discussed. The related papers in recent

years according to the reaction type were covered focusing upon catalytic mechanism and comparison of these new types of Lewis acids with other conventional Lewis acids. Successful catalytic asymmetric reactions involved Aldol reaction, Mannich-type reaction, Michael reaction, ene reaction, allylation reaction, ring-opening reaction, Diels-Alder reaction, 1,3-dipolar cycloadditions and other cycloaddition reaction, Friedel-Crafts alkylation, Nazarov reaction as well as other miscellaneous reaction et al. This kind of Lewis acid catalyzed reaction could be available not only in many organic solvents but also in aqueous media. These properties will lead to really environmentally friendly chemical processes. The promise of chiral scandium complexes in asymmetric catalysis has not yet been fulfilled and effective chiral ligands are still proving elusive, then this area presents significant challenges for some time to come.

Chapter 2 - The addition of scandium oxide to dispenser cathodes (namely Scandate cathodes), which are typically comprised of a porous tungsten matrix impregnated with Ba-Ca-aluminate, improves the emission by a factor of tens to hundreds under the same operating temperature. The fabrication, emission property and emission mechanism of Scandate cathodes have been reviewed. Four types were summarized in this paper: the traditional impregnated Scandate cathode, "top-layer" impregnated Scandate cathode, impregnated mixed matrix Scandate cathode and pressed Scandate cathode. It was found that decreasing the grain size from micrometer to sub-micrometer could enhance the cathode emission performance. Mixed matrix Scandate cathode prepared with scandium oxide doped tungsten powder which has the characteristic of superfine Sc_2O_3 particles dispersing uniformly over and among sub-micrometer W grains, might be the main type of Scandate cathodes in the future. The emission models for explaining the conspicuous emission performance were summarized. Although the operating mechanism of Scandate cathodes is still unclear, it is accepted that the emission is correlated with a surface multilayer/monolayer of Ba-Sc-O. The layer is formed after proper activation by diffusion of free or ionic Sc together with Ba and O from the interior of the cathode to its surface. The correlation between the emission properties of scandate cathodes and their surface features has been established.

Chapter 3 - The present paper deals with comparison of mechanisms of scandium recovery by phosphorus-containing inorganic and organic adsorbents as well as by organophosphorus solvent extractants and ones supported on TVEX porous carrier.

Using ^{31}P NMR method (magic angle rotation), mechanism of Sc recovery by titanium and zirconium phosphates is determined for diluted hydrochloric,

sulfuric and nitric solutions. It is revealed that the presence of three types of functional groups results in scandium sorption at the expense of cation exchange, formation of coordinate bonds with P=O groups as well as by both mechanisms with chelate formation. Prevailing of particular recovery mechanism depends upon acid and pH value.

It is found that the mechanism of scandium recovery by organic ion-exchange resins defines in many ways by the type of functional groups and their spatial distribution in polymer matrix of the resin. Thus, three mechanisms are defined for Sc sorption from hydrochloric solutions by different ion-exchange resins using ^{31}P NMR method (magic angle rotation). According to the first mechanism, scandium is sorbed with formation of coordinated bond with ionite functional group and remaining its hydration shell as $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ ion. By the second adsorption mechanism scandium ions are sorbed with formation of one ionic bond while formation of two ionic bonds with two groups is typical for the third mechanism. For the second and third mechanisms the number of water molecules decreases in Sc first coordination sphere.

Using ^{31}P , ^{34}Sc NMR method, comparison is made for mechanisms of scandium extraction by liquid organophosphorus extractants and ones incorporated in TVEX polymer carrier.

The difference in scandium extraction by liquid DEHPA (di-2-ethyl hexyl phosphoric acid) and TVEX-DEHPA is established. It is shown that during Sc recovery by TVEX-DEHPA the complexes are formed typical both for solvent extraction and sorption by phosphorus-containing ion-exchange resins.

Chapter 4 – Objectives- The aim of this study was to compare the effectiveness of five power lasers (CO₂, diode, KTP, ErCr:YSGG, and Nd:YVO₄) in laser assisted uvulopalatoplasty and find potential role of laser crystal compounds on the patients recovery.

Methods- This is a prospective study of 100 patients who were treated for snoring by laser assisted uvulopalatoplasty with either CO₂ (n=21), diode (n=19), KTP (n=21), ErCr:YSGG (n=21) or with Nd:YVO₄ laser (n=18).

Results- The statistical significance ($P < 0.01$) of differences in age, BMI and apnea-hypopnea index before and after the surgery among the lasers was assessed using the Student's t-test with the PROC GLM procedure of SAS. Differences in sex ratios among the lasers were analyzed with the Chi-square test with the PROC FREQ procedure of SAS. Difference in snoring score before and after the surgery among the lasers has been tested by the Kruskal-Wallis test with the PROC NPAR1WAY procedure of SAS.

The number of days of pain medication use and the time to return to normal diet were used as indicators of recovery from surgery. Pain medications were used on average for 10.1, 6.5, 6.5, 4.1 and 4.9 days and the times to return to normal diet were on average 8.6, 6.7, 6.8, 4.5 and 5.9 days in the CO₂, diode, KTP, ErCrYSGG and Nd:YVO₄ groups, respectively.

Conclusions- Differences in post op recovery were observed. Proband treated with ErCrYSGG laser, laser with scandium enriched crystal, recovered more quickly than the Nd:YVO₄, diode, KTP and CO₂ group.

Chapter 5 - Rare earth elements have been widely used in high-technology products, such as permanent magnets, fluorescent materials, and new ceramics, as well as in computers, mobile telephones, plasma displays, magneto-optical disks, high-powered lasers, fluorescent lamps, and hybrid cars. In addition, rare earth elements are used in the glass, petroleum, and nuclear industries, as well as in various medical fields.

Chapter 6 - Scandium (Sc): Chemical abstract service (CAS) numbers # 7440-20-2; atomic weight 45.0 is a soft, silvery metallic transition element of atomic number 21 that turns yellowish or pinkish when exposed to air. It appears between calcium (Ca) and titanium (Ti) in the periodic table, and acts like boron (B), aluminum (Al) and titanium (Ti). Now, Sc is highly industrial strategic element and its main application by weight is in the improvement of the thermal property of Al alloy for baseball bats, bicycle frames and handguns. Sc have been believed to be non-toxic and environment friendly, however, recently health hazards in animal experiment or occupational and industrial exposure to Sc dust are reported.

Chapter 7 - Scandium nitride (ScN) and aluminum nitride (AlN) are novel semiconducting materials with tremendous potential for optoelectronic applications. While AlN's bandgap lies in the UV at 6 eV, ScN's bandgap is around 2–2.4 eV. Combinations of these semiconductors can cover most of the visible spectrum (from the UV/violet to up to the color red). This makes the alloying of AlN with ScN an interesting alternative to Al_xIn_{1-x}N or In_xGa_{1-x}N, the latter of which is currently used for a.o. 2 T. Bohnen, G.W.G. van Dreumel, P.R. Hageman et al. white light LEDs. The drawback of InN is its poor thermal and chemical stability, whereas ScN is extremely inert and stabile.

In this chapter the authors will introduce the first ever semiconducting Sc_xAl_{1-x}N alloy in the form of nanowires. These nanowires were grown on ScN films, deposited by hydride vapor phase epitaxy on silicon carbide substrates. Though their fabrication was unintentional, we can explain the growth of these Sc_xAl_{1-x}N nanowires via the formation of nanosized metallic droplets of aluminum on the ScN film. These droplets then acted as catalysts

under which the nanowires formed during the final stages of the growth process.

The structural properties of these $\text{Sc}_x\text{Al}_{1-x}\text{N}$ nanowires on ScN films were examined by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), energy dispersive analysis of X-rays (EDX), and X-ray diffraction (XRD). The optical properties were investigated by single nanowire cathodoluminescence (CL).

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Chapter 1

CHIRAL SCANDIUM COMPLEXES IN CATALYTIC ASYMMETRIC REACTIONS

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ABSTRACT

Catalytic asymmetric reaction is an important subject in modern organic chemistry. The development of high efficient and environmental friendly catalysts is an important effort in the study of asymmetric catalysis to construct potentially useful chiral molecules. Scandium complex has shown extraordinary high catalytic activity in many organic reactions which may be attributed to its small ionic radii compared with other rare-earth metal complexes. Another characteristic feature of Sc(III) complex is that it's stable and reusable as Lewis acid catalyst which is different from traditional Lewis acids such as AlCl_3 , TiCl_4 , $\text{Ti}(\text{O}i\text{Pr})_4$ etc. The combination of magnetic properties with a chiral ligand resulted in the novel applications in asymmetric catalysis with high ee's and convenient experimental conditions. Many kinds of chiral ligands, such as bipyridine, bis(oxazolinyl)pyridine compound, *N,N'*-dioxide compound etc., have been evaluated based on their scandium complexes in asymmetric reactions. In this chapter, useful asymmetric transformations employing chiral scandium complex as Lewis-acid catalysts are discussed. The related papers in recent years according to the

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reaction type were covered focusing upon catalytic mechanism and comparison of these new types of Lewis acids with other conventional Lewis acids. Successful catalytic asymmetric reactions involved Aldol reaction, Mannich-type reaction, Michael reaction, ene reaction, allylation reaction, ring-opening reaction, Diels-Alder reaction, 1,3-dipolar cycloadditions and other cycloaddition reaction, Friedel-Crafts alkylation, Nazarov reaction as well as other miscellaneous reaction et al. This kind of Lewis acid catalyzed reaction could be available not only in many organic solvents but also in aqueous media. These properties will lead to really environmentally friendly chemical processes. The promise of chiral scandium complexes in asymmetric catalysis has not yet been fulfilled and effective chiral ligands are still proving elusive, then this area presents significant challenges for some time to come.

INTRODUCTION

Scandium(III) ion lies on the borderline between lanthanide-early transition metal-aluminum and is the most Lewis acidic as the smallest rare-earth-metal cation [1]. The application of scandium complex in organic transformations was scarce probably due to the less reserve and difficulties in separation until scandium trifluoromethanesulfonate was first introduced as a promising reusable Lewis acid in Diels-Alder reaction by Kobayashi group [2]. And then, the unique characteristics of $\text{Sc}(\text{OTf})_3$ which feature advantages as stability, recovery and reusability have drawn intense attentions in the catalytic organic synthesis [3]. The electronic properties of scandium cation also offer its remarkably excellent outcomes in many organic reactions compared with traditional transition metals even with other lanthanide metals. In general, scandium(III) exhibits high coordination numbers as 6 and 7 which are highly advantageous for assembling various chiral and achiral ligands around the metal ions, thus creating an integrated chiral space in which the stereochemistry of the reaction might effectively be controlled. In Figure 1 is summarized the chiral ligands which have been commonly efficiently used to *in situ* form the chiral scandium complexes. The highlighted chiral ligands include bidentate BINOL derivatives with O-donors, tridentate pybox with N-donors, tetradentate *N,N'*-dioxides with O-donors as well as tetradentate bipyridine-alcohol with N,O-donors et al.

Throughout there is an emphasis on catalytic asymmetric reactions, and although there is necessarily a degree of overlap with some of the recent reviews [4], the intention is to provide an update and where appropriate focus

on the structures of the chiral ligand-scandium complex as well as the reaction mechanism.

1. ASYMMETRIC ALDOL REACTION

Several examples of Sc(III) complex catalyzed asymmetric aldol reactions of silyl enolates with aldehydes and pyruvates have been examined either in organic solvent or in water.

Chiral cationic Lewis acid complexes $[\text{Sc}(\text{pyridyl-bis}(\text{oxazolinyl}))(\text{Cl}_2)\text{SbF}_6]$ were found to be effective catalysts for the *anti*-selective Mukaiyama aldol reaction by Evans group [5a]. The exploration of counterion of the catalyst showed that $[\text{Sc}((S,S)\text{-Ph-pybox})(\text{Cl}_2)\text{SbF}_6]$ complex **1**, formed *in situ* by treatment of the $[\text{Sc-pybox}](\text{Cl})_3$ complex, could obtain highly selective addition of thiosilylketene acetals to ethyl glyoxylate compared with that of $[\text{Sc}((S,S)\text{-Bn-pybox})](\text{OTf})_3$ complex (Figure 2). The addition of a range of alkyl- and alkoxy-substituted (*Z*)-thiosilylketene acetals was conducted by 5-10 mol% **1** at -10 to -78 °C to give malate derivatives with high *syn* diastereoselectivity (*dr* \geq 92:8) and enantioselectivity (90-99% ee). This scandium complex catalyst served to complement both the relative and absolute stereochemistry observed with the $[\text{Sn}((S,S)\text{-Bn-box})](\text{OTf})_2$ catalyst which afforded the *anti* aldol products [5b].

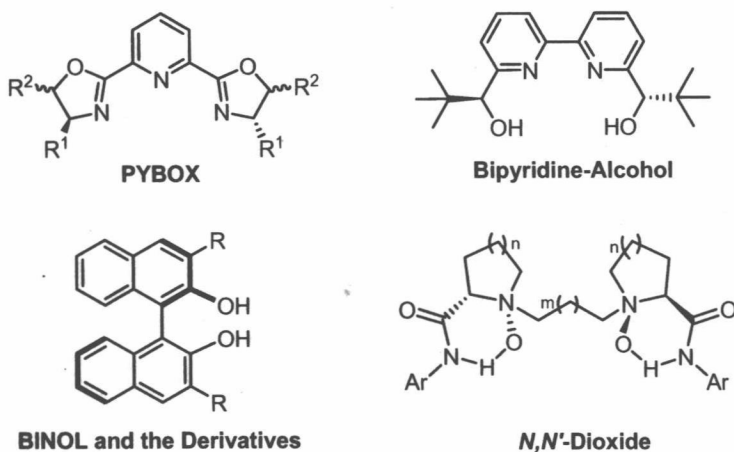


Figure 1. Represented chiral ligands

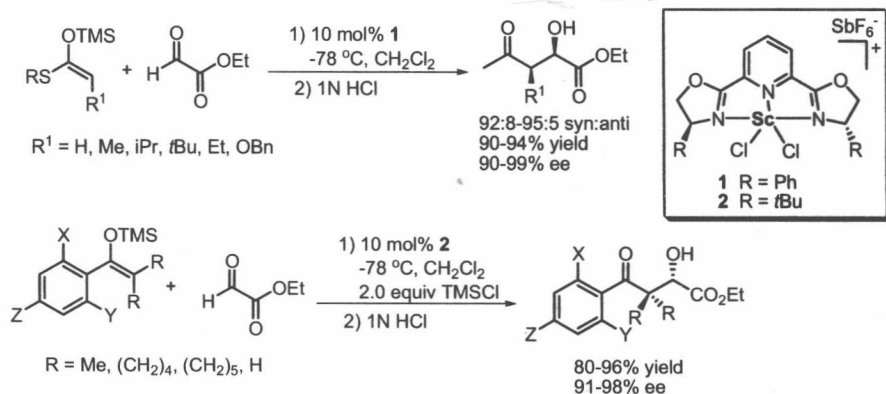


Figure 2. Sc(III)-pybox complex catalyzed asymmetric Aldol reactions

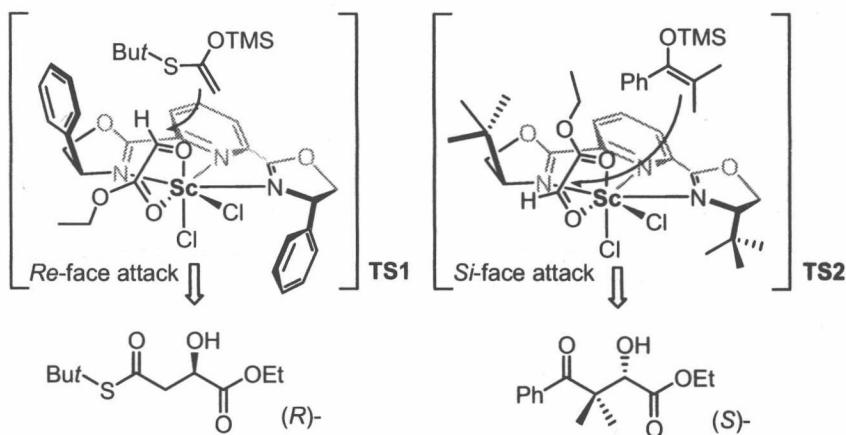


Figure 3. The rationalized transition state to elucidate the difference in stereoselectivity

[Sc((*S,S*)-*t*Bu-pybox)](Cl)₂ SbF₆ complex **2** was evaluated as catalyst for enantioselective glyoxylate aldol process of a variety of enolsilane nucleophiles derived from aryl ketones to provide the α -hydroxy- γ -ketoesters (Figure 2). The addition of chlorotrimethylsilane was essential to facilitate the catalyst turnovers with 91-98% ee and 80-96% yield. Substituted and unsubstituted pantolactone derivatives have been efficiently synthesized using this asymmetric aldol reaction as the key step [5c].

Interestingly, the enolsilane addition catalyzed by **2** afforded the opposite sense of chiral induction from that of thiosilylketene acetal catalyzed by complex **1**. The difference in stereoselectivity was rationalized by different

transition state structures of complexes **1** and **2** docked with ethyl glyoxylate (Figure 3). Steric environment within the chiral pocket of the scandium catalyst might explain the preference for the location of ethyl glyoxylate in the complex (one is bound in the apical position in TS1 and the other is in the equatorial position in TS2).

Sc(OTf)₃ or Lu(OTf)₃ complexed with ligand pybox was also found to be efficient catalysts for the enantioselective Mukaiyama-aldol reaction between 1-phenyl-1-trimethylsilyloxyethene and pyruvates [6].

Taking advantage of the particular properties of Sc(OTf)₃, such as the strong Lewis acidity and stability in aqueous media, Kobayashi group achieved successful catalytic asymmetric hydroxymethylation of silicon enolates by 3-Sc(OTf)₃ complex with a formaldehyde aqueous [7]. Optically active α -hydroxymethylated carbonyl compounds were afforded with up to 90% yields and 94% ee in H₂O/THF. X-ray analysis of 3-ScBr₃ complex showed that ligand adopted a pentagonal bipyramidal structure in which the hydroxyl groups and nitrogens of ligand **3** coordinated to Sc(III) in a tetradentate manner (Figure 4). The new catalytic system provides guide to various kinds of catalytic asymmetric C-C bond formation reactions in aqueous media.

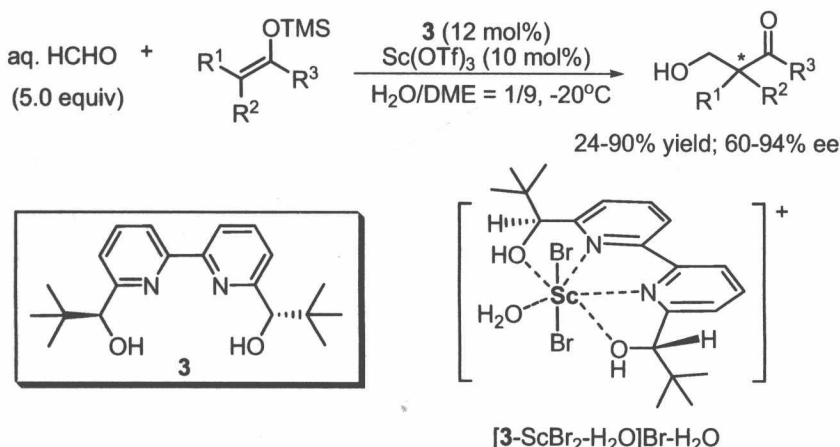


Figure 4. Chiral scandium complex catalyzed asymmetric hydroxymethylation reaction