THE PREPARATION AND CHARACTERIZATION OF SOME NEW ORGANOSCANDIUM COMPOUNDS

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ABSTRACT

THE PREPARATION AND CHARACTERIZATION OF
SOME NEW ORGANOSCANDIUM COMPOUNDS

By

Jeffrey A. Witt

Thermally stable organoscandium compounds of the general formula R_3Sc have been prepared containing triphenylmethyl, trimethylsilylmethyl, pentafluorophenyl, tolyl and benzyl groups. Compounds of uncertain composition containing scandium and naphthalyl and t-butyl groups have also been prepared. Infrared, mass spectral, elemental and ^1H nmr techniques were used where possible to characterize these compounds.

Polymeric structures are proposed for these compounds with the scandium (III) ion in a 4 or 5 coordinate environment. Normal 2 electron 2 center bonds and 2 electron 3 center bonds are proposed for the terminal and bridging ligands respectively. The ability of the trimethylsilylmethyl and pentafluorophenyl compounds to form dioxane complexes lends further support to the proposed coordinatively unsaturated polymeric structures.

All of the compounds isolated as solids are decomposed by the addition of dilute nitric acid but are not pyrophoric in air.

Reactions between scandium metal and the alkylhalides triphenylchloromethane, benzylbromide and t-butylbromide have produced products of uncertain composition and unusual properties. Further investigations concerning the composition and structure of these products are necessary before any conclusions can be reached.

The triphenylmethyl and benzyl compounds of scandium act as catalysts for the polymerization of styrene in the absence of other metals, halides or other organometallic compounds. Further studies to determine whether these and other organoscandium compounds may act as catalysts in hydrogenation reactions are indicated.

THE PREPARATION AND CHARACTERIZATION OF SOME NEW ORGANOSCANDIUM COMPOUNDS

By

Jeffrey A. Witt

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To Sue

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INTRODUCTION

In 1938 Plets[1] reported the isolation of $(C_2H_5)_3ScO(C_2H_5)_2$. However, recent attempts to repeat the synthesis were unsuccessful[2,3] and it is doubtful that the compound was actually prepared.

The first authentic report of the isolation of an organoscandium compound was made in 1956 by Birmingham and Wilkinson.[4] They obtained tricyclopentadienylscandium, $(C_5H_5)_3Sc$, by sublimation from the product of the reaction between anhydrous scandium chloride and sodium cyclopentadienide. It is a yellow solid and the authors proposed that the bonding in the compound was ionic because of the instantaneous liberation of cyclopentadiene upon the addition of water.

Hart and coworkers[3] reported the synthesis of triphenylscandium, $(C_6H_5)_3Sc$, and tris(phenylethynyl)scandium, $(C_6H_5\text{-}C\equiv C\text{-})_3Sc$ in 1968. The compounds were prepared by the reaction between anhydrous scandium chloride and the corresponding organolithium compound and were brown, non-sublimable and pyrophoric in air. Because of the insolubility and involatility of these compounds, the authors concluded that they were not monomeric.

The most recent paper concerning the synthesis of new organoscandium compounds was by Coutts and Wailes[5] in 1970. The authors reported the isolation of dicyclopentadienylscandium chloride, $(C_5H_5)_2ScCl$, by sublimation of the product of the reaction between anhydrous scandium chloride and magnesium cyclopentadienide. On the basis of ebulliometric molecular weight measurements, they proposed a dimeric structure with bridging chloride ions. The authors also prepared four new compounds by replacing the chloride ion with acetate, acetylacetonate, allyl and phenylethynyl ions. On the basis of ebulliometric and infrared data, they proposed that dicyclopentadienylscandium acetate has a dimeric structure with bridging acetate ions and (dicyclopentadienyl)phenylethynylscandium is at least a dimer. The ^1H nmr spectrum of (allyl) dicyclopentadienylscandium confirmed the symmetrical nature of the allyl group in the proposed monomeric structure, and dicyclopentadienylscandium acetylacetonate was also proposed to be monomeric on the basis of its molecular weight in boiling benzene and infrared absorptions characteristic of bidentate acetylacetonate.

Shortly after the report of the synthesis of dicyclopentadienylscandium chloride, Smith and Atwood[6] reported its crystal and molecular structure. Their study confirmed the presence of bridging chloride ions in the dimeric molecule and showed that the cyclopentadienide ions exhibited penta-hapto-coordination.

In 1965, Kirmse and Zwietasch[7] reported that scandium chloride would form complexes with olefins such as tetramethylethylene, cyclohexene, and 1,5-hexadiene. They also found that olefins such as 1,1-diphenylethylene and 1,3-cyclohexadiene formed oligomers in the presence of scandium chloride.

A patent[8] granted in 1959 claimed the use of a solution of scandium chloride and phenylmagnesium bromide as a catalyst for ethylene polymerization. Although it was not completely understood what made the system catalytically active, it was proposed that a complex was formed that was capable of coordinating ethylene or similar olefins. The nature of this complex was not discussed however.

It had been accepted for some time that transition metal-carbon bonds were relatively weak, but could be stabilized by using π accepting ligands.[9,10] A more recent theory proposed that the function of these ligands was to block coordination sites on the metal.[11] Since stable compounds have been prepared that do not contain stabilizing ligands, it now appears that a judicious choice of ligand will eliminate the need for supporting ligands.[11,12]

There are several criteria to be considered in choosing a ligand. An anionic ligand that is able to delocalize its charge, such as the benzyl ion, will be less likely to be oxidized.[13] If the β atom of the anionic ligand has no

readily transferable groups, there will be less chance of an alkene elimination reaction taking place.[11,12] An anionic ligand that is bulky could block coordination sites on the metal and prevent possible decomposition reactions involving attack at the metal-carbon bond.[14] These criteria, as well as mechanisms for possible decomposition reactions, have been summarized by Braterman and Cross.[15]

A primary aim of investigating the area of organoscandium chemistry is to prepare stable organoscandium compounds and determine whether they can act as catalysts in reactions such as polymerization of olefins.

EXPERIMENTAL

A. REAGENTS AND SOLVENTS

Benzene, diethylether, 1,4-dioxane, hexane and petroleum ether were purchased from J. T. Baker Chemical Company and dried and deoxygenated over sodium before use. Magnesium (Fisher Scientific Company), lithium (Matheson Coleman and Bell) and sodium (Matheson Coleman and Bell) were used as purchased.

2-Bromo-2-methylpropane (t-butylbromide), p-bromotoluene and α-bromotoluene (benzylbromide) were used as purchased from Matheson Coleman and Bell. Naphthalene (Mallinckrodt), iodopentafluorobenzene (PCR, Inc.) and chloromethyltrimethylsilane (PCR, Inc.) were also used as purchased. Triphenylchloromethane (PCR, Inc.) was purified by sublimation before use.

Anhydrous scandium chloride was prepared from scandium oxide (Roc/Ric, 99.9%) by the method of Melson and Stotz.[16] Scandium foil was used as purchased from Alfa, Inc.

B. GENERAL TECHNIQUES

All operations were carried out where possible in a moisture and oxygen free nitrogen atmosphere provided by a Vacuum Atmospheres "Dri-Lab, Dri-Train" system.

C. PHYSICAL MEASUREMENTS

Infrared spectra in the region 4000-250 cm^{-1} were recorded with a Perkin-Elmer Model 457 infrared spectrophotometer using nujol mulls between CsI plates. Mass spectra were determined with a Hitachi-Perkin-Elmer RMU-60 Spectrometer. ^{1}H nmr spectra were recorded with a Varian HA-100 spectrometer.

Elemental analyses for scandium were determined by hydrolysis of the sample and igniting the residue to scandium oxide. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

D. SYNTHESES

1. Tris(triphenylmethyl)scandium (III)

An excess of freshly cut sodium metal was added to a flask containing 50 ml. diethylether and 2.51 grams (9 mmoles) triphenylchloromethane, $(C_6H_5)_3CCl$. The solution immediately became yellow thus indicating the presence of the triphenylmethyl radical.[17] After half an hour, the solution became red which indicated the presence of the triphenylmethyl anion.[18] The solution was filtered and the filtrate added to a flask containing 0.46 grams (3 mmoles) scandium chloride. The solution was very dark after two hours stirring and the solvent was removed under reduced pressure. The dark solid remaining was extracted with 50 ml benzene, filtered and the filtrate taken to dryness under

reduced pressure. The brown solid obtained was placed in a sublimator and heated under vacuum at 120° for several hours to remove any volatile impurities. Less than 0.5 grams of brown tris(triphenylmethyl)scandium, (III), I, remained; yield 20%. Rather than generate the triphenylmethyl anion with sodium metal, an alternate reaction using scandium metal was chosen. An excess of triphenylchloromethane and 0.1 grams (2.2 mmoles) scandium foil were placed in a pressure tube. The pressure tube was evacuated and heated at 140° for four days in a vertical position. The brown solid at the bottom of the pressure tube was extracted with 50 ml benzene, filtered and the filtrate taken to dryness. The brown solid obtained was placed in a sublimator and heated at 180° for 20 hours under vacuum to remove unreacted triphenylchloromethane or volatile impurities such as hexaphenylethane; yield 0.3 grams 17%.

2. Tris(trimethylsilylmethyl)scandium (III)

An excess of chloromethyltrimethylsilane, $(CH_3)_3SiCH_2Cl$, was added to a flask containing 75 ml diethylether and 0.29 grams (12 mmoles) magnesium. The mixture was heated periodically until all the magnesium had reacted. The resulting solution was added to a flask containing 0.61 grams (4 mmoles) scandium chloride and stirred overnight at room temperature. The solvent was removed under reduced pressure and the white solid remaining was extracted twice

with 150 ml of warm hexane and filtered. The two filtrates were combined and the hexane removed under reduced pressure yielding 0.78 grams of tris(trimethylsilylmethyl)scandium, III, II; yield 64%.

Anal. calc. for $((CH_3)_3SiCH_2)_3Sc$: Sc, 14.7%. Found: Sc, 15.7%.

a. Tris(trimethylsilylmethyl)scandium (III) (1,4 dioxane)

A solution, as prepared above, was stirred overnight and the solvent removed under reduced pressure. The white solid remaining was extracted with two 100 ml portions of petroleum ether and filtered. The filtrates were combined and almost all of the petroleum ether was removed under reduced pressure leaving a gelatinous substance. A portion of this product was redissolved in 75 ml of petroleum ether and 15 ml of 1,4 dioxane were added. A white precipitate formed immediately which was filtered off and dried under vacuum, IIa.

Anal. calc. for $((CH_3)_3SiCH_2)_3Sc(C_4H_8O_2)$: Sc, 11.4%. Found: Sc, 11.0%.

3. Tris(pentafluorophenyl)scandium (III)

A flask containing 75 ml diethylether, 0.145 grams (6 mmoles) magnesium and 1.76 grams (6 mmoles) iodopentafluorobenzene was heated periodically until all of the magnesium had reacted. The resulting solution was added to a flask containing 0.31 grams (2 mmoles) scandium chloride and

stirred overnight at room temperature. The solvent was removed under reduced pressure, leaving a dark tarry substance which was placed in a sublimator. The sublimator was heated at 150° under vacuum, and a colorless liquid was observed condensing on the coldfinger and dripping down to the bottom of the sublimator. A modified sublimator, shown in Figure 1, was used to collect the fraction of liquid with a boiling point from 130-140°, III.

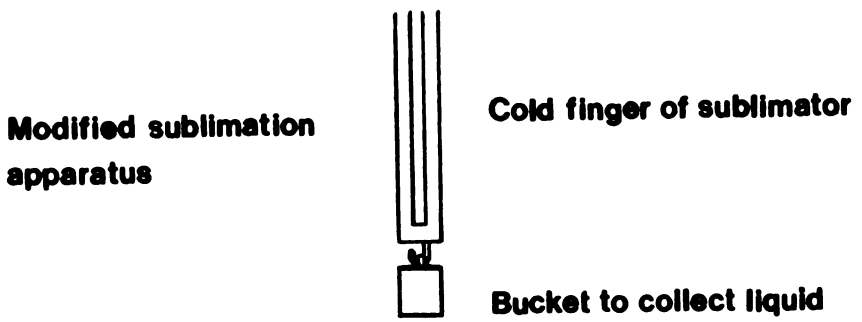


Figure 1. Modified sublimation apparatus.

a. Tris(pentafluorophenyl)scandium (III) (1,4-dioxane)

The solid remaining in the sublimator was extracted with 100 ml of a 5:1 mixture of diethylether and 1,4-dioxane. The solution was filtered to remove precipitated magnesium salts and the volume of the filtrate reduced. High boiling petroleum ether was added and a dark brown solid precipitated

and was filtered off and dried under vacuum; yield .3 grams of IIIa.

4. Tris(tolyl)scandium (III)

An excess of p-bromotoluene and 0.145 grams (6 mmoles) magnesium were added to a flask containing 75 ml diethylether. The solution was heated periodically until all of the magnesium had reacted and added to a flask containing 0.31 grams (2 mmoles) scandium chloride. Initially the resulting solution was yellow, but after stirred overnight at room temperature it became brown. The solvent was removed under reduced pressure leaving a brown solid. The brown solid was extracted with 50 ml benzene, filtered to remove magnesium salts, and the filtrate taken to dryness under reduced pressure. The brown solid obtained from the filtrate was again extracted with 50 ml of benzene. During a slow filtration of the solution, a great deal of yellowish brown solid came out of solution and was collected on the filter and dried under vacuum. Analysis of powder obtained showed that the sample contained 15.6% scandium; theoretical 14.2% for $(CH_3C_6H_4)_3Sc$. The filtrate from which the powder was obtained was allowed to evaporate to dryness in the dry box producing 0.1 grams of small yellowish brown crystals, IV.

5. Tris(benzyl)scandium (III)

To a flask containing 75 ml diethylether were added 0.145 grams (6 mmoles) magnesium and an excess of benzyl-bromide, $C_6H_5CH_2Br$. The solution was heated periodically until all the magnesium had reacted, added to a flask containing 0.31 grams (2 mmoles) scandium chloride and stirred overnight at room temperature. The solvent was removed under reduced pressure leaving a brown solid. The solid was extracted with 75 ml benzene and the solution filtered to remove magnesium salts. The filtrate was taken to dryness under reduced pressure and the brown solid obtained again extracted with 75 ml benzene. During a slow filtration a great deal of brown powder came out of solution and was collected on the filter. Evaporation of the filtrate left 0.1 grams of brown tris(benzyl)scandium (III), v; yield 18%.

6. Preliminary Results

a. Reaction between Sc^{3+} and the naphthalenide ion

An excess of lithium ribbon and 0.76 grams (6 mmoles) naphthalene were added to a flask containing 75 ml diethyl-ether. After half an hour of stirring, the solution was green, thus indicating the presence of the naphthalenide anion.[5] The solution was added to a flask containing 0.31 grams (2 mmoles) scandium chloride and stirred at room temperature for 3-5 hours. The solution was brown and the solvent was removed under reduced pressure. The brown solid remaining was extracted with 100 ml benzene and the solution

was filtered. Hexane was added to the filtrate and a light brown precipitate formed which was collected by filtration and dried under vacuum. The amount of solid, VIa, obtained was 0.15 grams.

b. Reactions between Sc^{3+} and the t-butyl ion, and scandium metal with t-butylbromide

To a flask containing 75 ml diethylether were added 0.85 grams (6 mmoles) 2-bromo-2-methylpropane, $(CH_3)_3CBr$, and 0.38 grams (6 mmoles) n-butyllithium. The solution was stirred for an hour at room temperature and added to a flask containing 0.31 grams (2 mmoles) scandium chloride. The solution was stirred for 3 hours and the solvent was removed under reduced pressure.

50 ml of benzene was added to the solid and the solution was filtered. Hexane was added to the filtrate and a tan powder precipitated which was filtered from the solution and dried under vacuum. The product, VIb, .09 grams, was placed in a sublimator and gradually, under vacuum, heated to 150°. Examination of the cold finger revealed that nothing had sublimed, which indicated that no t-butyllithium had been present in the sample.[19]

An alternate method of preparing tris(t-butyl)scandium (III) was also attempted. 50 ml of 2-bromo-2-methylpropane, 50 ml of high boiling petroleum ether and 0.09 grams (2 mmoles) scandium metal were placed in a flask and heated at 75° for 3-5 days. The solution was taken to dryness under

reduced pressure and 50 ml benzene was added to the solid that remained. The solution was filtered and high boiling petroleum ether was added to the filtrate. The solid precipitate that formed was filtered from the solution and dried under vacuum. The amount of solid, VIc, obtained was .05 grams.

c. Reaction between scandium metal and benzylbromide

50 ml of colorless benzylbromide and 0.09 grams (2 mmoles) scandium metal were placed in a flask, and after heating at 75° for 3-5 days the solution was brown in color. The solution was filtered to remove unreacted scandium metal and scandium bromide. High boiling petroleum ether was added to the filtrate and the dark tar which precipitated was filtered and dried under vacuum. The amount of blackish solid obtained, VId, was .15 grams.

RESULTS AND DISCUSSION

Reactions between scandium (III) and a series of organic anions have produced thermally stable, moisture sensitive organoscandium compounds. The anions were chosen because they fulfill the criteria of being bulky enough to shield the metal, charge delocalization is possible, and no readily transferable groups on the β atom, or because other organometallic compounds have been prepared using the anion. The reactions were undertaken with the aim of preparing compounds containing scandium-carbon sigma bonds.

None of the compounds reported herein are pyrophoric in air, although all those isolated as solids reacted immediately with dilute nitric acid except tris(triphenylmethyl)scandium (III) which reacted slowly. The reaction presumed to be responsible for this behavior is that of the anionic ligands with H^+ to form the corresponding hydrocarbons. The phenyl and phenylethynyl compounds of scandium are pyrophoric in air, but no explanation of the differing behavior is possible at this time.

Carbon analyses for all of the compounds isolated as solids, I-VIb excluding III, were low. In addition, the carbon to hydrogen ratio was low for all of the analyses except for VIb. Carbide formation is thought

to be one of the factors involved, as was reported for the phenyl and phenylethynyl compounds, but it is apparently not the only factor to be considered.

The triphenylmethyl group satisfies the three criteria listed earlier, and it was, perhaps, for these reasons that the triphenylmethyl group was used to prepare compounds of calcium[18] and nickel.[20] Hexaphenylethane was added to either calcium amalgam or a nickel (0) complex to prepare the compounds. The first reaction utilized to prepare tris (triphenylmethyl)scandium (III) did not make use of scandium metal, but involved a reaction between the triphenylmethyl anion and scandium (III). A large excess of sodium was used to prepare the anion, because a stoichrometric amount merely produces hexaphenylethane by means of a Wurtz reaction, which readily dissociates to form triphenylmethyl radicals.[17]

The reactions between scandium chloride and triphenylmethylsodium and scandium metal and triphenylchloromethane both produced a brown, nonsublimable solid, I. The phenyl and phenylethynyl compounds are also brown, nonsublimable solids but are insoluble, whereas I is soluble in benzene and produces a brown solution. The solution is unstable, however, and decomposes on standing to give a yellow solution of triphenylmethyl radicals.

The infrared spectrum of tris(triphenylmethyl)scandium (III) contained bands of weak intensity at 522 and 426 cm^{-1} in addition to the expected absorptions of the triphenylmethyl group.

The mass spectrum of I did not contain a parent ion peak. However, the temperature needed to produce a spectrum was sufficiently high, 300-395°, that extensive decomposition had taken place, as evidenced by large peaks corresponding to hexaphenylethane, m/e = 486, and its fragments. Peaks were observed corresponding to ScL_2^+ and ScL^+, m/e = 531 and 288 respectively.

The reaction between scandium metal and triphenylchloromethane was more successful than expected in that tris(triphenylmethyl)scandium (III) was not the only product obtained. As shown in Figure 2, three distinct products were observed.

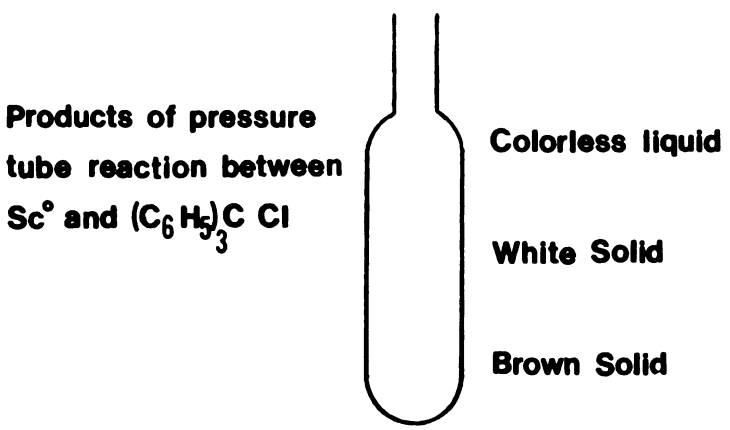


Figure 2. Products of pressure tube reaction.

The brown solid was a mixture of scandium chloride, tris(triphenylmethyl)scandium (III), and unreacted scandium metal and triphenylchloromethane. The white solid has been identified as hexaphenylethane on the basis of infrared and mass spectral data. The mass spectrum of the clear liquid had peaks corresponding to $(C_6H_5)_3CH^+$ and $(C_6H_5)_3C^+$, m/e = 244 and 243 respectively, but nothing heavier was observed. The infrared spectrum of the liquid had a few absorptions similar to those of I, but was significantly different in that additional absorptions at 1662 vs, 1620 sh, 1319 s, 942 s, 720 m, and 375 w (br) cm^{-1} were observed along with much stronger absorptions at 920 s, 640 s, and 605 s cm^{-1}. The spectrum is no closer to resembling that of I than it is those of hexaphenylethane or triphenylmethylsodium.

Because of the rather unusual characteristics of the clear liquid, an attempt was made to prepare more of it for further study. A few crystals of colorless triphenylchloromethane were near the neck of the pressure tube, and as the reaction progressed, some of the liquid condensed on the crystals of triphenylchloromethane and produced a brown solid. Since tris(triphenylmethyl)scandium (III) is a brown solid, it was concluded that the liquid contained scandium. As of this date, no conclusions have been reached concerning the composition of the liquid or the oxidation state of the scandium present in it.

In recent years, the trimethylsilylmethyl group has been found to be useful in preparing thermally stable organometallic compounds and complexes.[11,12,21-23] This group fulfills the criteria of being bulky enough to shield the metal and having no readily transferable groups on the β atom. The reaction used to synthesize tris(trimethylsilylmethyl)scandium (III), II is similar to that used for other transition metals, but the product could not be induced to sublime.

The infrared spectrum of II contained the expected absorptions of the ligand along with absorptions at 3360 w, 1620 w, and 430 sh cm^{-1} which indicated that some decomposition had taken place, and peaks at 530 sh and 505 m cm^{-1}. On the basis of the infrared spectrum, it was not surprising that the amount of scandium found was higher than that calculated on the basis of $((CH_3)_3SiCH_2)_3Sc$. Water molecules could attack the Sc-C bonds and produce tetramethylsilane and scandium hydroxide.

As was mentioned earlier, II could not be induced to sublime, thus it was not surprising that the mass spectrum of II did not contain a parent ion peak. The heaviest peak observed corresponded to $((CH_3)_3SiCH_2)_2^+$ or L_2^+, m/e = 174. In addition to decomposition fragments of L_2^+, peaks were observed for ScL^+ and Sc^+, m/e = 132 and 45 respectively. Due to the insolubility of tris(trimethylsilylmethyl) scandium (III) once it has been isolated as a solid, it was impossible to obtain an ^1H nmr spectrum of it.

The dioxane complex of II, IIa, is a 1:1 complex on the basis of the scandium analysis. The infrared spectrum of IIa had all of the absorptions found for II along with bands for dioxane, including a strong band at 340 cm^{-1} assigned to ν (Sc-O).[24]

The mass spectrum of IIa was similar to that of II and I in that no parent ion peak was observed and peaks corresponding to L_2^+ and ScL^+, m/e = 174 and 132 respectively, were observed. Two other peaks at m/e = 219 and 220 were observed that corresponded to ScL_2^+ and ScL (dioxane)$^+$ respectively. Peaks heavier than m/e = 220 were observed but could not be assigned.

The pentafluorophenyl group has been widely used for preparing compounds and complexes of transition metals and main group metals.[25] More recently, tris(pentafluorophenyl)-indium (III) and several complexes of this compound have been prepared.[26,27]

When tris(pentafluorophenyl)indium (III) is sublimed at 140-150° onto a room temperature probe it condenses as a liquid. Tris(pentafluorophenyl)scandium (III), III, is a liquid that condenses at 130-140° onto a room temperature probe. The mass spectrum of III had a fairly strong parent ion peak, m/e = 546, as well as peaks corresponding to ScL_4^+ and ScL_2^+, m/e = 713 and 379 respectively. There was no large peak corresponding to L_2^+, $(C_6F_5)_2^+$ m/e = 334, as there was in the mass spectrum of a lower boiling fraction, 60-125°.

The infrared spectrum of the liquid remaining on the cold finger in the first sublimation attempt was very complex, indicating that several compounds were present. The mass spectrum of this liquid indicated the presence of L_2ScF^+, L_2ScI^+, L_3Sc^+, L_2^+ and LH^+. The infrared spectrum did have two absorptions of weak to medium intensity at 560 and 580 cm^{-1} that could not be assigned as absorptions of the pentafluorophenyl group.

The infrared spectrum of the brown dioxane complex, IIIa, was very similar to that of the indium complex which was prepared in the same manner. In addition to the expected absorptions of the ligands present, a very broad peak of medium intensity was observed at 520 cm^{-1}. The mass spectrum of IIIa also did not contain a parent ion peak, but peaks corresponding to ScL_2^+, LH^+, dioxane$^+$, and Sc^+ were observed, m/e = 379, 168, 88 and 45 respectively.

The tolyl group was chosen to prepare an organoscandium compound because the phenyl compound has been prepared and the two compounds should be very similar. The phenyl compound is a yellowish brown, insoluble and involatile solid, and tris(tolyl)scandium (III), IV, is a yellowish brown, insoluble and involatile solid.

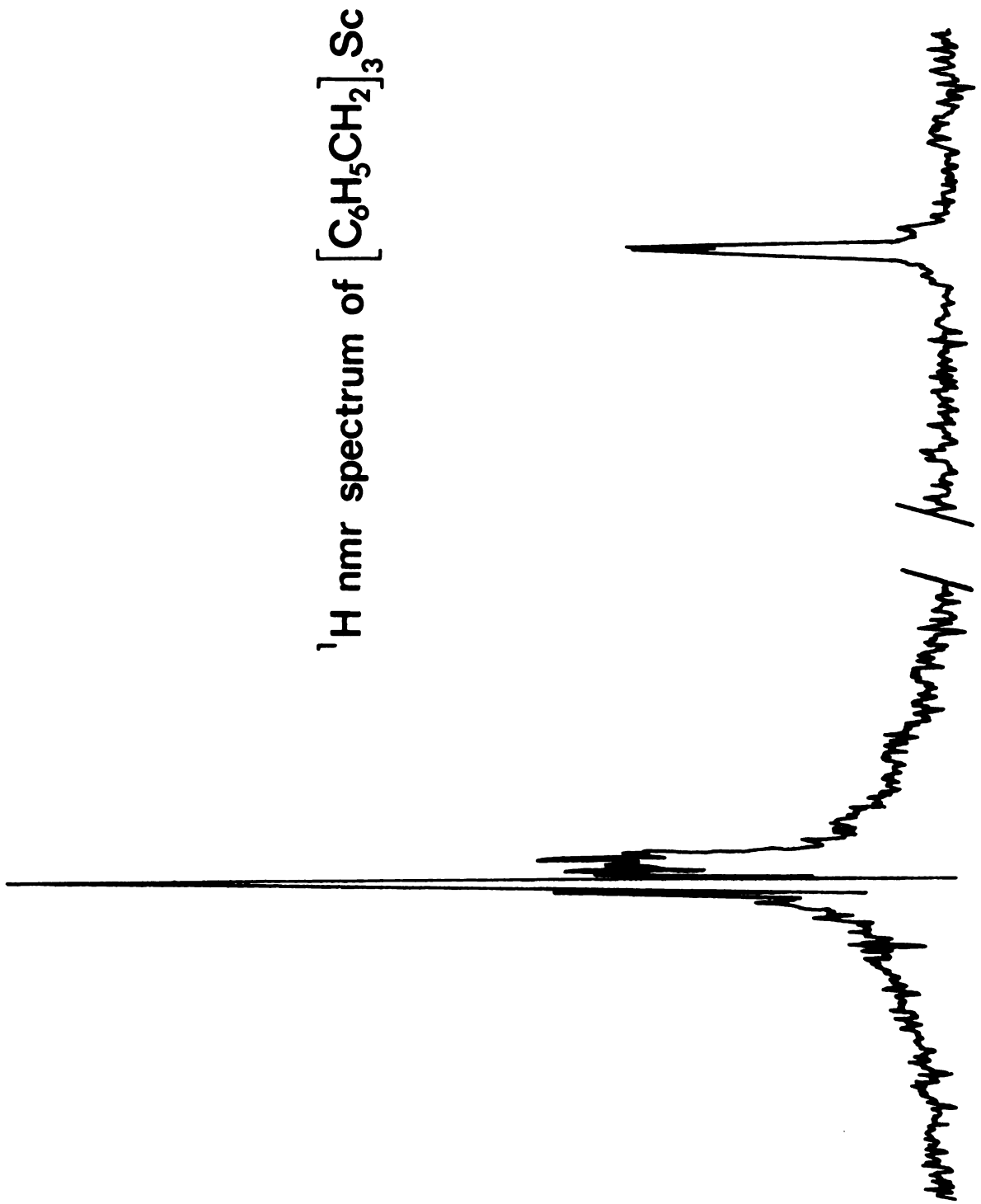
The infrared spectrum of IV contained the expected absorptions for the ligand in addition to a broad peak of medium intensity at 542 cm^{-1}, a broad, weak peak at 3300 cm^{-1}, ν (O-H); and a shoulder at 400 cm^{-1}, ν (Sc-O). The presence

of the last two bands mentioned indicated that partial decomposition had taken place and could account for the high value for scandium in the analysis.

The lowest temperature at which a mass spectrum could be obtained was 220°, and, as expected, no parent ion peak was observed. The major peaks in the spectrum were assigned to $(CH_3C_6H_4)_2^+$ and its fragments. Other peaks observed, m/e = 136, 91 and 45, were assigned to ScL^+, L^+ and Sc^+ respectively.

The benzyl ion has been used to prepare thermally stable organometallic compounds such as tetrabenzyltitanium.[13] The benzyl ion fulfills the criteria in that it is bulky enough to shield the metal to some extent, there are no readily transferable groups on the β atom, and charge delocalization is possible. The methyl group only fulfills the second criterion and tetramethyltitanium decomposes above -78°.

Like I, IV, and the phenyl and phenylethynyl compounds of scandium, tris(benzyl)scandium (III), V, is a brown, involatile solid. It is slightly soluble in deuterochloroform, and an ^1H nmr spectrum was obtained as shown on the following page. It contained a complex multiplet 7.15 ppm from TMS, $(CH_3)_4Si$, corresponding to the aromatic proton absorption, and a sharp singlet 2.9 ppm from TMS for the methylene proton absorption. The ^1H nmr spectrum of tetrabenzyltitanium had two multiplets at 6.42 and 6.81 ppm from TMS and a sharp singlet at 2.57 ppm respectively.


^{1}H nmr spectrum of $[C_6H_5CH_2]_3Sc$
7.15 δ PPM
2.9 δ PPM

The infrared spectrum of V contained the expected absorptions of the benzyl group in addition to a broad peak of medium intensity at 512 cm^{-1}. The mass spectrum of this involatile solid had peaks corresponding to L^+ and Sc^+, m/e = 91 and 45 respectively.

The infrared spectrum of the product obtained from the reaction between scandium chloride and lithium naphthalenide, VIa, had a broad peak of medium intensity at 525 cm^{-1} in addition to the expected absorptions of the ligand. The mass spectrum of VIa had peaks corresponding to $C_{10}H_8^+$ and Sc^+, m/e = 128 and 45 respectively.

The infrared spectrum of VIb, the product of the reaction between scandium chloride and t-butyllithium, had a broad absorption of medium intensity at 540 cm^{-1} in addition to the expected bands of the ligand. The mass spectrum of VIb had peaks corresponding to ScL^+ and L^+, m/e = 102 and 57 respectively.

Recent reports have shown that gallium and indium metals will undergo some type of reaction in the presence of alkyl-halides.[28,29] The results indicate that mixed compounds are formed, RMX_2 and R_2MX (M = Ga, In; X = Br, I; R = CH_3, CH_3CH_2, $CH_3CH_2CH_2$). In view of these reports, and the successful reaction between scandium metal and triphenyl-chloromethane, reactions between scandium metal and benzyl-bromide and t-butylbromide were attempted. In both cases, the surface of the metal immediately became discolored and indicated some sort of reaction.

The infrared spectrum of the benzyl product, VId, had absorptions at 280 m (br), ν (Sc-Br),[24] 497 m (br) and 545 sh cm^{-1} in addition to the expected absorptions of the ligand. The infrared spectrum of the t-butyl product, VIc, had a broad, strong absorption at 1575 cm^{-1} and no absorptions were observed below 600 cm^{-1} except for the beginning of a broad band of medium intensity estimated to be at 220 cm^{-1}.

The mass spectrum of VId at 115° had peaks corresponding to $C_6H_5CH_2Br^+$, ScL^+, L^+ and Sc^+, m/e = 172 and 170, 136, 91 and 45 respectively. The mass spectrum of VIc from 210-300° had a small peak at m/e = 57, $(CH_3)_3C^+$, which was one of a series of peaks of decreasing intensity from m/e = 55-59. Another peak of equally low intensity was observed at m/e = 45, Sc^+.

On the basis of infrared and mass spectra, VId is similar to tris(benzyl)scandium (III) but has both scandium-carbon and scandium-bromine interactions.

The infrared spectrum was very similar to those reported for the mixed products of gallium and indium, and it is concluded that VId is a mixture of $RScBr_2$ and R_2ScBr (R = $C_6H_5CH_2$) with benzylbromide impurities.

The infrared and mass spectra do not give conclusive evidence on the composition of VIc. The lack of any absorptions in the expected metal-carbon absorption region indicates the absence of the t-butyl group in the product. This is not an unreasonable result, as the

possibility of an elimination reaction to form 2-methylpropene, $(CH_3)_2C=CH_2$, is much higher than in the reaction between scandium chloride and t-butyllithium. If the elimination reaction occurs, then the product obtained could be a mixed one of hydrogen and bromine with scandium. The broad band, circa 220 cm^{-1}, can then be assigned to ν (Sc-Br) and the band at 1575 cm^{-1} can be assigned to a scandium-hydrogen interaction. A titanium compound has been prepared that contains bridging hydride ions,[30] di-μ-hydrido-bis(cyclopentadienyl)titanium (III), and the authors assigned a broad, strong absorption observed at 1450 cm^{-1} to the antisymetric stretch vibration.

Table 1 lists the absorptions of the compounds prepared thus far in the expected metal-carbon absorption region.

It was concluded, on the basis of their insolubility, involatility and infrared spectra, that the phenyl and phenylethynyl compounds of scandium were not monomeric.[3] The absorptions reported for these compounds in the metal-carbon region, in a preliminary communication in the case of the phenyl compound,[31] are very similar to the absorptions of the compounds whose preparations are reported herein. However, no assignments were made for the phenyl and phenylethynyl compounds.

For polymeric or dimeric structures, two scandium-carbon stretching frequencies or a broad band should be observed due to the difference in strength of the two types of bonds

Table 1. Infrared Absorptions in the Metal-Carbon Region

Compound	Absorptions in Metal-Carbon Region
$[(C_6H_5)_3C]_3Sc$	522 w-m, 426 w-m
$[(CH_3)_3SiCH_2]_3Sc$	530 sh, 505 m (br)
$[(CH_3)_3SiCH_2]_3Sc(C_4H_8O_2]$	530 sh, 505 m (br)
$(C_6F_5)_3Sc$	580 w, 560 w
$(C_6F_5)_3Sc(C_4H_8O_2)$	520 m (br)
$(CH_3C_6H_4)_3Sc$	542 m (br)
$(C_6H_5CH_2)_3Sc$	512 m (br)
$Sc(C_{10}H_7)_n$	525 m (br)
$Sc[(CH_3)_3C]_n$	540 m (br)
$(C_6H_5CH_2)ScBr_2$ $(C_6H_5CH_2)_2ScBr$	545 sh, 497 m (br)
$(C_5H_5)_3Sc$	370 s, 325 m, 296 m
$(C_6H_5C\equiv C)_3Sc$	540 sh, 516 m, (ref. 3)
$(C_6H_5)_3Sc$	490 (ref. 31)

as shown in Figure 3. The terminal ligands have a normal

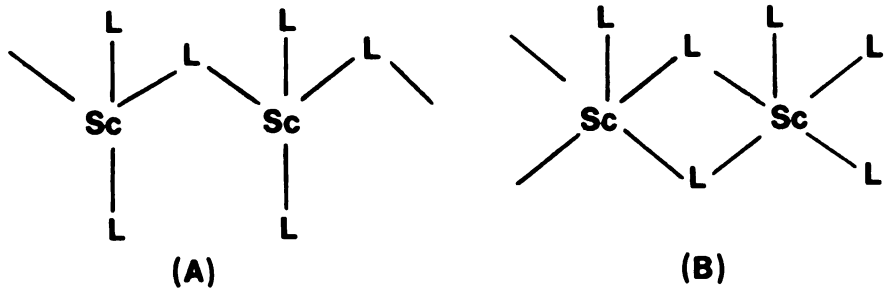


Figure 3. Possible structures of polymeric organoscandium compounds.

two election two center bond and the bridging ligands will take part in two electron three center bonds. For all of the compounds reported herein except for VIc, either two absorptions or a broad absorption were observed in the metal-carbon region which are assigned to ν (Sc-C) and are indicative of dimeric or polymeric structures. In addition, the fact that the mass spectrum of tris(pentafluorophenyl)-scandium (III) had peaks corresponding to ScL_4^+, ScL_3^+ and ScL_2^+ is further support for the at least dimeric structure proposed for these compounds.

The slightly higher absorptions assigned to ν (Sc-C) for $(C_6F_5)_3Sc$ are reasonable because of the increased stability of the compound due to the high electronegativity of the pentafluorophenyl group. Presumably, the addition of a dioxane molecule would weaken these strong bonds more noticeably than it would for a hydrocarbon ligand.

The increased stability of a metal-carbon bond caused by using a very electronegative ligand such as the pentafluorophenyl group is not enough to account for the extremely high values for ν (In-C) assigned by Deacon and Parrott, 792 and 788 cm^{-1}.[26] Other workers have prepared organoindium compounds using hydrocarbon ligands such as methyl, ethyl and n-propyl anions,[29,32] with ν (In-C) assigned to absorptions in the range of 455-575 cm^{-1}, and it is concluded that the assignments made by Deacon and Parrott are incorrect.

The infrared spectrum of sodium cyclopentadienide has no absorptions of even medium intensity below 600 cm^{-1}. The infrared spectrum of $(C_6H_5)_3Sc$ has three bands of at least medium intensity, which would indicate, on comparison with other organoscandium compounds, that it too is polymeric with bridging cyclopentadienyl groups. A recent study of $(C_5H_5)_3Sc$ confirmed that its structure is polymeric in the solid state with bridging cyclopentadienyl groups.[33]

Table 2 shows the mass spectral data for the organoscandium compounds reported herein and three lanthanide cyclopentadienides.

Table 2. Mass Spectral Data

Compound	Peaks Observed					
$[(C_6H_5)_3C]_3Sc$		ScL_2^+	L_2^+	ScL^+	L^+	Sc^+
$[(CH_3)_3SiCH_2]_3Sc$			L_2^+	ScL^+	L^+	Sc^+
$[(CH_3)_3SiCH_2]_3Sc$ diox.		ScL_2^+				
		$ScL(diox)^+$	L_2^+	ScL^+	L^+	Sc^+
$(C_6F_5)_3Sc$	ScL_4^+	ScL_3^+	ScL_2^+		L^+	Sc^+
$(C_6F_5)_3Sc$ diox.			ScL_2^+		diox. $C_6F_5^+$	Sc^+
$(CH_3C_6H_4)_3Sc$				L_2^+	ScL^+	L^+	Sc^+
$(C_6H_5CH_2)_3Sc$					L^+	Sc^+
$Sc(C_{10}H_7)_n$					L^+	Sc^+
$Sc[(CH_3)_3C]_n$				ScL^+	L^+	Sc^+
$RScBr_2 + R_2ScBr$ R = $C_6H_5CH_2$				ScL^+	L^+	Sc^+
$(C_5H_5)_3Sc$		ScL_3^+	ScL_2^+		ScL^+		Sc^+
$(C_5H_5)_3M$		ML_3^+	ML_2^+		ML^+		M^+

M = Nd, Yb, Sm (ref. 35)

The mass spectra are consistent with the polymeric structure proposed on the basis of infrared data, insolubility and involatility for the compounds reported here. Either of the structures shown in Figure 3 correlates with the mass spectral data, the observed fragments arising from the initial cleavage at the weaker bridging bonds with further fragmentation dependent on the strength of the bonds between the scandium and the remaining ligands.

The fragmentation patterns observed for the compounds at temperatures under 200° suggests that decomposition is a result of electron impact rather than thermal decomposition, since extensive fragmentation has also been observed for peralkylchromium (IV) compounds when the electron impact technique is used.[34]

The mass spectra for the lanthanide cyclopentadienides[35] exhibit similar intensities for the peaks listed compared to those of $(C_5H_5)_3Sc$. The samarium compound has been shown to be polymeric in the solid state, with bridging cyclopentadienides.[36] In the absence of further evidence this would imply that the scandium, neodymium and ytterbium compounds are also polymeric. The infrared spectrum and the recent crystal structure study have shown that the scandium compound is indeed polymeric with bridging cyclopentadienide groups.

One of the primary reasons for attempting to prepare organoscandium compounds is to determine whether they will act as catalysts in olefin polymerization reactions. The most important property of a homogeneous catalyst is a vacant coordination site.[36] Other criteria that must be met for a rapid rate of polymerization are: it must be a kinetically labile system for rapid attachment of substrate and removal of product, and the catalyst should be soluble in nonpolar solvents.[37]

Organoscandium compounds are coordinatively unsaturated with respect to the scandium and they are initially soluble in nonpolar solvents. Since Sc(III) has a $3d^0$ configuration, organoscandium compounds are relatively labile and can act as catalysts in olefin polymerization reactions. It has been reported that a solution containing scandium chloride and phenylmagnesiumbromide does act as a catalyst for polymerizing ethylene,[8] but it has also been reported that scandium chloride alone could cause olefins such as 1,3-cyclohexadiene to oligomerize.[7] It is therefore necessary to determine whether a nonhalide containing organoscandium compound will act as a catalyst.

A benzene solution of styrene and tris(triphenylmethyl) scandium (III), 100:1, was allowed to stand at room temperature for 3-5 days and taken to dryness under reduced pressure. The mass spectrum of the solid remaining had peaks corresponding to $(C_6H_5CH{=}CH_2)_n^+$, n = 1 and 4.

A solution of 9.1 grams styrene in benzene was added to 5 ml of a saturated benzene solution of tris(benzyl) scandium (III) and allowed to stand at 50° for 3-5 days. The solvent was removed under reduced pressure and the solid obtained was identified by its infrared spectrum as polystyrene.

A similar experiment was attempted using tris(trimethylsilylmethyl)scandium (III) that had been isolated as a solid and was consequently no longer soluble. The infrared spectrum of the solid obtained indicated that no polystyrene was present. Presumably tris(trimethylsilylmethyl)scandium (III) would also act as a catalyst if the extraction solution used in its isolation is used directly.

The infrared spectra of tris(triphenylmethyl)scandium (III) and tris(benzyl)scandium (III) did not have any absorptions attributable to the presence of halides. Hence, these are the first reactions where a scandium compound with only organic ligands present acts as a catalyst.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

On the basis of the data presented in this thesis, the following can be concluded:

1. Stable organoscandium compounds containing trimethylsilylmethyl, triphenylmethyl, pentafluorophenyl, tolyl, benzyl, naphthalyl, and t-butyl anions have been prepared that contain scandium-carbon bonds. The bonds in these compounds are not inherently weak, but are subject to attack due to the coordinatively unsaturated environment about the scandium.

2. Organoscandium compounds are polymeric with terminal and bridging ligands. Further studies to determine whether the scandium is 4 or 5 coordinate for various ligands may enable predictions to be made concerning the choice of one ligand over another for better catalytic properties.

3. Soluble organoscandium compounds do act as catalysts in olefin polymerization reactions in the absence of any other metals or organometallic compounds. Further work is needed to determine

optimum ratios and reaction conditions. It was determined that $(C_6H_5CH_2)_3TiCl$ polymerized ethylene faster than $(C_6H_5CH_2)_4Ti$,[13] hence an investigation concerning the catalytic properties of mixed compounds, R_nScX_{3-n}, should be made.

4. Organoscandium compounds of uncertain composition have been prepared. Further characterization of the colorless liquid and black solid, from the reactions between scandium metal and triphenylchloromethane and benzylbromide respectively, is needed to determine what type of environment the scandium ion is in and what the compositions of these products are.

5. A compound of uncertain composition has been isolated as the product of the reaction between scandium metal and t-butylbromide. A comparison of the infrared and mass spectral data for $[(C_5H_5)_2TiH]_2$ and $[(C_5H_5)_2ScH]_2$ would give some indication of the strength of the scandium-hydrogen interaction and would make an accurate assignment of the strong, broad band at 1575 cm^{-1} in the infrared spectrum of VIc possible. The preparation of $[(C_5H_5)_2ScH]_2$ has not been reported, but it may be possible to prepare it from a reaction between $[(C_5H_5)_2ScCl]_2$ and a compound such as CaH_2. If this compound can be prepared, it would

be worthwhile to determine whether it and similar organoscandium compounds would act as catalysts for hydrogenation reactions.

B I B L I O G R A P H Y

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