FEATURE ARTICLE

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Recent developments in the non-cyclopentadienyl organometallic and related chemistry of scandium

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Up to the early to mid 1990s the organometallic chemistry of scandium was dominated by cyclopentadienyl derivatives. This present article highlights advances in the synthesis and reactivity of non-cyclopentadienyl organometallic and related compounds of scandium. These include: compounds containing arene and other η^x-C_xR_x ligands; compounds with macrocyclic and *fac*-L_3 ligands; compounds with polydentate ligands that incorporate amide donors; compounds with bidentate, monoanionic N,N′ donor ligands; and compounds with iminophenolate, bis(phenoxide) and some other anionic O-donor ligands.

Introduction

The first organoscandium compound, [Cp_3Sc], was reported by Wilkinson and Birmingham in 1956.[1] Between that time and the early to mid 1990s the organometallic chemistry of scandium was dominated by cyclopentadienyl systems. This chemistry has been the subject of several reviews and the reader is referred to these for further details.[2–8] Just as for the Groups 4 to 6 transition metals[9–14] and heavier Group 3 and lanthanide metals,[15–21] the organometallic and related chemistry of scandium in non-cyclopentadienyl ligand environments has enjoyed much recent interest.

Philip Mountford gained a DPhil degree at the University of Oxford and Balliol College (1986 to 1989) under the supervision of Professor M. L. H. Green. He remained at Oxford as a Junior Research Fellow at Wolfson College (1989 to 1992), Departmental Demonstrator in the Inorganic Chemistry Laboratory (1990 to 1992), and Lecturer at Keble College (1990 to 1992). In 1992 he was appointed to a lectureship at the University of Nottingham, and in 1998 he returned to Oxford where he is a Reader in Inorganic Chemistry and a Tutorial Fellow at St Edmund Hall. He is a Fellow of the Royal Society of Chemistry, and a past recipient of the Royal Society of Chemistry's Sir Edward Frankland Fellowship. During 2003 he was visiting professor at the Université Louis Pasteur, Strasbourg, France and also at the Université Bordeaux I, France. His research interests centre around studies of the synthesis, structure, bonding and reactivity of organometallic and coordination compounds of the transition metals.

Ben Ward was formerly a DPhil student in the Mountford group and was a graduate of Nottingham University from where he received an MSci degree in 1999 having spent his final year research project with Dr Polly Arnold. His doctoral research was mainly on the chemistry of Group 6 imido complexes with diamido-amine ligands, as well as using the same types of ligand in developing organometallic and related chemistry of Group 3. He is currently a Leverhulme post-doctoral fellow in the Mountford group working on new organometallic scandium and yttrium chemistry. In September 2003 he will take up a post-doctoral position in Professor Gade's group at the Université Louis Pasteur, Strasbourg, France.

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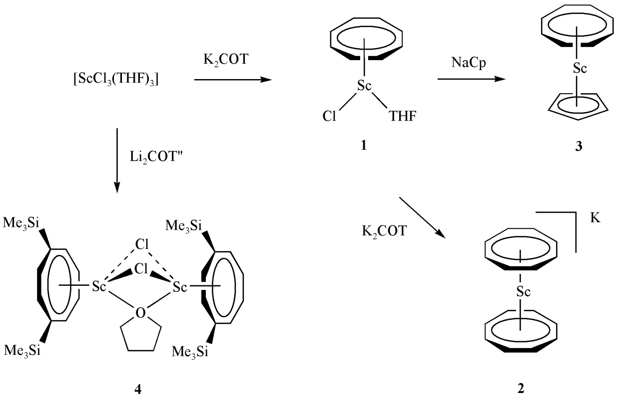
The purpose of our review is to highlight this new chemistry of scandium. The last reviews[4,22] specifically to focus on scandium (but not specifically on non-cyclopentadienyl organometallic chemistry) covered literature up to the middle to end of 1998. Edelmann[23] and Piers[24] have very recently reviewed non-cyclopentadienyl chemistry of the Group 3 and lanthanide metals in general, but our present, comparatively concise contribution covers specifically scandium's non-cyclopentadienyl organometallic and related chemistry as described in the literature up to the end of 2002.

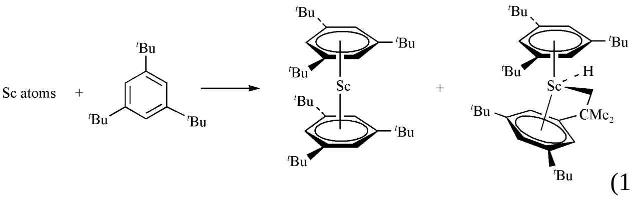
Scandium compounds with arene and other η^x-C_xR_x ligands

One of the earliest non-cyclopentadienyl organoscandium complexes was reported in 1976 by de Liefde Meijer.[25] It was found that [$ScCl_3(THF)_3$] reacts with one molar equivalent of dipotassium cyclooctatetraene (K_2COT) to afford [Sc(COT)Cl(THF)] (**1**). Further reaction with either a second equivalent of K_2COT or NaCp affords the sandwich complexes K[$Sc(COT)_2$] (**2**) or [Sc(COT)Cp] (**3**) respectively. Cloke *et al*[26] used the modified cyclooctatetraene derivative Li_2COT'' ($COT'' = 1,4\text{-}C_8H_6(SiMe_3)_2$) which reacts with [$ScCl_3(THF)_3$] to afford the dimeric product [$\{Sc(COT'')Cl\}_2(THF)$] (**4**) which contains bridging chloride and semi-bridging THF ligands (Scheme 1).



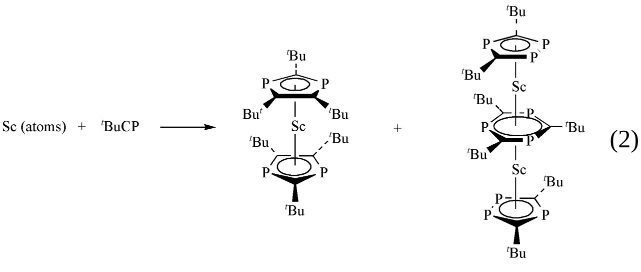
Scheme 1

Cloke *et al*[21] have also shown that a number of bis(η^6-arene) scandium sandwich compounds can be prepared by the co-condensation of scandium vapour with the appropriate arenes. These complexes tend to be thermally unstable, with decomposition temperatures ranging from −30 to 120 °C. In one specific example, the co-condensation of scandium vapour with 1,3,5-tri-*tert*-butylbenzene afforded a mixture of two compounds. The first a Sc^0 sandwich complex $[Sc(\eta^6\text{-}2,4,6\text{-}C_6H_3{}^tBu_3)_2]$ (**5**), and the second a Sc^{II} sandwich complex $[Sc(\eta^6\text{-}2,4,6\text{-}C_6H_3{}^tBu_3)(\eta^6\text{-}2,4\text{-}C_6H_3{}^tBu_2CMe_2CH_2)H]$ (**6**) which has undergone C–H activation at a *tert*-butyl group on one of the rings (eqn. (1)).



5 **6**

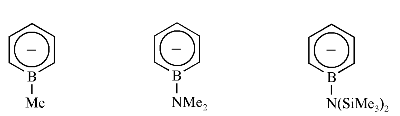
Cloke and Nixon and coworkers have reported[27,28] that the co-condensation of scandium vapour with *tert*-butylphosphaalkyne also results in the formation of new classes of scandium complex. In this reaction, two compounds are formed. The first, $[Sc\{\eta^5\text{-}P_2(C^tBu)_3\}_2]$ (**7**), is a scandium(II) complex supported by a bis(1,3-diphospha-2,4,5-tri-*tert*-butylcyclopentadienyl) ligand environment. This was the first example of a stable scandocene(II) species. The second product, $[Sc_2\{\eta^5\text{-}P_3(C^tBu)_2\}_2\{\eta^6\text{-}P_3(C^tBu)_3\}]$ (**8**), is a novel triple decker dinuclear scandium(I) complex as shown in eqn. (2). Since



7 **8**

complexes **7** and **8** are formed in approximately equimolar quantities, the number of phosphorus atoms and ^{t}BuC groups is equal, showing that the number of ^{t}BuCP units consumed is conserved.

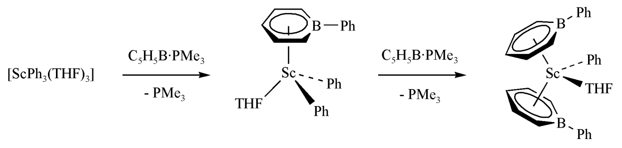
Another class of arene ligand that has recently received much attention is the boratabenzene ligands. The group of Herberich has shown[29,30] that the lithium salts of a number of boratabenzene derivatives react with $ScCl_3$ in refluxing toluene to afford a range of scandium chloride complexes, the nature of which is heavily influenced by the steric requirements of the boratabenzene B-substituent (see **9–11** in Chart 1). The methyl-substituted ligand **9** and the dimethylamide-substituted ligand **10** react to form dinuclear products $[Sc_2(\eta^6\text{-}C_5H_5BR)_4(\mu\text{-}Cl)_2]$ with bridging chloride ligands. Only in the case of the bulky bis(trimethylsilylamide)-substituted ligand **11** does the resulting complex, namely $[Sc\{\eta^6\text{-}C_5H_5BN(SiMe_3)_2\}_2Cl]$, exist as a monomeric species.



9 **10** **11**

Chart 1

Bazan has recently reported the reaction of $[ScPh_3(THF)_2]$ with $C_5H_5B{\cdot}PMe_3$ which affords the boratabenzene-supported diphenyl complex $[Sc(\eta^6\text{-}C_5H_5BPh)Ph_2(THF)]$ (**12**). This reacts with a second equivalent of $C_5H_5B{\cdot}PMe_3$ to afford the sandwich complex $[Sc(C_5H_5BPh)_2Ph(THF)]$ (**13**, Scheme 2).[31]



12 **13**

Scheme 2

Scandium compounds with macrocyclic and *fac*-L_3 ligands

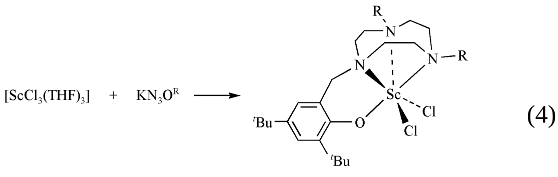
Triazacyclononane compounds

In 1997 Bercaw and coworkers described the use of the 1,4,7-trimethyl-1,4,7-triazacyclononane ($Me_3[9]aneN_3$) ligand system in scandium chemistry.[32] $[ScCl_3(THF)_3]$ reacts with $Me_3[9]aneN_3$ in acetonitrile solution to afford $[Sc(Me_3[9]aneN_3)Cl_3]$ (**14**). The correct choice of solvent for this reaction is critical, since the reaction gives lower yields in solvents other than MeCN. Cyclopentadienyl derivatives of **14** could not be prepared. However, **14** does react with three molar equivalents of MeLi to afford the trimethyl compound $[Sc(Me_3[9]aneN_3)Me_3]$ (**15**, eqn. (3)). The compound **15** is rather unreactive towards unsaturated organic substrates (*e.g.* olefins, acetylenes, acetonitrile), but does react with dihydrogen under forcing conditions (4 atm., 80 °C) to afford what is presumed to be a trihydride complex.

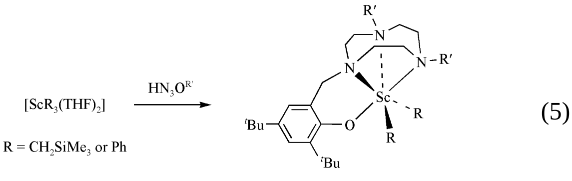
14 **15**

The trimethyl compound **15** can be activated by treatment with $[PhNMe_2H][BAr^F_4]$ ($Ar^F = C_6F_5$). When the reaction is carried out in THF, methane and free *N*,*N*-dimethylaniline are observed, the organometallic product being tentatively described as $[Sc(Me_3[9]aneN_3)Me_2(THF)_n][B(Ar^F)_4]$ (**16**) which has been shown to catalyse the polymerisation of ethylene and the oligomerisation of 1-pentene. Reaction of **15** with BAr^F_3 affords a different species which is likely to be an activated complex with a bridging methyl group, namely $[Sc(Me_3[9]aneN_3)Me_2(\mu\text{-}Me)B(Ar^F)_3]$ (**17**). Compound **17**, like **16**, catalyses the polymerisation of ethylene and the oligomerisation of 1-pentene. Furthermore, the 1-pentene oligomer obtained from **16** has identical properties to that obtained from **17**.

Mountford *et al.* have recently described related scandium complexes containing triazacyclononane ligands possessing single pendant phenoxide arms.[33–35] Reactions of $[ScCl_3(THF)_3]$ with the potassium salts of these macrocyclic ligands afford the *cis*-dichloride compounds $[Sc(N_3O^R)Cl_2]$ (R = Me **18** or ^{i}Pr **19**, eqn. (4)).[33] Reaction of **18** with $LiCH_2SiMe_3$ gives the *cis*-dialkyl derivative $[Sc(N_3O^{Me})(CH_2SiMe_3)_2]$, but this and related σ-hydrocarbyl compounds are more easily prepared by protonolysis routes summarised in eqn. (5).[34,35]



R = Me (**18**) or ^{i}Pr (**19**)

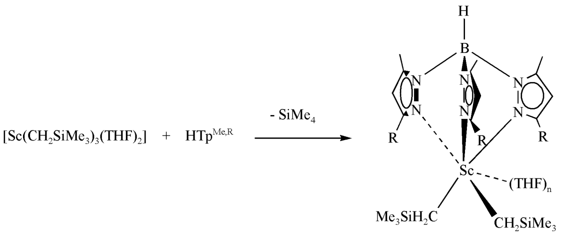


R' = Me or ^{i}Pr; R = CH_2SiMe_3 (**20**) or Ph (**21**)

The bis(trimethylsilyl) compounds **20** are reasonably thermally stable at ambient temperature whereas the diphenyl homologues [Sc(N$_3$O^R)Ph$_2$] **21** rapidly decompose with concomitant evolution of C_6H_6.

Tris(pyrazolyl)hydroborate and tris(pyrazolyl)methane compounds

Piers *et al.* have shown that reaction of the potassium salts of tris(pyrazolyl)hydroborate ligands [B(3-Me-5-RPz)$_3$]$^-$ (Tp^{Me,R}, R = Me or ^{t}Bu. Pz = 1,2-C$_3$HN$_2$) with ScCl$_3$ affords the corresponding dichloride compounds [Sc(Tp^{Me,R})Cl$_2$(THF)$_n$] (R = Me, n = 1 **22**; R = ^{t}Bu, n = 0 **23**).[36] Alkylation of **22** and **23** with lithium reagents resulted in the formation of dialkyl products but these were always contaminated with the lithium salt of the tris(pyrazolyl)hydroborate ligand, namely LiTp^{Me,R}. An alternative strategy was employed to prepare certain of the target dialkyl compounds. Thus treatment of *in-situ* generated [Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$] with the protonated ligands HTp^{Me,R} afforded the corresponding bis(trimethylsilylmethyl) complexes **24** and **25** (eqn. (6)) with concomitant elimination of tetramethylsilane.



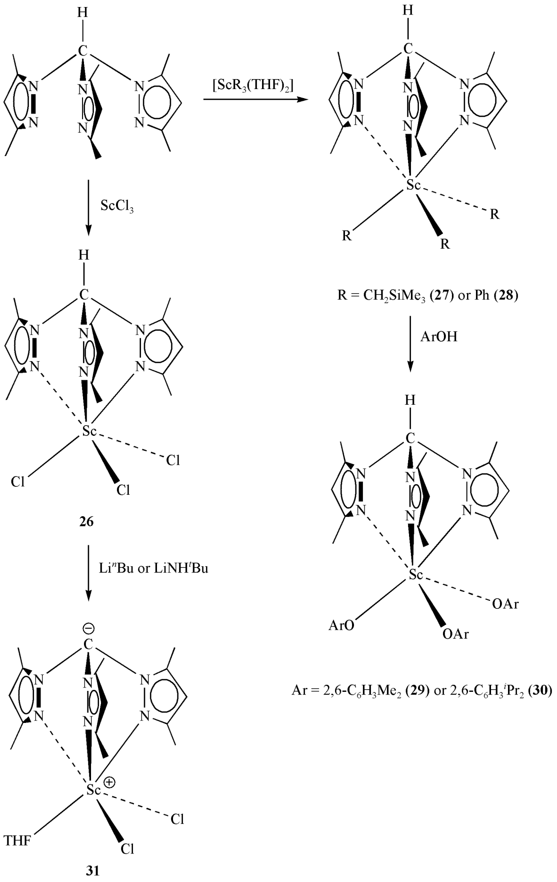
(6)

R = Me, n = 1 (**24**); R = ^{t}Bu, n = 0 (**25**)

Work of a similar nature has been carried out recently by Mountford *et al.* using the neutral *fac*-coordinating tris(pyrazolyl)methane ligands HC(3,5-Me$_2$Pz)$_3$.[37] This chemistry is summarised in Scheme 3. Thus reaction of HC(3,5-Me$_2$Pz)$_3$ with [ScCl$_3$(THF)$_3$] or [ScR$_3$(THF)$_2$] (R = CH$_2$SiMe$_3$ or Ph) affords the trichloride complex [Sc{HC(3,5-Me$_2$Pz)$_3$}Cl$_3$] (**26**) or tri-alkyl or -phenyl compounds [Sc{HC(3,5-Me$_2$Pz)$_3$}R$_3$] (R = CH$_2$SiMe$_3$ **27** or Ph **28**), respectively. Protonolysis of **27** with *ortho*-substituted phenols results in the formation of tris(phenoxide) compounds [Sc{HC(3,5-Me$_2$Pz)$_3$}(OAr)$_3$] (Ar = 2,6-C$_6$H$_3$Me$_2$ **29** or 2,6-C$_6$H$_3$^{i}Pr$_2$ **30**). Reaction of the trichloride complex **26** with either butyllithium or lithium *tert*-butylamide results in the formation of a zwitterionic compound [Sc{C(3,5-Me$_2$Pz)$_3$}Cl$_2$(THF)] (**31**) in which the tris(pyrazolyl)methane ligand has been deprotonated at the apical position.

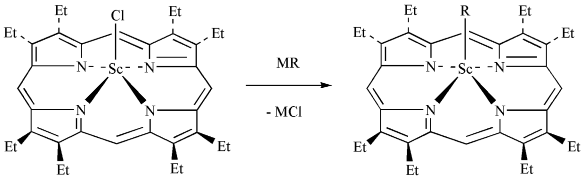
Porphyrin compounds

Although the first scandium complex supported by a porphyrin ligand was reported in 1971,[38] it was not until 1988 that Haushalter[39] undertook the first attempts at using these ligands in the context of organoscandium chemistry. Reaction of H$_2$TTP (TTP = dianion of tetratolylporphyrin) with ScCl$_3$ in refluxing chloronaphthalene affords [Sc(TTP)Cl] (**32**). Attempts to prepare a cyclopentadienyl derivative resulted only in the isolation and crystallographic characterisation of the bridging oxo compound [Sc$_2$(μ-O)(TTP)$_2$].



Scheme 3

In 1990, Arnold *et al*. reported that Li$_2$OEP (OEP = dianion of octaethylporphyrin) reacts with [ScCl$_3$(THF)$_3$] to afford the versatile monochloride [Sc(OEP)Cl] (**33**) analogous to that reported by Haushalter.[40] This compound readily undergoes chloride ligand metathesis to afford a wide range of derivatives [Sc(OEP)R] (R = Me, CH(SiMe$_3$)$_2$, N(SiMe$_3$)$_2$, Cp, C$_5$H$_4$Me or Cp*; eqn. (7)).[41] The OEP ligand provides a platform for supporting reaction chemistry of organoscandium complexes. For example, Arnold *et al.* have shown that the methyl derivative [Sc(OEP)Me] reacts readily with carbon dioxide or acetone to afford the corresponding acetate and *tert*-butoxide complexes, respectively.



(7)

33

R = Me, CH(SiMe$_3$)$_2$, N(SiMe$_3$)$_2$, Cp, C$_5$H$_4$Me or Cp*

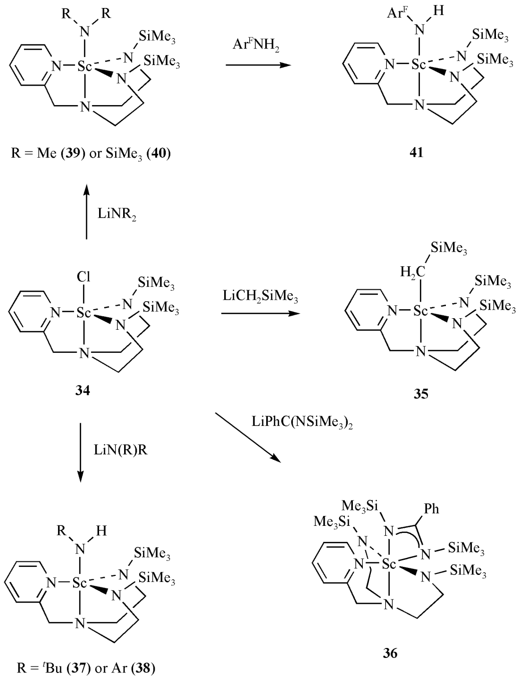
Scandium complexes with polydentate ligands that incorporate amide donors

Compounds with triamidoamine ligands

Recently, Scott and coworkers have reported on the use of a triamidoamine ligand N(CH$_2$CH$_2$NSiMe$_2$^{t}Bu)$_3$$^{3-}$ with scandium.[42] Reaction of [ScCl$_3$(THF)$_3$] with one molar equivalent of the trilithium amide affords the corresponding triamidoamine-supported scandium “ate” complex, incorporating one equivalent of lithium chloride. Sublimation of this complex at high vacuum affords the monomeric salt-free compound [Sc{N(CH$_2$CH$_2$NSiMe$_2$^{t}Bu)$_3$}].

Compounds with tetradentate diamido-donor ligands

Triamidoamine complexes of scandium cannot be further functionalised at the metal with anionic ligands such as alkyl groups. One solution to this problem is to replace one of the anionic amide arms of a triamidoamine ligand by a neutral amine donor. One ligand derived from this change is the potentially tetradentate diamidodiamine ligand $(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NSiMe_3)_2$ (N_2NN') reported by Mountford *et al.*[34,43] The Group 3 chemistry associated with this ligand is illustrated in Scheme 4. Thus, reaction of Li_2N_2NN' with $ScCl_3$ affords the scandium chloride $[Sc(N_2NN')Cl]$ (**34**). Compound **34** undergoes halide metathesis reactions with a variety of lithium alkyl and amide reagents to afford complexes containing alkyl (**35**), benzamidinate (**36**), and primary (**37**, **38**) and secondary amide (**39**, **40**) ligands. Compound **39** reacts with pentafluoroaniline to give the perfluorinated amide complex **41**. The monoalkyl compound **35** can also be prepared by reaction of the protio-ligand H_2N_2NN' with $[Sc(CH_2SiMe_3)_3(THF)_2]$.

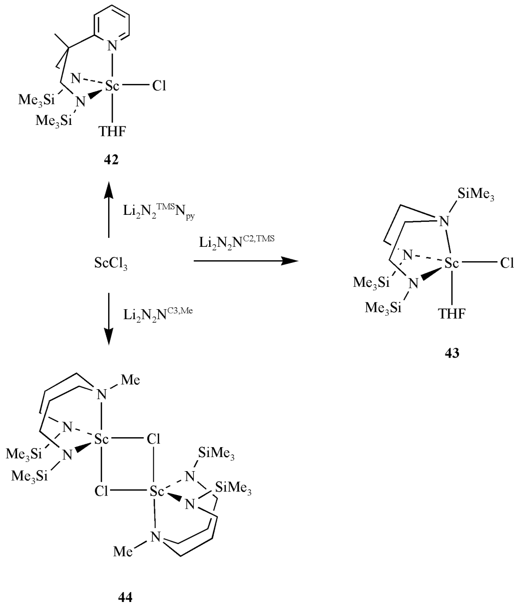


Scheme 4

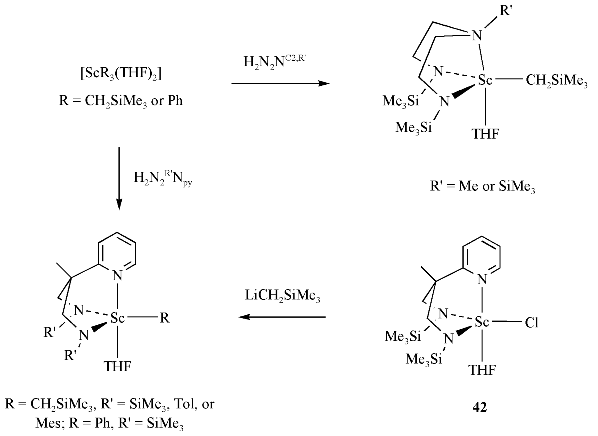
Compounds with tridentate diamido-donor ligands

Very recently, Gade and Mountford have reported on the use of various tridentate diamide-donor ligands as supporting ligands in organometallic and related chemistry of scandium.[44] Reaction of $Li_2N_2{}^{TMS}N_{py}$ or $Li_2N_2N^{C2,TMS}$ with $ScCl_3$ in THF afforded the five-coordinate derivatives $[Sc(N_2{}^{TMS}N_{py})Cl(THF)]$ **42** and $[Sc(N_2N^{C2,TMS})Cl(THF)]$ **43** where $N_2{}^{TMS}N_{py} = MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ and $N_2N^{C2,TMS} = Me_3SiN(CH_2CH_2NSiMe_3)_2$ (Scheme 5). The corresponding reactions for the amino *N*-methylated two-carbon analogue $N_2N^{C2,Me}$ ($N_2N^{C2,Me} = MeN(CH_2CH_2NSiMe_3)_2$) or of the amino *N*-silylated three-carbon chain analogue $N_2N^{C3,TMS}$ ($N_2N^{C3,TMS} = Me_3SiN(CH_2CH_2CH_2NSiMe_3)_2$) afforded no tractable products. In contrast, reaction of $ScCl_3$ with the three-carbon chain species $Li_2N_2N^{C3,Me}$ ($N_2N^{C3,Me} = MeN(CH_2CH_2CH_2NSiMe_3)_2$) cleanly gave the THF-free dinuclear, chloride-bridged compound $[Sc_2(N_2N^{C3,Me})_2(\mu\text{-}Cl)_2]$ **44**.

Organometallic analogues with these tridentate diamide-donors have also been reported (Scheme 6). Reactions of $H_2N_2{}^{R'}N_{py}$ ($N_2{}^{R'}N_{py} = MeC(2\text{-}C_5H_4N)(CH_2NR')_2$ where R′ = SiMe$_3$, Tol or Mes) and $H_2N_2N^{C2,R'}$ (R′ = Me or SiMe$_3$) with $[ScR_3(THF)_2]$ (R = CH_2SiMe_3 or Ph) in benzene gave $[Sc(N_2{}^{R'}N_{py})R(THF)]$ (R = CH_2SiMe_3, R′ = SiMe$_3$, Tol or Mes; R = Ph, R′ = SiMe$_3$) and $[Sc(N_2N^{C2,R'})(CH_2SiMe_3)(THF)]$ (R′ = Me or SiMe$_3$). The alkyl derivative $[Sc(N_2{}^{TMS}N_{py})(CH_2SiMe_3)(THF)]$ could also be prepared by the reaction of **42** with $LiCH_2SiMe_3$. Reaction of $[Sc(CH_2SiMe_3)_3(THF)_2]$ with $H_2N_2N^{C3,Me}$ afforded no tractable product, and with $H_2N_2N^{C3,TMS}$ in deuterobenzene the labile compound $[Sc(N_2N^{C3,TMS})(CH_2SiMe_3)(THF)]$ was observed by ^1H NMR spectroscopy but could not be isolated.



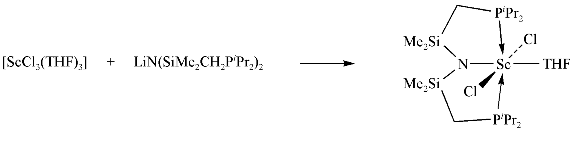
Scheme 5



Scheme 6

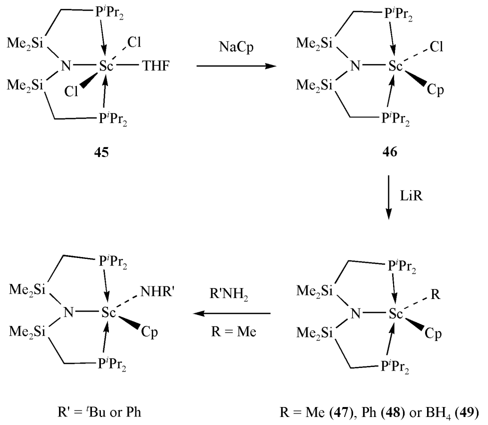
Compounds with amido-diphosphine ligands

Fryzuk *et al.* have recently reported on the use of an amido-diphosphine ligand to access new organoscandium chemistry.[45] Reaction of $LiN(SiMe_2CH_2P^iPr_2)_2$ with $[ScCl_3(THF)_3]$ in toluene at 100 °C affords the scandium dichloride complex $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}Cl_2(THF)]$ (**45**, eqn. (8)). Compound **45** can be alkylated to form dimethyl, diethyl, and bis(trimethylsilylmethyl) derivatives. However reaction of these with iodomethane, dihydrogen, carbon monoxide, nitriles, isonitriles and silanes were unsuccessful and gave rise to mixtures of products. Reaction of the neutral dialkyl compounds with ethylene afforded polyethylene.



(8)

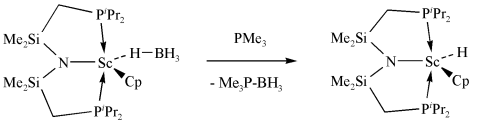
Reaction (Scheme 7) of the dichloride $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}Cl_2(THF)]$ (**45**) with one equivalent of NaCp gave $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}CpCl]$ (**46**) which in turn undergoes



Scheme 7

chloride metathesis reactions with lithium reagents RLi (R = Me, Ph or BH_4) to afford the compounds $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}CpR]$ (R = Me **47**, Ph **48**, BH_4 **49**).[46] The methyl compound **47** reacts with *tert*-butylamine or aniline to give the corresponding primary amido compounds $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}Cp(NHR')]$ (R′ = ^{t}Bu or Ph). These amido compounds were also prepared by the reaction of $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}CpCl]$ (**46**) with LiNHR′ (R = ^{t}Bu or Ph).

The reaction of $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}CpMe]$ **47** with ethylene gave polyethylene. The borohydride complex $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}Cp(BH_4)]$ (**49**) reacts with PMe_3 to afford $BH_3{\cdot}PMe_3$. It is presumed that the other product of the reaction is the scandium hydride complex $[Sc\{N(SiMe_2CH_2P^iPr_2)_2\}CpH]$ (**50**, eqn. (9)).



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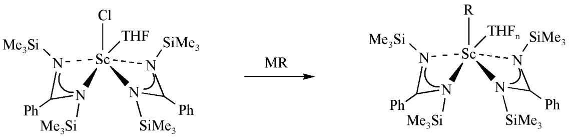
(9)

Scandium compounds with bidentate, monoanionic N,N′ donor ligands

Compounds with amidinate ligands

In 1996 Edelmann[47] and Arnold[48] independently reported the synthesis and chemistry of benzamidinate-supported scandium complexes. The complexes were synthesised by the reaction of two molar equivalents of the alkali metal salt of a benzamidinate ligand with $[ScCl_3(THF)_3]$ affording $[Sc\{PhC(NSiMe_3)_2\}_2Cl(THF)]$ (**51**). Arnold *et al.* went on to develop the reactions of **51** which afforded the compounds $[Sc\{PhC(NSiMe_3)_2\}_2R(THF)_n]$ (R = CH_2SiMe_3 **52**, NHAr **53** or BH_4 **54**) (eqn. (10)). Compound **52** reacts with trimethylsilylacetylene to



51

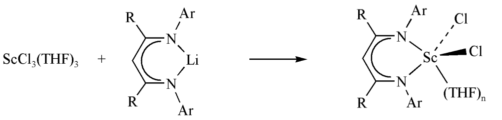
R = CH_2SiMe_3 (**52**), NH-2,6-$C_6H_3{}^iPr_2$ (**53**) or BH_4 (**54**)

(10)

afford the η^1-acetylide complex $[Sc\{PhC(NSiMe_3)_2\}_2(CCSiMe_3)]$, and with dihydrogen to afford the dinuclear hydride complex $[Sc_2\{PhC(NSiMe_3)_2\}_4(\mu\text{-}H)_2]$ (**55**). Diphenyl acetylene inserts into the Sc–H bond of **55** to give the metallated stilbene derivative $[Sc\{PhC(NSiMe_3)_2\}_2(\eta^1\text{-}C_2HPh_2)]$.

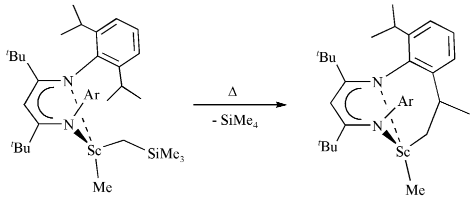
Compounds with β-diketiminato ligands

An area that has received considerable attention recently is the use of *N,N′*-disubstituted β-diketiminato ligands to develop organoscandium chemistry. Piers *et al.* have reported that reaction of Li[ArNC(R)CHC(R)NAr] (Ar = 2,6-$C_6H_3{}^iPr_2$, R = Me or ^{t}Bu) with $[ScCl_3(THF)_3]$ in refluxing toluene affords $[Sc\{ArNC(R)CHC(R)NAr\}Cl_2(THF)_n]$ (R = Me, n = 1 **56**; R = ^{t}Bu, n = 0 **57**) (eqn. (11)).[49] Piers has shown that the dichloride complex **56** can be readily alkylated with alkali metal alkyl reagents.[50] The base free dimethyl compound $[Sc\{ArNC(^tBu)CHC(^tBu)NAr\}Me_2]$ (**58**) undergoes conproportionation with the dichloride **57** to afford the monomethylmonochloride compound $[Sc\{ArNC(^tBu)CHC(^tBu)NAr\}(Cl)Me]$ which can in turn be alkylated with trimethylsilylmethyl lithium to give the mixed alkyl species $[Sc\{ArNC(^tBu)CHC(^tBu)NAr\}Me(CH_2SiMe_3)]$ (**59**). This alkyl compound is thermally unstable, and heating solutions of it in benzene-d_6 results in the elimination of $SiMe_4$ and intramolecular C–H activation of one of the aryl substituents on the ligand backbone forming **60** (eqn. (12)).



(11)

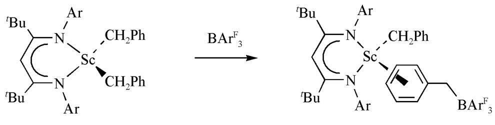
R = Me, n= 1 (**56**) or ^{t}Bu, n = 0 (**57**)



59 **60**

(12)

The dialkyl compounds $[Sc\{ArNC(^tBu)CHC(^tBu)NAr\}R_2]$ (R = Me **58** or CH_2Ph **61**) can be activated with BAr^F_3. Reaction of this borane with **61**[49] results in the formation of a contact ion pair **62** where the benzyl ligand that has been abstracted by the boron from the metal centre and has re-coordinated to the scandium in a π-type fashion (eqn. (13)).



61 **62**

(13)

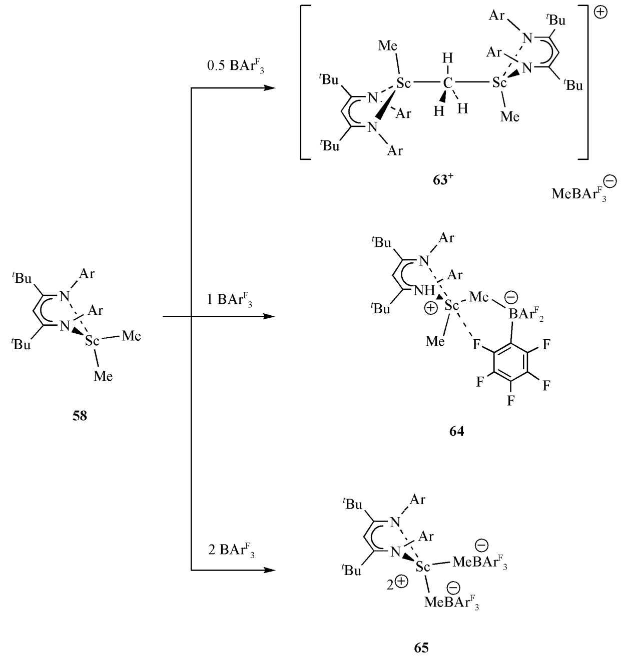
Reaction of the dimethyl compound $[Sc\{ArNC(^tBu)CHC(^tBu)NAr\}Me_2]$ (**58**) with varying amounts of BAr^F_3 results in a range of activated complexes (Scheme 8).[51] Reaction of **58** with 0.5 molar equivalents of borane affords the methyl-bridged cationic dimer $[Sc_2\{ArNC(^tBu)CHC(^tBu)NAr\}_2Me_2(\mu\text{-}Me)]^+$ (**63**$^+$, anion $[MeB(Ar^F)_3]^-$). Reaction with a single equivalent of borane results in a contact ion pair, where the $[MeBAr^F_3]^-$ anion stabilises the cationic scandium by coordination through a bridging methyl group as well as an *ortho*-fluorine interaction (**64**). Reaction of **58** with two molar equivalents of borane affords a complex (**65**) with two Sc-(μ-Me)-B linkages.

Roesky has also described the use of β-diketiminato ligands with chelating amine pendant arms.[52] Thus reaction of $[ScCl_3(THF)_3]$ with the lithium salt of such a β-diketiminato ligand affords the corresponding dichloride complex $[Sc\{Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2\}Cl_2]$, but attempts to prepare scandium alkyl complexes were unsuccessful. Reaction with $NaN(SiMe_3)_2$ resulted in the isolation of a dimeric complex which was the product of ligand degradation.

Scandium compounds with iminophenolate and bis(phenoxide) ligands

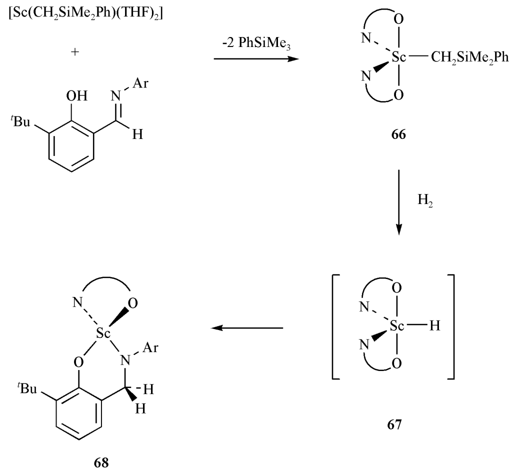
Compounds with iminophenolate ligands

The use of iminophenolate ligands in organoscandium chemistry is an area of research that has received little attention until



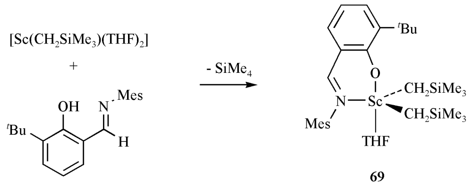
Scheme 8

very recently. The first example of this ligand type being used with scandium was reported by Piers *et al.*,[53,54] whereby reaction of $[\mathrm{Sc(CH_2SiMe_2Ph)_3(THF)_2}]$ with two equivalents of an iminophenol according to Scheme 9 affords the scandium alkyl compound $[\mathrm{Sc\{O\text{-}2,6\text{-}C_6H_3(^tBu)CHNAr\}_2(CH_2SiMe_2Ph)}]$ (**66**) (Ar = 2,6-$\mathrm{C_6H_3{}^iPr_2}$). Compound **66** reacts with dihydrogen to afford the transient hydride $[\mathrm{Sc\{O\text{-}2,6\text{-}C_6H_3(^tBu)CHNAr\}_2H}]$ (**67**) which undergoes insertion of the imine group of the ligand into the Sc–H bond giving **68**. Compound **66** also undergoes thermolysis which gives rise to C–H activation of one of the ligand *iso*-propyl groups which then rearranges to afford a heterocyclic amide complex.



Scheme 9

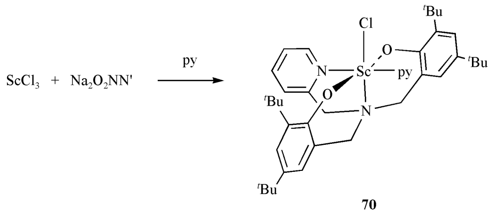
Bochmann has reported that the reaction of the scandium trialkyl $[\mathrm{Sc(CH_2SiMe_3)_3(THF)_2}]$ with a single equivalent of an iminophenol affords the scandium dialkyl complex **69** (eqn. (14)). This compound is active in the ring opening polymerisation of ε-caprolactone.[55]



(14)

Compounds with bis(phenoxide) ligands

Another group of tetradentate donor with similarities both to the diamidodiamine and to the iminophenolate ligands discussed above are the bis(phenoxide)diamine ligands. Mountford *et al.* have reported that the disodium salt $\mathrm{Na_2O_2NN'}$ (eqn. (15), $\mathrm{O_2NN'} = (2\text{-}\mathrm{C_5H_4N})\mathrm{CH_2N(CH_2\text{-}3,5\text{-}C_6H_2{}^tBu_2O)_2}$) reacts with $\mathrm{ScCl_3}$ in THF in the presence of pyridine to afford the chloride complex $[\mathrm{Sc(O_2NN')Cl(py)}]$ (**70**).[34] Reaction of compound **70** with $\mathrm{LiCH_2SiMe_3}$ in the presence of pyridine affords the alkyl derivative $[\mathrm{Sc(O_2NN')(CH_2SiMe_3)(py)}]$ (**71**). An easier route to the THF analogue of **71**, namely $[\mathrm{Sc(O_2NN')(CH_2SiMe_3)(THF)}]$ was *via* reaction of $[\mathrm{Sc(CH_2SiMe_3)_3(THF)_2}]$ with $\mathrm{H_2O_2NN'}$, with concomitant elimination of tetramethylsilane.



(15)

Scandium compounds with silsesquioxane ligands

Silsesquioxane ligands have received attention in the past as soluble models for silica-supported lanthanide (including yttrium) heterogeneous catalysts.[56,57,58] However, very recently there has been a report in the literature of these ligands being used for the first time to support scandium. Edelmann[59] has reported that reaction of $[\mathrm{Sc(\eta^5\text{-}C_5Me_5)(acac)_2}]$ with the cyclohexyl silsesquioxane derivative $\mathrm{(C_6H_{11})_7Si_8O_{12}OH}$ affords the dinuclear complex $[\mathrm{Sc_2\{\mu\text{-}(C_6H_{11})_7Si_8O_{12}O\}_2(acac)_4}]$, establishing that these ligand are suitable supports for scandium.

Concluding remarks

It is clear that organoscandium chemistry in a range of non-cyclopentadienyl environments has undergone huge advances over the last 10 years and an impressive range of compounds of various types have been prepared. While it is highly likely that further new (to scandium) ligand classes will continue to be developed, it is also evident that a major focus will and should be an exploration of the reaction (including catalytic) chemistry of these new systems.

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