A new family of monocyclopentadienyl organoscandium *bis*-alkyls supported by a bulky trialkylphosphine oxide ancillary[1]

Lee D. Henderson, Glen D. MacInnis, Warren E. Piers, and Masood Parvez

Abstract: Treatment of the oligomeric compound $[Cp^*ScCl_2]_n$ ($Cp^* = C_5Me_5$) with tri-*tert*-butylphosphine oxide in THF leads to the monocyclopentadienyl scandium dichloride $[Cp^*(t\text{-}Bu_3P{=}O)ScCl_2]$ as a monomeric, THF-free solid in 72% yield. This compound can be alkylated with MeLi to give the corresponding dimethyl derivative, $[Cp^*(t\text{-}Bu_3P{=}O)ScMe_2]$, **1**. The crystal structures of these two compounds have been done and reveal a three-legged piano stool geometry about the scandium center. The coordinated phosphine oxide ligand exchanges with free donor in both compounds via an associative mechanism, as indicated by the activation parameters ($\Delta H^{\ddagger}$ = 6.4–8.4 kcal mol^{-1}; $\Delta S^{\ddagger}$ = –22.5 to –26.6 eu). Thus, the $Cp^*(t\text{-}Bu_3P{=}O)$ ligand set provides a stable platform for organoscandium chemistry. This was demonstrated by the activation of **1** by treatment with $B(C_6F_5)_3$ to form the fully characterized contact ion pair $[Cp^*(t\text{-}Bu_3P{=}O)ScMe]^+[MeB(C_6F_5)_3]^-$, **2**, which is an active ethylene polymerization catalyst.

Key words: organoscandium compounds, olefin polymerization, cationic complexes.

Résumé : Le traitement du produit oligomère $[Cp^*ScCl_2]_n$ ($Cp^* = C_5Me_5$) avec de l'oxyde de tri-*tert*-butylphosphine, dans le THF, conduit à la formation du dichlorure de monocyclopentadiénylscandium, $[Cp^*(t\text{-}Bu_3P{=}O)ScCl_2]$, isolé avec un rendement de 72 %, sous la forme monomère et exempt de THF. Ce composé peut être alkylé avec du MeLi pour donner le dérivé diméthylé correspondant, $[Cp^*(t\text{-}Bu_3P{=}O)ScMe_2]$, **1**. On a déterminé les structures cristallines de ces deux composés qui comportent une géométrie en banc de piano à trois pattes autour du centre scandium. Le ligand oxyde de phosphine qui est coordiné s'échange avec un donneur libre dans les deux composés, par le biais d'un mécanisme associatif suggéré par les paramètres d'activation ($\Delta H^{\ddagger}$ = 6,4 à 8,4 kcal mol^{-1}; $\Delta S^{\ddagger}$ = –22,5 à –26,6 ue). Ainsi, l'ensemble de ligand $Cp^*t\text{-}Bu_3P{=}O$ fournit une plate-forme stable pour la chimie de composés organiques du scandium. Ceci a été démontré par l'activation de **1** par traitement avec du $B(C_6F_5)_3$ qui conduit à la formation de la paire d'ions de contact complètement caractérisé, $[Cp^*(t\text{-}Bu_3P{=}O)ScMe]^+[MeB(C_6F_5)_3]^-$ (**2**), qui est un catalyseur actif pour la polymérisation de l'éthylène.

Mots clés : composés organiques du scandium, polymérisation des oléfines, complexes cationiques.

[Traduit par la Rédaction]

Introduction

Suitable ligand environments for group 3 metal bis-alkyl functions free from occluded salts or coordinating solvent molecules are rare; this lack of abundance has prevented development of the chemistry of organo group 3 dialkyls to the same degree as the extensively explored group 4 dialkyls (1). A notable exception is the bulky β-diketiminato (nacnac) ligand framework (**A**) and related structures (2), which supports the chemistry of base-free scandium dialkyls (3) and cationic scandium alkyls (4) but cannot eliminate the need for THF ligation in analogous organoyttrium chemistry (5). Despite the success of this ligand ancillary and its derivatives (6), new environments are of interest in the continued expansion of this area of early transition-metal organometallic chemistry.

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Dedicated to Professor Edward Piers on the occasion of his 65th birthday and for his many contributions to chemistry in Canada.

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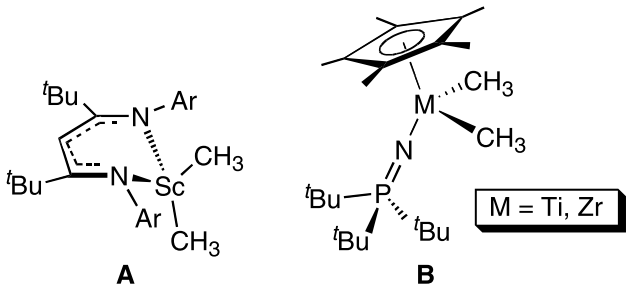

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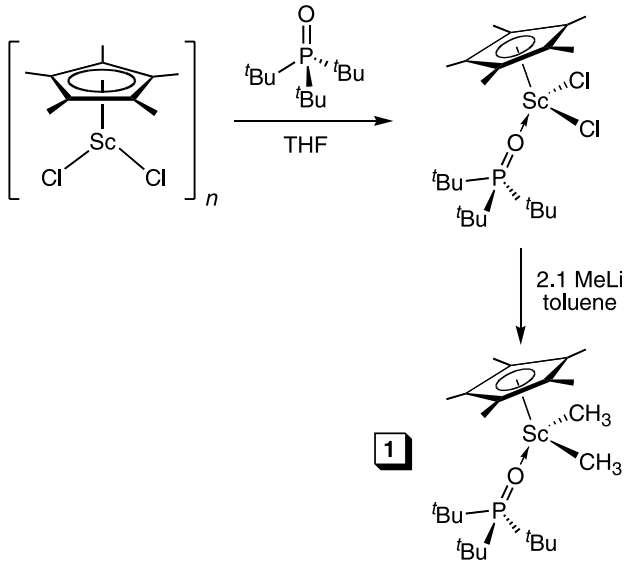
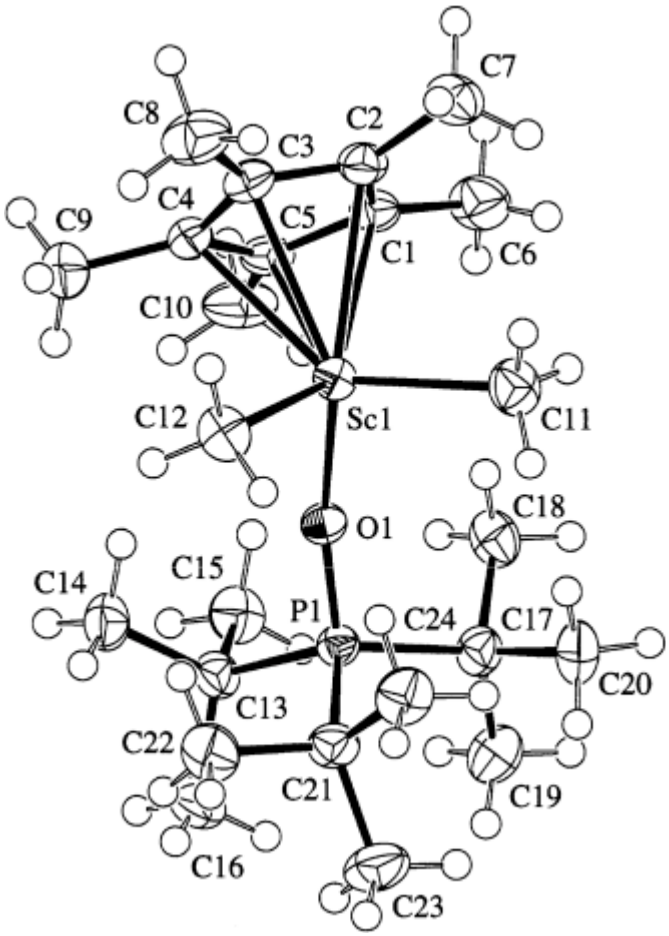
Scheme 1.



Inspiration for possible organo group 3 ligand environments can be found in successful areas of group 4 metal chemistry. Stephan and co-workers (7) and others (8) have demonstrated the efficacy of the bulky phosphinimide ligand t-$Bu_3P{=}N^-$ as a steric replacement for the Cp* ligand ($C_5Me_5^-$), following a strategy originally tendered by Wolczanski and co-workers (9) and embodied in the tri-*tert*-butylmethoxide "tritox" ligand system. Thus, the organotitanium and zirconium compounds **B** are sterically analogous to the more well-known permethylmetallocenes but with a somewhat more open environment in the immediate vicinity of the metal center, which confers high reactivity. Since dialkyl group 3 chemistry requires a monoanionic ancillary ligand set, either the Cp* or the phosphinimide ligand must be neutralized to transfer this general ligand environment to scandium or yttrium. Herein we describe the preparation and some preliminary chemistry of [Cp*(t-$Bu_3P{=}O$)$ScMe_2$], **1**, a new THF-free organoscandium dimethyl complex incorporating a bulky phosphine oxide ligand as a Cp* equivalent.

The synthesis of **1** is straightforward and shown in Scheme 1.[4] Treatment of $[Cp^*ScCl_2]_n$ (10), which possesses an ill-defined oligomeric structure, with t-$Bu_3P{=}O$ (11) leads to deoligomerization and formation of [Cp*(t-$Bu_3P{=}O$)$ScCl_2$] in good yield on a multigram scale. Downfield shifts in the ^1H and ^{31}P NMR spectra (by 0.18 ppm and 24.5 ppm, respectively) are observed for the coordinated t-$Bu_3P{=}O$ relative to the free ligand, mirroring trends observed in other $R_3P{=}O$ coordination compounds of scandium (12). Notably, the material is isolated free of THF even though the reaction is performed in this normally persistent solvent, attesting to the steric satisfaction provided by the Cp* – phosphine oxide combination to the Lewis-acidic scandium center. The dichloride is readily methylated when treated with MeLi in toluene, giving **1** in 45% isolated yield

Fig. 1. Molecular structure of [Cp*(t-$Bu_3P{=}O$)$ScMe_2$], **1**, with hydrogen atoms omitted for clarity. Selected metrical parameters are given below; numbers in parentheses are analogous distances and angles for [Cp*(t-$Bu_3P{=}O$)$ScCl_2$]. Distances (Å): Sc(1)—$Cp^*_{centroid}$, 2.21(1) (2.159(4)); Sc(1)—O(1), 2.072(1) (2.0373(1)); Sc(1)—C(11), 2.251(2) (Sc(1)—Cl(1), 2.3906(6)); Sc(1)—C(12), 2.252(2) (Sc(1)—Cl(2), 2.3995(5)); O(1)—P(1), 1.5225(13) (1.5336(10)). Angles (°): Sc(1)-O(1)-P(1), 162.09(8) (161.12(6)); O(1)-Sc(1)-C(11), 103.22(7) (101.01(3)); O(1)-Sc(1)-C(12), 100.16(7) (100.02(3)); C(11)-Sc(1)-C(12), 104.48(8) (105.54(2)).

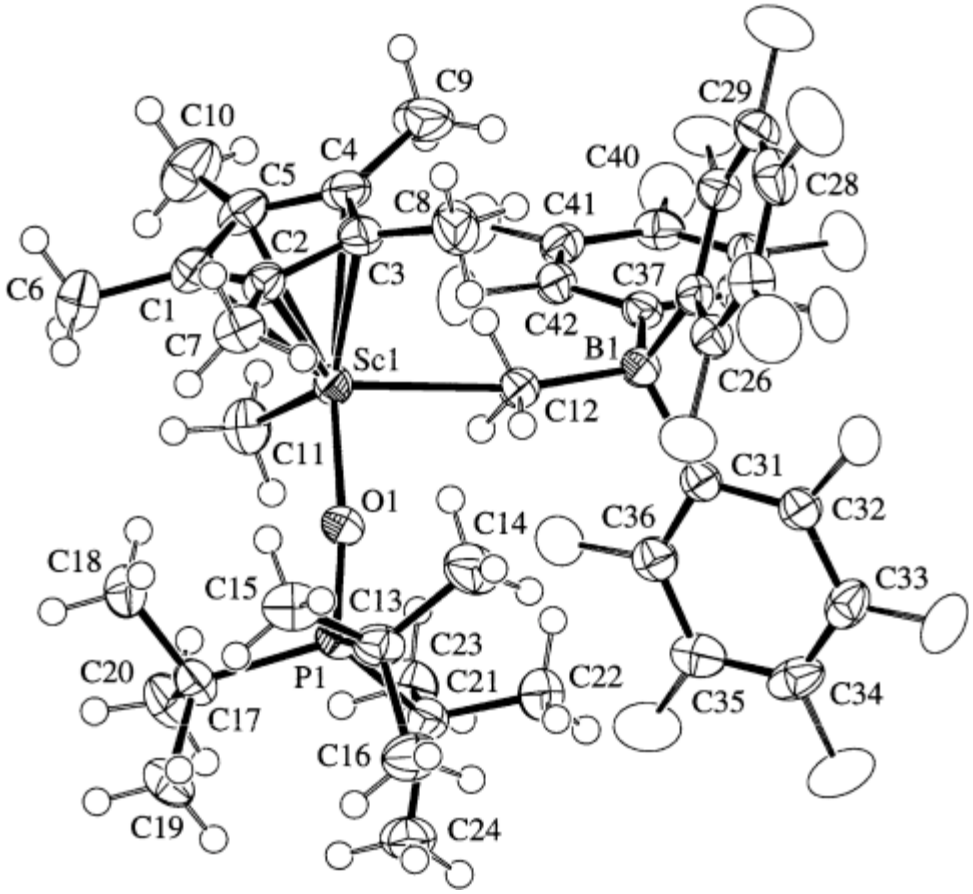


(^1H NMR (Sc—Me) = –0.36 ppm; ^{31}P NMR = 82.2 ppm). Care must be taken not to expose this compound to excess MeLi, to avoid the formation of a side product that we believe to be the scandate complex $[Cp^*ScMe_3]^-[Li]^+$.

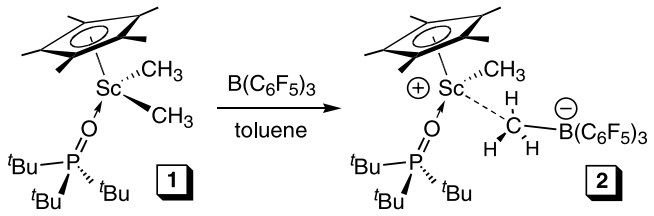
Both **1** and its dichloride precursor are monomeric in the solid state as determined by X-ray crystallography; the structure of **1** is shown in Fig. 1, along with selected metrical parameters for both compounds for comparative purposes. The structures are grossly similar to that reported for [Cp*(t-$Bu_3P{=}N$)$TiCl_2$] (7*a*), with the phosphine oxide ligand occupying a roughly equivalent region of coordination space to that of the Cp* ligand in a tetrahedral environment. The

[4] Full experimental details on the synthesis and characterization of new compounds can be found in the Supporting information. Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 215982–215984 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 2. Molecular structure of $[Cp^*(t\text{-}Bu_3P{=}O)ScMe]^+[MeB(C_6F_5)_3]^-$, **2**, with hydrogen atoms omitted for clarity. Selected bond distances (Å): Sc(1)—$Cp^*_{centroid}$, 2.155(1); Sc(1)—O(1), 2.0370(13); Sc(1)—C(11), 2.201(2); Sc(1)—C(12), 2.529(11); O(1)—P(1), 1.536(13); B(1)—C(12), 1.658(7). Selected bond angles (°): Sc(1)-O(1)-P(1), 167.49(8); Sc(1)-C(12)-B(1), 170.00(11); O(1)-Sc(1)-C(11), 102.10(7); O(1)-Sc(1)-C(12), 95.06(5).



Scheme 2.



Sc(1)-O(1)-P(1) angles are about the same for both compounds and are bent slightly away from the Cp* ligand. The Sc(1)—O(1) distances are comparable with those of other phosphine oxide complexes of scandium (12) and intermediate between the typical distances for scandium alkoxides (≈1.90 Å (13)) and scandium ethers (≈2.20 Å (14)). In **1**, the Sc(1)—O(1) distance is elongated relative to the dichloride, reflecting the lower Lewis acidity of the Cp^*ScMe_2 fragment.

Despite the accessibility of these new organoscandium compounds, the dative nature of the phosphine oxide – scandium linkage raises concerns about the kinetic stability of this ligand and its suitability as an ancillary. Indeed, for both the dichloride and **1**, the coordinated $t\text{-}Bu_3P{=}O$ ligand exchanges with free ligand on the NMR timescale. The barriers to exchange, as measured by the coalescence method (15) using variable temperature ^1H NMR spectra, was 11.9(5) kcal mol^{-1} (253 K) for $[Cp^*(t\text{-}Bu_3P{=}O)ScCl_2]$ and 17.7(5) kcal mol^{-1} (363 K) for the less Lewis-acidic dimethyl derivative **1**. The activation parameters were determined by analysis of the rate constants at various temperatures using EXSY methods (16) and the $\Delta S^{\ddagger}$ values are –22.4(8) and –26.6(6) eu for the dichloride and **1**, respectively. These values are consistent with an associative mechanism for ligand exchange and indicate that the compounds are stable towards dissociation of the ligand under ambient conditions. It should be noted, however, that compound **1** decomposes to unknown products when heated to temperatures above 80 °C in toluene, a process that is accelerated in the donor solvent THF.

Treatment of **1** with 1 equiv of $B(C_6F_5)_3$ in toluene leads to a soluble contact ion pair, $[Cp^*(t\text{-}Bu_3P{=}O)ScMe]^+[MeB(C_6F_5)_3]^-$, **2** (Scheme 2), demonstrating that the Cp^*–$t\text{-}Bu_3P{=}O$ ligand set can deliver a stable platform for organometallic chemistry. Although phosphine oxide adducts of $B(C_6F_5)_3$ are known (17), the ^{11}B NMR chemical shift for **2** (–15.2 ppm) and the small difference between the *meta* and *para* fluorine signals in the ^{19}F NMR spectrum ($\Delta_{m,p}$ = 4.1 ppm (18)) clearly establishes **2** as a contact ion pair deriving from methide abstraction (19). Separate, nonexchanging signals for Sc-Me (–0.07 ppm) and B-Me (1.09 ppm, br) in-

dicate that this abstraction is irreversible, at least on the NMR timescale; a similar lack of Sc-Me–B-Me exchange is observed in the organoscandium methyl cation of complex **A** (4*b*). The structure was confirmed by X-ray analysis of colourless crystals of **2** grown from toluene; an ORTEP diagram is shown in Fig. 2, along with selected distances and angles. The carbon-boron distance in the anion is 1.658(7) Å, comparable with that observed in the contact ion pair formed from the β-diketiminato complex **A** (4*b*). In contrast to the nacnac system, however, there are no close Sc···F contacts, and the Sc(1)···C(12) contact of 2.529(11) Å is much closer than the 2.703(6) Å observed in the ion pair formed from **A**. In addition, the B(1)-C(12)-Sc(1) angle of 170.00(11)° is more characteristic of a metallocenium ion pair (19). The decreased steric congestion about scandium relative to **1** allows for a slightly more linearly coordinated phosphine oxide ligand (Sc(1)-O(1)-P(1) = 167.49(8)°).

Compound **2** is relatively thermally stable in solution, and preliminary experiments indicate that **2** is a highly active ethylene polymerization catalyst at room temperature and 1 atm (1 atm = 101.325 kPa) of ethylene (1.3×10^5 g mol^{-1} h^{-1} of polyethylene). However, polymerizations carried out at higher temperatures indicated a decline in activity presumably due to catalyst decomposition, either thermally or via catalyst interaction with the solvent and with monomer feed scrubbers present in the medium.

In summary, we have prepared a new dimethyl scandium derivative with a ligand environment that mimics the metallocene set (20) but provides two reactive hydrocarbyl ligands with which to develop new organoscandium chemistry. The facile preparation of these novel compounds offers an opportunity to open new areas of organoscandium chemistry.

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