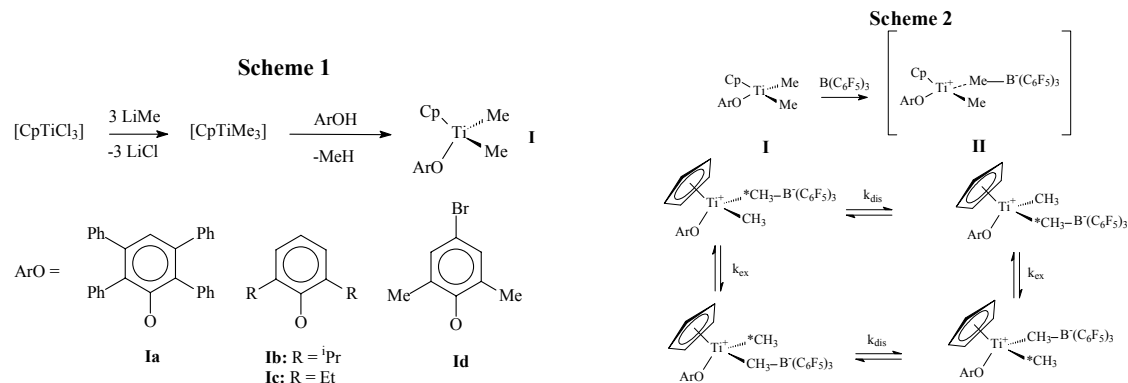


Research results are the areas of catalyst precursor synthesis, catalyst fluxionality, catalyst stability, polymerization of α -olefins as well as the chemistry of Group IV and Group V metal centers with aryloxide and arylsulfide ligands.

Synthesis and Activation of Titanium Catalyst Precursors.

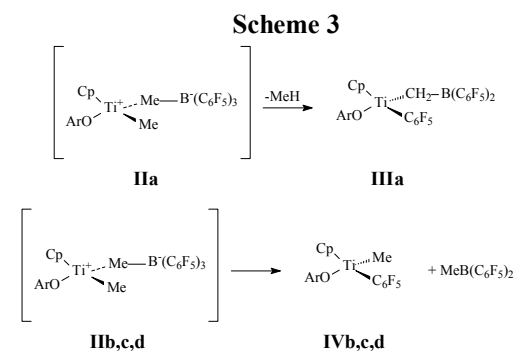
A more efficient route to the synthesis of the titanium dimethyl precursors (**I**) has been developed. This procedure has allowed the synthesis of a large number of aryloxide and arylsulfide compounds. Substrates which have been the focus of detailed study are shown in **Scheme 1**.



Activation of these dimethyl compounds with $[B(C_6F_5)_3]$ leads to a series of cationic methyl compounds (**II**) which will polymerize a range of olefins. In aromatic hydrocarbon solvents, the fluxionality of these catalysts has been studied by 1H NMR spectroscopy. The activation energy for the exchange of methyl groups between boron and titanium has been measured (**Scheme 2**). Furthermore it has recently been observed that incomplete activation results in a mixture of substrate dimethyl and cationic methyl titanium compounds (**I + II**) which undergo complete scrambling of methyl signals.

Catalyst Deactivation.

We have identified two distinct processes for the deactivation of these catalysts. The deactivation pathway is dependent on the nature of the ancillary aryloxide ligand. With bulky 2,3,5,6-tetraphenylphenoxides, a clean first order elimination of methane occurs with formation of a discrete organometallic product (**III**, **Scheme 3**). This compound is inactive for any further reaction with olefin or activator. VT-NMR studies of the kinetics of this decomposition were undertaken, and the enthalpy and entropy of activation were estimated to be 15.8(5) kcal mol⁻¹ and -22(5) cal mol⁻¹ K⁻¹, respectively. In contrast the decomposition of the 2,6-dimethyl-4-bromo, 2,6-diethyl and 2,6-di-isopropylphenoxides occurs to produce the monomethyl compound **IV**, (**Scheme 3**) via C_6F_5 abstraction from the anion. The kinetics of this process are complicated as C_6F_5 abstraction can also occur from the $[MeB(C_6F_5)_2]$ intermediate (**Scheme 3**).



Polymerization Studies.

We have focused our initial polymerization studies on the polymerization of 1-hexene by the four catalysts **Ia-d**. Kinetic studies of the polymerization of 100 equivalents by NMR spectroscopy show dramatic aryloxide dependence. The 2,3,5,6-tetraphenylphenoxide **Ia** rapidly polymerizes the olefin even at -30 °C. As the bulk of the aryloxide decreases, so the rate of polymerization decreases. At ambient temperature, catalysts **Ib**, **Ic** and **Id**, do not completely consume the olefin due to the deactivation process outlined above. Analysis of the

Table 1 Characterization of poly(1-hexene) made by [CpTi(OAr)Me₂]/[B(C₆F₅)₃] catalyst systems.

Catalyst precursors	poly(1-hexene)								
	25 °C			0 °C			-30 °C		
	k _{obs} (s ⁻¹)	M _n (Dalton)	PDI	k _{obs} (s ⁻¹)	M _n (Dalton)	PDI	k _{obs} (s ⁻¹)	M _n (Dalton)	PDI
Ia	N/A	12,100	1.14	N/A	12,500	1.1	2.7 x 10 ⁻³	12,600	1.09
Ib	N/A	5,000	1.60	2.1 x 10 ⁻³	6,600	1.36	3.5 x 10 ^{-4a}	6,800 ^a	1.24 ^a
Ic	N/A	4,600	1.81	1.9 x 10 ⁻³	5,500	1.49	4.4 x 10 ^{-4a}	4,600 ^a	1.36 ^a
Id	N/A	2,500	1.91	7.0 x 10 ⁻⁴	3,300	2.08	9.5 x 10 ⁻⁵	3,000	1.52

Note: ^a Polymerization was carried out at -20 °C.

polymers obtained in this kinetic study (**Table 1**) show narrow polydispersities and an increase in polymer molecular weight as the bulk of the aryloxide increases.

Isolation and Chemistry of Tantalum(V) Complexes of

Optically Active 3,3'-Disubstituted-1,1'-bi-2,2'-Naphthoxide Ligands.

Chiral complexes offer the promise of inducing asymmetric transformations, and accordingly we set out to synthesize tantalum complexes of optically resolved, chelating 1,1'-bi-2,2'-naphthyloxy ligands bearing substituents in the 3,3' positions. Preparations were successful when dimethyl amido ligands served as the leaving groups. In particular, we isolated several *cis*-dichloro-bis(binaphthoxido)tantalate(V) complexes as diethylammonium salts. Interestingly, ¹H-NMR studies suggest that the tantalum complexes remain six-coordinate in DMSO-d₆, but that they are in equilibrium with the neutral five-coordinate form in benzene-d₆. In line with this model, treatment with excess diethylammonium chloride will shift the equilibrium toward the dichloro complex. On the other hand, treatment with one eq. of (trimethylsilyl)methyl-Grignard per chloride leads to formation of the five-coordinate, mono-alkyl complex along with one eq. of TMS. Thus, we have charted viable pathways for the preparation of catalyst precursors of tantalum involving chiral, binaphthoxido ligands with a variety of co-ligands and different coordination geometries.

The Nature of Aryloxide and Arylsulfide Ligand Bonding in Dimethyltitanium Complexes Containing Cyclopentadienyl Ligation.

Cyclopentadienyl (Cp) ligation is ubiquitous in group 4 organometallic chemistry. Since the introduction of Cp₂TiCl₂ in 1953, the broad applicability of titanocenes has been studied for derivatives containing a range of alkyl, aryl, and heteroatom-substituted Cp rings, as well as ansa-titanocenes that have the two Cp rings linked by a bridging group. We have previously reported bis(aryloxide) titanium and zirconium compounds of the type [(ArO)₂MR₂] (R=Me, CH₂Ph) and mixed Cp/aryloxide titanium compounds of the type CpTi(OAr)R₂ (R=Me, CH₂Ph). The aryloxide ligand can adopt a bonding motif isolobal with that of cyclopentadienyl, potentially bonding in a σ²π⁴ fashion. A key property of these ligands is their tunability, as a wide collection of phenols offering a unique and diverse set of steric and electronic alternatives

are commercially available or can be readily synthesized. Given the abundance of $\text{CpTi}(\text{OAr})\text{R}_2$ complexes, we are not aware of any examples of $\text{CpTi}(\text{SAr})\text{R}_2$ analogues being synthesized or characterized. In this paper, we have reported the syntheses of novel $\text{CpTi}(\text{SAr})\text{Me}_2$ complexes where $\text{SAr} = \text{SC}_6\text{H}_2\text{Me}_{3-2,4,6}$ and $\text{SC}_6\text{H}_2^1\text{Pr}_{3-2,4,6}$ along with their x-ray crystal structures. Through a collaboration with the Chemical Engineering Department at Purdue University, we have performed DFT calculations on $\text{CpTi}(\text{OAr})\text{Me}_2$ and $\text{CpTi}(\text{SAr})\text{Me}_2$ complexes. Comparisons between Ti-O and Ti-S bonding have been made. Bonding in the arylsulfide systems was found to be significantly different from bonding in the aryloxy systems. The aryloxy ligands exhibited wide Ti-O-Ar angles (≥ 150 degrees) with the Ar group oriented proximal to the Cp group. DFT computations revealed two conformers for the arylsulfide systems. Arylsulfides with the Ar group proximal to the Cp group had a predicted Ti-S-Ar angle of ~ 120 degrees while those with the Ar group distal to the Cp group had a measured and predicted Ti-S-Ar angle of ~ 100 degrees. The titanium arylsulfide ligand bond is primarily a covalent sp^3 hybridized single bond with two lone pairs residing on the sulfur atom. In contrast to the titanium arylsulfide bond, the titanium aryloxy bond is primarily sp hybridized, and three of the oxygen lone pairs interact weakly with the titanium metal center.

Alkylation of Mixed Halide and 2,6-Diarylphenoxide Complexes of Niobium and Tantalum.

Mixed chloro-aryloxy complexes of niobium and tantalum [$\text{M}(\text{OAr})_x\text{Cl}_{5-x}$] are important starting materials in the chemistry of these elements. For example, we have demonstrated that they are useful precursors for reagents capable of activating unsaturated organic substrates. They also react to provide d^0 -alkyl and hydrido-aryloxides useful for effecting hydrogenation of simple arenes and aryl-phosphines. By means of Grignard reagents, we have thoroughly investigated the stepwise alkylation of a series of niobium and tantalum chloro-alkoxide complexes in the current grant period.

All chlorides of the type $\text{Ta}(\text{OAr})_2\text{Cl}_3$ adopt a square pyramidal (sp) geometry whereas tris-alkyl analogues characteristically assume a trigonal bipyramidal (tbp) geometry. We have characterized a series of dichloro-mono(benzyl) and chloro-bis(benzyl) derivatives and determined that they, too, adopt a tbp geometry. In contrast, derivatives obtained with one equivalent of cyclopentyl- or cyclohexyl-Grignard assume a sp geometry with the carbon donor in an axial coordination position. Treatment of the corresponding $\text{Ta}(\text{OAr})_2\text{Cl}_3$ complex with benzyl-Grignard yielded a mixture of products including a monochlor-bis(benzyl) complex isomorphous with the tantalum analogue. Other products formed included an alkyl, alkylidene and a bis(alkyl) niobium(IV) complex. Hydrogenolysis of a mixture of the latter complexes in the presence of PMe_3 led to isolation of a all-*trans*, six-coordinate, d^1 niobium(IV) bis(hydrido)-bis(aryloxy)-bisphosphine complex. The complex exhibits a ten-line ESR signal (^{93}Nb , $I=9/2$), and it gives a single $\nu(\text{Nb-H})$ stretching vibration in the infrared spectrum. In all, we have reported a half-dozen or more crystal structures in the course of this work.

Publications.

- 1) Formation of Neutral and Cationic Methyl Derivatives of Titanium Containing Cyclopentadienyl and Aryloxy Ancillary Ligation. Fenwick, A. E.; Phomphrai, K.;

- Thorn, M. G.; Vilardo, J. S.; Trefun, C. A.; Hanna, B.; Fanwick, P. E.; Rothwell, I. P. *Organometallics*, **2004**, *23*, 2146-2156.
- 2) Structural and stereochemical aspects of the group 4 metal chemistry of constrained-geometry 2-(indenyl)phenoxide ligation. Turner, L.E., Thorn, M.G., Fanwick, P.E., and Rothwell, I.P. *Organometallics*, **2004**, *23*, 1576-1593.
 - 3) The nature of aryloxide and arylsulfide ligand bonding in dimethyltitanium complexes containing cyclopentadienyl ligation. Manz, T.A., Fenwick, A.E., Phomphrai, K., Rothwell, I.P., and Thomson, K.T. *Dalton Transactions*, **2005**, 668-674.
 - 4) Polymerization of 1-hexene by cationic methyl derivatives of half-sandwich aryloxide titanium complexes; Aryloxide dependent activity and deactivation. Phomphrai, K.; Fenwick, A. E.; Fanwick, P. E.; Rothwell, I. P. *Manuscript in preparation*.
 - 5) Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. A germanium-silver complex containing a Ge-Ag bond, Ag[Ge(OC₆HPh₄-2,3,5,6)₃-(AgOSO₂CF₃)]·4C₆H₆. *Acta Cryst.* **2002**, *E58*, m718-m720.
 - 6) Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. Novel germanium(II) binaphthoxide complexes: synthesis and crystal structure of (*R,R*)-[Ge{OC₂₀H₁₀(OSiMe₃)-2'-(SiMe₃)₂-3,3'}₂] and (*R*)-[Ge{O₂C₂₀H₁₀(SiMe₂Ph)₂-3,3'}{NH₃}]; catalytic function of Ge[N(SiMe₃)₂]₂ for the mono-silylation of 3,3'-disubstituted-1,1'-bi-2,2'-naphthols. *J. Chem. Soc., Dalton Trans.* **2002**, 2948–2950.
 - 7) Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. Isolation and chemistry of Tantalum(V) compounds containing two resolved 3,3'-disubstituted-1,1'-bi-2,2'-naphthoxide ligands. *Organometallics* **2002**, *21*, 484-490.
 - 8) Schweiger, S. W.; Salberg, M. M.; Pulvirenti, A. L.; Freeman, E. E.; Fanwick, P. E.; Rothwell, I. P. Studies of the alkylation of niobium and tantalum halides containing 2,6-diarylphenoxide ancillary ligation. *J. Chem. Soc., Dalton Trans.* **2001**, 2020–2031.