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Chelating Aryloxide Ligands in the Synthesis of Titanium, Niobium, and Tantalum Compounds: Electrochemical Studies and Styrene Polymerization Activities

Lucyna Michalczyk,[1a] Susan de Gala,[1b] and Joseph W. Bruno*,[1a]

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459, and Department of Chemistry, Yale University, New Haven, Connecticut 06511

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The chelating trisphenol ligands tris(2-hydroxyphenyl)amine (**1**H_3) and tris(2-hydroxy-4,6-dimethylbenzyl)amine (**2**H_3) proved to be excellent precursors for the chelating phenoxides, and the latter has been used to prepare a series of cyclopentadienylmetal derivatives of early transition metals. For niobium and tantalum, reactions with $CpMCl_4$ lead to the compounds CpMCl(**1**) and CpMCl(**2**). An X-ray diffraction study of CpNbCl(**1**) establishes a pseudo-octahedral structure with a *trans* disposition of the η^5-cyclopentadienyl ring and the nitrogen atom of the chelating ligand. Similar reactions of $CpTiCl_3$ lead to the CpTi(**1**) and CpTi(**2**) analogues. Electrochemical experiments provide useful information on the reduction potentials of the compounds, from which it is clear that ligand **2** is a stronger donor than is **1**. At the same time, it appears that chelate ring size is important; while the reduction of complexes containing **1** are largely reversible, those of complexes containing **2** are irreversible. This is interpreted to mean that the six-membered rings in the latter are opening during reduction, a process involving formal loss of an aryloxide from the metal center. In an attempt to correlate this solution reactivity with catalytic efficiency in a bond-forming process, the compounds were screened for activity as styrene polymerization catalysts in the presence of methylaluminoxane cocatalyst. While the niobium and tantalum analogues were inactive, the titanium compounds of **1** showed high activity and appreciable selectivity for the preparation of syndiotactic polystyrene.

Introduction

Aryloxides are extremely versatile ligands for transition metals since proper ring substitution patterns allow for substantial modification of steric and electronic properties.[2,3] As a result, they have been utilized extensively in the preparation of group IV[4] and group V[5−7] compounds, for which a variety of tetravalent and pentavalent compounds are known. Rothwell has shown that the use of sterically demanding aryloxides can lead to unimolecular compounds of general formula $M(OAr)_xCl_{5-x}$ and that niobium and tantalum aryloxides can support a variety of complex geometries.[5−7] In addition, aryloxides have proven useful as ancillary ligands in the production of metal hydrides, compounds containing the hard base aryloxides and the soft, polarizable hydride ligands.[6,8,9] These and related compounds have been used extensively in the stereospecific hydrogenation of arene rings[3,8,10] and in a variety of intramolecular C−H activation reactions.[11]

While aryloxides are usually used to stablize high oxidation states, it has proved possible to prepare low-valent derivatives exhibiting a range of oxidation states.[12,13] Likewise, related low-valent siloxide derivatives are known; Wolczanki's use of $(tert\text{-butyl})_3SiO-$ (silox) ligands[14] has allowed the isolation of $(silox)_3Ta$,[15,16] a highly unsaturated and reactive Ta(III) compound. This species is known to engage in a variety of bond

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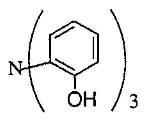
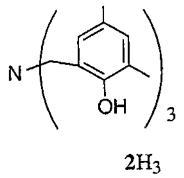
activation processes; most notable of these is the facile scission of carbon monoxide into dicarbide and oxo groups.[17] While the corresponding niobium compound has eluded isolation, the adduct (silox)$_3$Nb(η^2-C,N-picoline) serves as a convenient source of this compound.[16] The niobium analogue has also been seen to engage in interesting processes involving atom transfer and heterocycle ring opening.

Chelated aryloxides have also been applied to the synthesis of useful niobium and tantalum compounds. The most intriguing of these are derivatives containing the calix[4]arene ligand and substituted derivatives. These species have been prepared for niobium[18]and tantalum[19] and have exhibited a range of useful chemistries. In the compounds Cp*Ta(calix[4]arene) the calixarene ligand leaves open a coordination site *trans* to the Cp*, and a variety of small ligands have been coordinated at this position. In addition, the calixarene bowl also allows for the addition of larger molecules, and inclusion complexes have been prepared in this way.[19] More recently, Floriani has shown that the niobium derivatives may be reduced and that the low-valent niobum calixarene derivatives are highly effective in the scission of nitrogen[20] and carbon monoxide[21] ligands.

The foregoing examples demonstrate the versatility of aryloxides of the group IV and V elements, for which the chelated derivatives are particularly effective in bond scission processes. We are interested in pursuing bond-forming reactions such as alkene polymerization and reductive coupling reactions, processes for which we anticipate the need for multiple *cis* coordination sites at the metal. For this reason we have initiated a study of chelating ligands containing aryloxide moieties, systems designed to incorporate the useful features of aryloxide coordination while linking the donor sites. We sought the use of trivalent ligands so as to provide for the inclusion of two additional (formally anionic) ligands within the metal coordination sphere. This has led us to consider the use of atrane[22] molecules derived from tris(2-hydroxyphenyl)amine (**1**H$_3$)[23] and tris(2-hydroxy-4,6-dimethylbenzyl)amine (**2**H$_3$).[24] Like the calix[4]arenes, these ligands are constrained to coordinate in one hemisphere of a metal coordination sphere, and the resulting complexes constitute good models for metal centers supported on an oxide surface. Ligands **1** and **2** have been used effectively in main group chemistry, and there are derivatives showing that the nitrogen center may be bound or free;[25] we are unaware of any applications involving transition metals, although a recent report indicates that the related compound triethanolamine adds to a Cp*Ti compound to give an active polymerization catalyst.[26] As an initial study of the use of aryloxide derivatives, we have prepared complexes of **1** and **2** with titanium, niobium, and tantalum; the goals of this study were to characterize ligand binding, understand the relative donor power of the ligands, and correlate these data with solution reactivity for the related group IV and group V compounds. Herein we describe these syntheses, a structural study, the use of voltammetric techniques to probe the electronics of ligand binding, and studies of the complexes in catalytic styrene polymerization.



1H$_3$



2H$_3$

Experimental Section

General Considerations. All manipulations involving metal complexes were carried out under an atmosphere of nitrogen which was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques were used to handle solutions, and solids were transferred in a Vacuum Atmospheres Corp. glovebox under purified nitrogen. Solvents toluene, hexane, and tetrahydrofuran (J.T. Baker) were distilled from sodium benzophenone ketyl under nitrogen. NbCl$_5$, TaCl$_5$, ZrCl$_4$, and TiCl$_4$ (Aldrich) were commercial materials and used as supplied. Compounds **1**H$_3$,[23] **2**H$_3$,[24] CpNbCl$_4$,[27] CpTaCl$_4$,[27] and CpTiCl$_3$[27] were prepared using literature methods.

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NMR spectra were obtained on a Varian Gemini 300 FT-NMR instrument, infrared spectra on a Perkin-Elmer Model 1600 FT-IR spectrophotometer, and voltammetric data with an EG&G VersaStat potentiostat interfaced to a PC. The electrolytic cell was evacuated on a Schlenk line and then loaded with a solution of 0.25 M $NBu_4^+PF_6^+$ in THF. The reference electrode was prepared by inserting a short (ca. 1/4 in.) length of 5 mm porous Vycor into a Teflon tube. This was filled with 0.1 M $AgNO_3/CH_3CN$ solution, into which a 16 gauge silver wire was immersed. The working electrode was a platinum disk, and the counter electrode was a platinum wire. The electrolytic solution was maintained under a nitrogen atmosphere by passing THF-saturated nitrogen through the cell. Background data were recorded for the solvent/electrolyte solution, then a THF solution of the appropriate organometallic compound was added to yield a concentration of 1 mM of analyte. Voltammetric data were obtained at various scan speeds ranging from 100 to 500 mV sec^{-1}. It proved impossible to obtain acceptable analytical data for complexes of **1** or **2**, even though many of the compounds were highly crystalline and very pure according to NMR analysis.

Synthesis of $Li_3$2. Solid **2**H_3 (1.4 g, 3.3 mmol) was added to a round-bottom gas inlet flask and degassed. Under a nitrogen purge, 50 mL THF was added via syringe. The solution was cooled to −78 °C in a dry ice−acetone bath, and a hexane solution of BuLi (0.64 g, 10 mmol) was added via syringe. The solution was stirred and allowed to warm to room temperature overnight. The THF was removed in vacuo, and 15 mL hexane was added to give a suspension. This was filtered to give 1.39 g of Li_3**2** as a colorless solid (88%). ^1H NMR (C_6D_6): 6.69 (s, 3H), 6.80 (s, 3H), 3.38 (br s, 6H), 2.24 (s, 9H), 1.92 (s, 9H).

Synthesis of CpNbCl(1) (3). In the glovebox, 0.45 g (1.49 mmol) of $CpNbCl_4$ and 0.44 g (1.49 mmol) of **1**H_3 were added to a gas inlet flask. On the Schlenk line, 50 mL of toluene was added and the solution stirred at room temperature for 14 h. At this time, the volume of toluene was reduced to ca. 2 mL, and 15 mL of hexane added. The resulting solution was cooled to 0 °C to precipitate a light orange solid, which was isolated by filtration. Yield: 0.5 g (69%). ^1H NMR ($CDCl_3$): 7.98 (m, 2H, Ar-H), 7.14 (m, 5H, Ar-H), 6.96 (m, 6H, Aryl C-H and Cp superimposed), 6.64 (m, 3 H, Ar-H), 6.53 (d, $J = 8$ Hz, 1 H, Aryl-H). IR (Nujol): 1486 (s), 1470 (s), 1284 (s), 1265 (s), 832 (s), 749 (m).

Synthesis of CpTaCl(1) (4). This compound was prepared via the method used for niobium analogue **3**. The result was a green-yellow solid isolated in 61% yield. ^1H NMR ($CDCl_3$): 7.43 (m, 3 H), 7.08 (m, 3H), 6.77 (s, 5H, Cp), 6.51 (m, 3H). IR (Nujol): 1490 (s), 1467 (m), 1289 (m), 1269 (m).

Synthesis of CpNbCl(2) (5). Solid $CpNbCl_4$ (0.17 g, 0.567 mmol) and Li_3**2** (0.25 g, 0.567 mmol) were added to a gas inlet flask in the glovebox. On the Schlenk line, 40 mL of THF was added via syringe and the solution was stirred for ca. 15 h. At this time, the solvent was removed in vacuo and 15 mL toluene was added. The resulting suspension was filtered under inert atmosphere to remove LiCl. The toluene was removed in vacuo, and 10 mL hexane was added. Cooling gave a red precipitate that was isolated by filtration: yield 0.26 g (74%). ^1H NMR (C_6D_6): 6.83 (s, 5H, Cp), 6.77 (s, 2H), 6.70 (s, 1H), 6.44 (s, 2H), 6.14 (s, 1H), 4.74 (d, $J = 13$ Hz, 2H, NCH), 3.27 (br. s, 2H, N-CH_2), 2.97 (d, $J = 13$ Hz, 2H, N-CH), 2.28 (s, 3H, Ar-Me), 2.17 (s, 6H, Ar-Me), 2.15 (s, 6H, Ar-Me), 2.04 (s, 3H, Ar-Me). IR (Nujol): 1495 (s), 1305 (m), 1292 (m), 1179 (s), 867 (s), 857 (s), 655 (m).

Synthesis of CpTaCl(2) (6). This compound was prepared via the method used for the niobium analogue **5**; the result was a yellow solid isolated in 60% yield. ^1H NMR (C_6D_6): 6.79 (s, 2 H), 6.741 (s, 5H, Cp), 6.68 (s, 1H), 6.43 (s, 2H), 6.08 (s, 1H), 4.87 (d, $J = 15$ Hz, 2 H, N−CH), 3.35 (s, 2H, NCH_2), 3.04 (d, J 15 Hz, 2H, N-CH), 2.29 (s, 3H, Ar-Me), 2.19 (s, 6H, Ar-Me), 2.17 (s, 6H, Ar-Me), 2.04 (s, 3H, Ar-Me). IR (Nujol): 1492 (s), 1250 (m), 1196 (s), 856 (m), 831 (m).

Synthesis of CpTi(1) (7). In the glovebox a gas inlet flask was charged with 0.5 g (1.7 mmol) of **1**H_3 and 0.37 g (1.71 mmol) of $CpTiCl_3$. On the Schlenk line, 50 mL of toluene was added via syringe. The solution was warmed to reflux for ca. 22 h, during which time it developed a pale orange color. The solution was purged with nitrogen to flush any residual HCl, then the volume was reduced to ca. 5 mL in vacuo. Hexane (15 mL) was added and the resulting solution cooled in an ice bath to precipitate a pale orange solid. Yield: 0.52 g (75%). ^1H NMR ($CDCl_3$): 7.44 (d, $J = 8$ Hz), 7.08 (m, 3H), 6.77 (s, 5 H, Cp), 6.75 (m, 3H), 6.51 (d, $J = 8$ Hz). IR (Nujol): 1283 (s), 1252 (s), 1103 (m), 1024 (m), 753 (s), 642 (m).

Synthesis of CpTi(2) (8). A round-bottom gas-inlet flask was equipped with a dropping funnel and reflux condenser. To this was added 60 mL of chloroform, 0.42 g (2.2 mmol) of $TiCl_4$, and 0.92 g (2.2 mmol) of **2**H_3. A solution of 1.22 mL (6.5 mmol) of triethylamine in 10 mL of chloroform was added dropwise. When addition was completed, the solution was refluxed for 5 h, giving a red heterogeneous mixture containing ClTi(**2**). The mixture was filtered to remove $[NEt_3H][Cl]$, and the solvent was removed in vacuo to give a red solid. To this was added 75 mL of acetonitrile, and the resulting suspension was filtered to give an orange solid. This was washed with hot acetonitrile, leaving an orange solid that was dried in vacuo. Yield: 0.81 g (74%) of ClTi(**2**). ^1H NMR (C_6D_6): 6.63 (s, 3H), 6.36 (s, 3H), 2.72 (s, 9H), 2.09 (s, 9H). IR (Nujol): 1471 (s), 1231 (s), 1214 (s), 859 (s), 613 (s). Subsequently, a gas-inlet flask was charged with 0.29 g (0.58 mmol) of ClTi(**2**) and 35 mL of THF. Another flask was charged with 0.051 g (0.58 mmol) of sodium cyclopentadienide and 20 mL of THF. The solution of ClTi(**2**) was cooled to −10 °C, and the NaCp solution was added dropwise. After addition, the solution was allowed to warm to room temperature and stirred for an additional 3 h. The solvent was removed in vacuo and 30 mL of benzene added, and the resulting suspension was filtered through Celite to remove NaCl. The solution was concentrated in vacuo, and ca. 10 mL of hexane added; the resulting solution was cooled to precipitate a yellow-orange solid, which was isolated by filtation and dried in vacuo. Yield: 0.047 g (15%). ^1H NMR (C_6D_6): 6.85 (s, 5H, Cp), 6.82 (s, 3H), 6.39 (s, 3H), 3.85 (d, $J = 14$ Hz, 3H, NCH-Ar), 2.43 (d, $J = 14$ Hz, 3H, NCH-Ar), 2.32 (s, 9H), 2.17 (s, 9H). IR (Nujol): 1475 (s), 1251 (s), 1159 (m), 857 (s), 841 (s), 792 (m), 673 (m), 552 (m).

Synthesis of [CpNb(1)][BF_4] (9). In the glovebox, **3** (0.18 g, 0.372 mmol) and $AgBF_4$ (0.072 g, 0.372 mmol) were added to a gas inlet flask. On the Schlenk line, 40 mL of THF was added and the reaction stirred for 2 days. At the end of this period, the pale yellow solution was filtered to remove AgCl, and most of the THF was removed in vacuo. Hexane was added and the solution cooled to precipitate a pale yellow solid, which was isolated by filtration (yield 0.10 g, 49%). ^1H NMR (CD_3CN): 8.07 (d, $J = 8$ Hz, 3H), 7.26 (d, $J = 8$ Hz, 2H), 7.16 (t, $J = 11$ Hz, 2H), 6.96 (m, 2H), 6.90 (s, 5H, Cp), 6.64 (m, 3H). IR (Nujol): 1485 (m), 1460 (s), 1375 (m), 1286 (m), 1265 (m), 1098 (m, br, BF_4).

Synthesis of [CpTa(1)][BF_4] (10). This compound was synthesized via the method used for the niobium analogue **9** and isolated as green oily solid. ^1H NMR (CD_3CN): 8.10 (d, $J = 8$ Hz, 3H), 7.29 (d, $J = 8$ Hz, 1H), 7.18 (m, 2H), 7.10 (m, 1H), 6.91 (m, 2H), 6.78 (s, 5H, Cp), 6.66 (m, 2H), 6.53 (m, 1H). IR (Nujol): 1467 (s), 1376 (s), 1290 (s), 1269 (s), 1248 (m), 1024 (m, br.), 836 (s), 751 (m).

Synthesis of [CpNb(2)(THF)][BF_4] (11). This compound was synthesized via the method used for compound **9** and isolated as a pale orange solid in 68% yield. ^1H NMR (C_6D_6): 6.85 (s, 2H), 6.78 (s, sh.), 6.76 (s, 5H, Cp), 6.46 (s, 2H), 6.26 (s, 1H), 3.92 (br S, 2H, N-CH), 3.55 (ca. 3H, THF), 3.33 (br S, 2H, N−CH), 3.06 (br. doublet, $J = 13$ Hz, N-CH), 2.31 (s, 3H, Ar-Me), 2.26 (s, 6H, Ar-Me), 2.19 (s, 6H, Ar-Me), 2.10 (s, 3H,

Table 1. Crystal Data for 3

empirical formula	$C_{23}H_{17}NO_3ClNb\cdot C_3H_6O$
fw	541.83
cryst color, habit	red, needle
cryst dimens	0.01 × 0.02 × 0.08 mm
cryst syst	monoclinic
lattice type	C-centered
lattice params	$a = 28.384(2)$ Å
	$b = 9.287(1)$ Å
	$c = 18.266(2)$ Å
	$\beta = 109.133(4)°$
	$V = 4549.0(7)$ Å^3
space group	$C2/c$ (No. 15)
Z value	8
D_{calc}	1.582 g/cm^3
F_{000}	2208.00
μ(Mo Kα)	6.80 cm^{-1}
temperature	−90(1) °C
residuals: R; R_w	0.046; 0.041
goodness of fit	1.32
no. of reflns	2987

Table 2. Bond Lengths and Angles for 3

Nb(1)−Cl(1)	2.461(2)	Nb(1)−C(3)	2.418(9)
Nb(1)−O(1)	1.970(5)	Nb(1)−C(4)	2.441(8)
Nb(1)−O(2)	1.978(5)	Nb(1)−C(5)	2.483(9)
Nb(1)−O(3)	2.009(6)	N(1)−C(11)	1.477(10)
Nb(1)−N(1)	2.369(7)	N(1)−C(12)	1.491(10)
Nb(1)−C(1)	2.456(10)	N(1)−C(18)	1.49(1)
Nb(1)−C(2)	2.444(9)		

Cl(1)−Nb(1)−O(1)	83.5(2)	O(3)−Nb(1)−N(1)	75.8(2)
Cl(1)−Nb(1)−O(2)	82.1(2)	Nb(1)−O(1)−C(6)	119.2(5)
Cl(1)−Nb(1)−O(3)	155.2(2)	Nb(1)−O(2)−C(17)	120.9(5)
Cl(1)−Nb(1)−N(1)	79.4(2)	Nb(1)−O(3)−C(23)	121.8(5)
O(1)−Nb(1)−O(2)	147.5(2)	Nb(1)−N(1)−C(11)	106.1(5)
O(1)−Nb(1)−O(3)	90.2(2)	Nb(1)−N(1)−C(12)	106.0(5)
O(2)−Nb(1)−O(3)	90.8(2)	Nb(1)−N(1)−C(18)	106.6(5)
O(1)−Nb(1)−N(1)	73.4(2)	O(2)−Nb(1)−N(1)	75.4(2)

Table 3. Voltammetric Data for Compounds 3−12.

compound	$E°$, V[a]
CpNb(**1**)Cl (**3**)	−1.36
CpTa(**1**)Cl (**4**)	−1.93
CpNb(**2**)Cl (**5**)	−1.62, −1.85
CpTa(**2**)Cl (**6**)	−2.13,[b] −2.27
CpTi(**1**) (**7**)	−1.66
CpTi(**2**) (**8**)	−1.85[b]
[CpNb(**1**)(THF)][BF_4] (**9**)	−1.58
[CpTa(**1**)(THF)][BF_4] (**10**)	−2.15
[CpNb(**2**)(THF)][BF_4] (**11**)	−1.88
[CpTa(**2**)(THF)][BF_4] (**12**)	−2.45, −2.90[b]

[a] 1 mM in THF with 0.25 M NBu_4PF_6, with potentials referenced to Ag/$AgNO_3$ reference electrode. Potentials are for reversible couples unless otherwise noted. [b] Irreversible processes. Potentials cited are cathodic peak potentials.

Table 4. Styrene Polymerization Data

run	catalyst	[cat], mM	Al/Ti	time, min	T_p, °C	yield PS, g	A (×10^{-6})	% sPS
1	**7**	1.24	500	30	50	0.374	1.38	82.4
2	**7**	1.24	1000	30	50	0.842	3.10	83.3
3	**7**	1.24	2000	30	50	0.837	3.09	98.1
4	**7**	1.24	500	30	90	0.383	1.40	68.1
5	**7**	1.24	500	30	80	1.075	3.90	91.5
6	**7**	1.24	1000	30	80	1.740	6.40	74.9
7	**7**	1.24	2000	30	70	1.051	3.90	79.3
8	**8**	0.94	500	30	75	0.194	0.94	55.7
9	**8**	0.94	1000	30	75	0.440	2.10	82.1
10	**8**	0.94	2000	30	75	0.973	3.70	79.2
11	**8**	0.94	1000	30	80	0.382	1.85	84.8
12	**8**	0.94	2000	30	50	0.202	0.98	50.5

Ar-Me), 1.38 (br s, ca. 3H, THF). IR (Nujol): 1495 (s), 1247 (m), 1200 (s), 1095 (s, br), 862 (s).

Synthesis of [CpTa(2)(THF)][BF$_4$] (12). This compound was synthesized via the method used for compound **9** and isolated as light brown solid in 51% yield. ^{1}H NMR (C_6D_6): 6.86 (s, 2H), 6.76 (s, 1 H), 6.69 (s, 5H, Cp), 6.46 (s, 2H), 6.19 (s, 1H), 4.06 (br S, 2H, N-CH), 3.56 (ca. 3H, THF), 3.31 (br S, 2H, N-CH), 3.12 (br doublet, $J = 12$ Hz, N-CH), 2.31 (s, 3H, Ar-Me), 2.28 (s, 6H, Ar-Me), 2.21 (s, 6H, Ar-Me), 2.10 (s, 3H, Ar-Me), 1.38 (br s, ca. 3H, THF). IR (Nujol): 1477 (m), 1375 (m), 1096 (s, br), 803 (s).

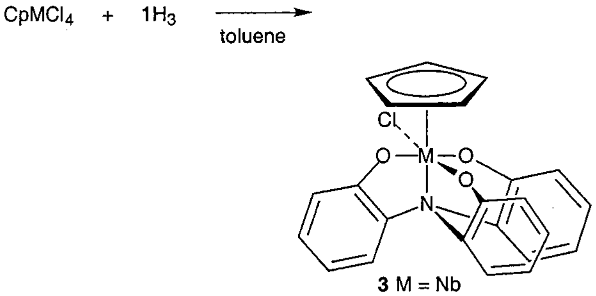
Styrene Polymerizations. These experiments were carried out in 100 mL gas inlet flasks equipped with magnetic stir bars. Styrene was stored over activated 3 Å molecular sieves for 3 days, distilled under nitrogen, then kept cold until used. Toluene, styrene (2.5 mL, 22 mmol), and the appropriate amount of a solution of MAO/toluene were added to the flask via syringe. The flask was immersed in an oil bath of the appropriate temperature and allowed to equilibrate for ca. 15 min. At this time, a solution containing ca. 0.01 g of catalyst (see Table 4) in 2 mL of toluene was added via syringe and the solution stirred under nitrogen for 30 min. The polymerization was terminated by the addition of methanol (10 mL) and a solution of 10% HCl in methanol (30−50 mL). The precipitated polymer was filtered, washed with methanol (ca. 150−300 mL), and then dried in vacuo to constant weight. The solid polymer was loaded into a Soxhlet extractor and extracted for 12 h with 2-butanone in order to determine the selectivity for syndiotactic polystyrene (sPS). The insoluble sPS was dried at elevated temperature until the weight was constant.

X-ray Study of 3. Compound **3** was crystallized for X-ray diffraction study by slow cooling of a saturated acetone solution. The bulk of the solution was removed from the resulting red needles, which were kept moist with solvent. A red needle having approximate dimensions 0.01 × 0.02 × 0.08 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using 10 (1° in ω, 10 s exposure, dezingered) data frames, corresponded to a C-centered monoclinic cell with dimensions $a = 28.384(2)$ Å, $b = 9.287(1)$ Å, $\beta = 109.133(4)°$, $c = 18.266(2)$ Å, and $V = 4549.0(7)$ Å^3. For $Z = 8$ and fw = 541.83, the calculated density is 1.58 g/cm^3. Based on the systematic absences of hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $C2/c$ (no. 15).

The data were collected at a temperature of −90 ± 1 °C to a maximum 2θ value of 43.9°. This was the maximum 2θ value of observed diffraction for this very small crystal. Two omega scans consisting of 57 and 40 data frames, respectively, were collected with a scan width of 2.0° and a detector-to-crystal distance, D_x, of 35 mm. A data set consisting of 2987 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ, for Mo Kα radiation is 6.8 cm^{-1}, and no absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. In the case of the methyl group hydrogens in the acetone solvent molecule, one hydrogen was located in the difference map and included at an idealized distance to set the orientation of the other two hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on 1631 observed reflections ($I > 3.00\sigma(I)$) and 298 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.046$ and $R_w = 0.041$. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.49 and −0.52 e$^-$/Å^3, respectively. Crystal data are collected in Table 1 and key bond lengths and angles in Table 2.

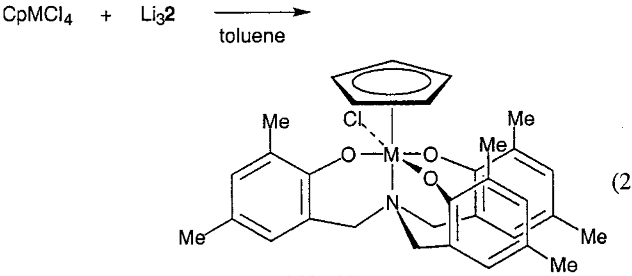
Results and Discussion

Synthesis of Cyclopentadienyl Derivatives. One aim of this project was to prepare cyclopentadienylmetal compounds containing chelating ligands **1** and **2**. We envisioned two routes to these species; one proceeds by constructing the Cp–M linkage first and adding the chelate ligand, and the other proceeds in the opposite sense. In fact, only the first of these proved useful in the preparation of the niobium and tantalum analogues, while the second was required for the titanium complex of **2**. Thus, while it was possible to prepare the M(**L**)Cl_2 (**L** = **1** or **2**) for niobium and tantalum, these compounds did not react cleanly with obvious sources of the cyclopentadienyl ligand; neither the sodium, lithium, or Grignard analogues proved useful. As such, we turned our attention to the reactions of the aryloxide ligands with known derivatives $CpMCl_4$. In fact, that approach proved out, and the desired niobium and tantalum compounds were obtained in yields greater than 60% in all cases (eqs 1, 2). For ligand **1** it proved possible to reflux the precursor **1**H_3 with $CpMCl_4$, a process that liberates 3 equiv of HCl. For the niobium and tantalum complexes of ligand **2** this approach led to impure compounds that proved difficult to purify. Instead, the ligand precursor **2**H_3 was first deprotonated with 3 equiv of butyllithium to give Li_3**2**. The latter salt reacted with $CpMCl_4$ to give clean samples of the desired compounds. While this sequence (deprotonation and reaction with metal halide) could presumably be carried out in a single pot, it is easy to isolate large quantities of Li_3**2** and store the salt for subsequent use. The preparation of titanium compound CpTi(**1**) (**7**) proceeded smoothly from the phenol ligand **1**H_3. However, a similar approach with **2** was unreliable, since this ligand tended to displace the cyclopentadienyl ligand from $CpTiCl_3$. For this reaction, the intermediate ClTi(**2**) was used in a reaction with NaCp; the yield of this reaction was lower than those obtained in the syntheses of **3**–**7**, but it was the only reliable route for the preparation of **8**. In general, the complexes containing **2** (e.g., **5**, **6**, and **8**) proved more soluble and easier to isolate and purify, while those of **1** (**3**, **4**, and **7**) tended to form better crystals for diffraction purposes. The niobium and tantalum compounds are depicted as containing octahedral metal centers, and this is consistent with the NMR data and the results of a diffraction study of **3**. The NMR spectra for **3** and **4** contain overlapping resonances for the four aromatic hydrogens, and the presence of the cyclopentadienyl group is evident from a singlet in the range ca. 6.7–7.0 ppm; the downfield shift of this signal is consistent with the presence of a pentavalent metal center. Compounds **5** and **6** contain a six-membered chelate ring, with an extra methylene group bridging the nitrogen center and the aryl rings; due to the presence of the arene methyl substituents, there are no three-bond couplings involving arene hydrogens and the aryl resonances appear as singlets. There are two sets of methyls and two sets of arene hydrogens present in a 2:1 ratio, reflecting the fact that one of the chelate arms is *trans* to chloride and two are *cis*. Signals for the hydrogens on the methylene bridges are also consistent with this geometry; those methylenes on chelate arms *cis* to chloride are diastereotopic and appear as two well-separated doublets. Conversely, the methylenes on the unique chelate arm *trans* to chloride are related by a mirror plane of symmetry and appear as a singlet. The titanium derivatives are expected to be five-coordinate, as seen for related compounds derived from triethanolamine.[26]



(1)

3 M = Nb
4 M = Ta



(2)

5 M = Nb
6 M = Ta

Structural Data for Compound 3. To gather information on the geometrical requirements for binding of the chelating ligands such as **1** and **2**, structural data were obtained for the niobium compound **3**. This compound was obtained in the form of red needles by slow cooling of a saturated acetone solution. The unit cell *C*2/*c* (no. 15) was found to contain eight molecules of **3** and acetone, so the correct empirical formula for the crystalline material is CpNb(Cl)(**1**)·Me_2CO. Crystal data are presented in Table 1, a summary of key bond lengths and angles are in Table 2, and the structure and atom-numbering scheme are given in Figure 1. Compound **3** may be seen to adopt a distorted octahedral geometry if the cyclopentadienyl group is considered to occupy a single coordination site. The position *trans* to the cyclopentadienyl is occupied by the linking nitrogen atom, and the four *cis* positions contain the oxygen atoms of **1** and the chloride. The bonding between the metal center and the cyclopentadienyl ligand is unexceptional, with Nb–C bond lengths ranging from 2.418(9) to 2.483(9) Å. The shortest of these is between Nb and C3, the carbon that sits over a space bisecting the O1–Nb–O3 angle. Indeed, it appears that the cyclopentadienyl ring tips slightly in this direction, as the Nb–C1 (2.456(10) Å) and Nb–C5 (2.483(9) Å) bonds are the longest of the set. The cyclopentadienyl C–C bonds range from 1.38(1) to 1.42(1) Å and the angles from 107.2(8)° to 108.6(8)°. The Nb–Cl bond length is 2.461(2) Å and the Nb–N bond length is 2.369(7) Å. This may be compared with the chelated compound Cp*-$Ti(N(CH_2CH_2O)_3)$, for which the Ti–N bond length is 2.342(9) Å;[26] as noted, this is likely to depend on the nature of the ligand *tran*s to the nitrogen. The Nb–O bond lengths in **3** range from 1.970(5) to 2.009(6) Å, with the longest of these (Nb–O3) for the oxygen situated

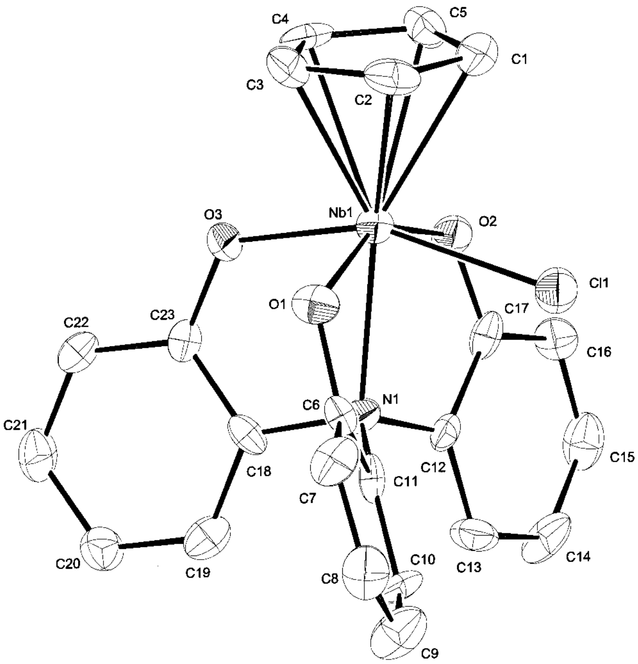


Figure 1. Molecular structure and atom-numbering scheme for **3**.

trans to the chloride ligand. There is clear evidence for distortion from a perfect octahedron, since the N−Nb−O angles, which range from 73.4(2)° to 75.8(2)°, are well off of the idealized 90°. Likewise the angles for the *trans* ligands are reduced from the ideal 180°; for O3−Nb−Cl1 this is 155.2(2)° and for O1−Nb−O2 it is 147.5(2)°. It is tempting to attribute this to chelate ring strain pulling the oxygen atoms out of the "equatorial" plane, but the N−Nb−O angles are not very different from the N−Nb−Cl angle of 79.4(2)°. This suggests that the oxygens and chlorine are simply moving away from the large cyclopentadienyl ligand.

Oxygen ligands have the potential to engage in π donation to early transition metal centers (the niobium center in **3** has a 16-electron count), and the structural ramifications of such an effect have been considered.[13,28,29] In these contributions it has been noted that M−O−C angles may vary widely in aryloxide compounds and that there is no necessary correlation between this angle and π bonding contibutions. Since one lone pair on oxygen resides in a p orbital situated perpendicular to the M−O−C plane, this lone pair can engage in pπ−dπ bonding with any M−O−C angle.[29] Nonetheless, the niobium−oxygen bond lengths in **3** (1.970(5)−2.009(6) Å) are on the long side for Nb(V) compounds; for $Nb(OAr)_5$ compounds the Nb−O bond lengths are typically 1.89−1.91 Å,[13] for $[Nb(OAr)_6]^-$ they are 1.95−1.98 Å,[13] and for $CpNb(OAr)Cl_3$ the Nb−O bond length is 1.872 Å.[7] The bond lengths for **3** are taken to indicate a reduced degree of pπ−dπ donation from the aryloxides. It remains to be seen if this effect holds for the complexes of **2**, in which the chelate rings contain six atoms.

Electrochemical Studies and Redox Chemistry. As an alternative means of assessing the electronics of ligand binding, voltammetric techniques were employed to determine redox behavior for the compounds discussed herein. These studies were carried out with a platinum disk electrode in THF solution, and potentials are referenced to the Ag/Ag^+ couple. Table 3 contains data for the reduction waves observed. Several observations result, and these will considered below.

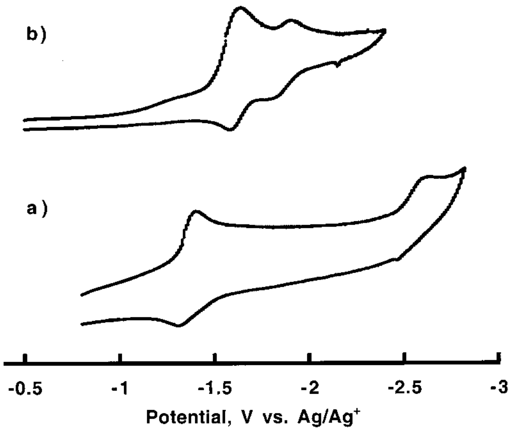


Figure 2. Cyclic voltammograms for (a) CpNb(**1**)Cl (**3**) and (b) CpNb(**2**)Cl (**5**).

The niobium and tantalum complexes of **1** (**3** and **4**, respectively) exhibit a wave that is apparently reversible and then a second, irreversible wave at more negative potential; the peak currents for the first reduction waves are comparable ($i_{p,c}/i_{p,a} \approx 1$), and the peak separations are ca. 70−80 mV, close to the value we observe for ferrocene under the same conditions of solvent and electrolyte. For niobium compound **3** (Figure 2a) the E° value is −1.36 V and for the tantalum analogue the E° value is −1.93 V. The difference here is nearly 0.6 V, reflecting the greater ease (thermodynamically) with which niobium is reduced. This is consistent with literature data for various $M(OAr)_5$ derivatives, which exhibit niobium E° values ranging from −1.4 to −1.5 V (vs Ag/Ag^+ in THF) and tantalum E° values of ca. −2.25 V.[13] Similarly, the compounds $M(silox)_3Cl_2$ exhibit reversible reductions for which the potentials E° are −1.42 and −2.18 V, respectively, for niobium and tantalum.[16] It is interesting to note that compounds **3** and **4** are somewhat easier to reduce than are the silox compounds, suggesting that the niobium centers in our compounds are more electron-deficient. This is consistent with the interpretation of the structural data given above.

The reversible voltammetric behavior suggests that there is no structural change accompanying reduction of **3** and **4**. However, compounds such as this sometimes lose chloride upon reduction, so we wondered if **3** and **4** were already ionized and existed as $[CpM(\mathbf{1})(THF)]^+Cl^-$ in THF solution. To test this hypothesis, we prepared the cationic analogues **9** and **10** for comparison. This was done by treating the chloride complex **3** or **4** with silver tetrafluoroborate (eq 3) and filtering off the precipitated silver chloride. The resulting compounds are the THF adducts; while varying amounts of this ligand are lost upon isolation and drying, it is reasonable to assume that the compound is fully coordinated in the THF solution used in the voltammetric studies. Compounds **9** and **10** also exhibited reversible reductions at a platinum electrode, but the potentials were

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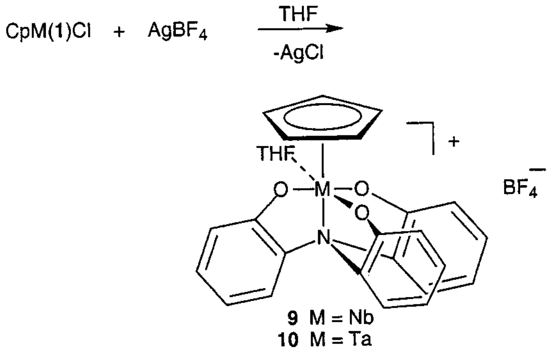
(28) Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963−968.

(29) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.

more negative than those seen for **3** or **4**. This is surprising, since the cationic analogues would be expected to reduce at less negative potentials. However,

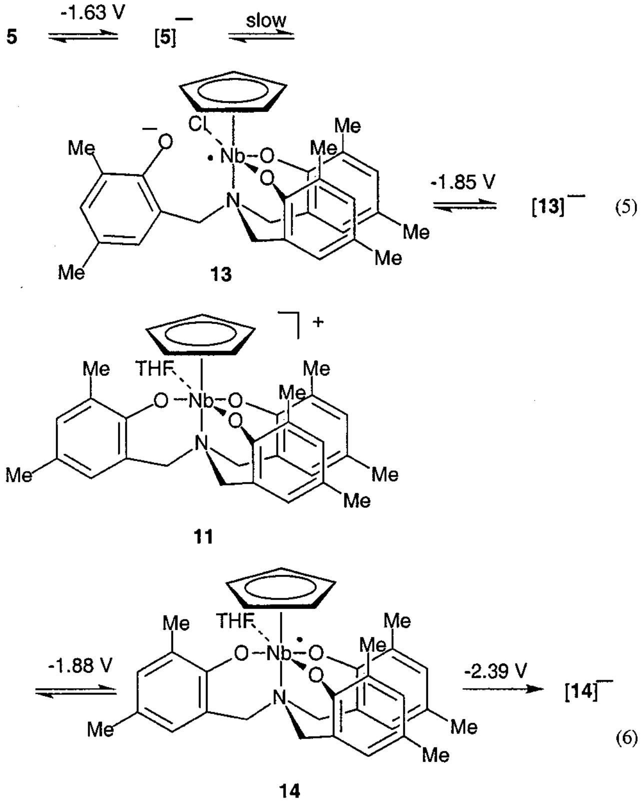


(3)

this behavior is seen for all of the series prepared in this study (Table 3) and presumably reflects the ability of the complexes to approach the electrode in a conformation leading to facile reduction. In any case, it is clear that the reductions seen for **3** and **4** do not correspond to those for **9** and **10**. The chloride ligands remain bound to the metal center even after reduction (eq 4), consistent with the behavior reported for $(\mathrm{silox})_3\mathrm{MCl}_2$.[16]

$$\mathrm{CpM(1)Cl} \underset{E^\circ}{\overset{\mathrm{THF}}{\rightleftharpoons}} [\mathrm{CpM}(\mathbf{1})\mathrm{Cl}]^- \tag{4}$$

Compounds **5** and **6** contain ligand **2**, and the data in Table 3 show electrochemical behavior different from that of **3** and **4**. First, the reductions observed for **5** and **6** are are not fully reversible, indicating that a chemical process occurs during or after the redox event. Niobium analogue **5** shows a quasi-reversible wave at −1.62 V and a second wave at −1.85 V (Figure 2b). Conversely, the tantalum analogue **6** shows an irreversible wave with a cathodic peak at ca. −2.1 V and follow-up reductions at −2.27 and −2.52 V; these latter two processes show some evidence for reversibility. Assuming a first $E°$ of ca. −2.2 V for **6**, its reduction is 0.5 V beyond that of **5**, consistent with the general trend for Nb and Ta analoges. In addition, both **5** and **6** are harder to reduce than are **3** and **4**; the niobium compounds differ by 0.26 V (−1.36 and −1.62 for **3** and **5**, respectively) and the tantalum compounds by ca. 0.27 V (−1.93 and −2.2 for **4** and **6**, respectively). Since ligand **2** contains donor methyl substituents and **1** does not, it is reasonable that complexes of **2** should be more electron rich and harder to reduce. The voltammograms for **5** and **6** suggest that a chemical process follows the first reduction and produces a species susceptible to facile second reduction;[30] for **5** this chemical process is competitive with the scan rate, and for **6** it is faster. An obvious explanation is that these compounds lose a chloride ligand upon reduction, so we prepared the cationic species $[\mathrm{CpM}(\mathbf{2})(\mathrm{THF})][\mathrm{BF}_4]$ (M = Nb, **11**; M = Ta, **12**) by treatment with AgBF_4 (as in eq 3). The resulting compounds exhibited reversible reductions at −1.88 V (**11**) and −2.45 V (**12**); note that the separation is 0.57 V, again consistent with the general trends seen in comparing niobium and tantalum analogues, and that the cationic species are again reduced at more negative potentials than are the neutral chloride compounds. In addition, both **11** and **12** exhibit a second irreversible wave, and the voltammetric data for niobium compounds are summarized in eqs 5 and 6. In eq 5, the



(5)

(6)

reduction of **5** is first seen to give **5**⁻, a process with a potential of −1.63 V. This anion slowly gives way to another species, **13**, which is reduced at −1.85 V. Conversely, the cation **11** exhibits a reversible reduction at −1.88 V to give a Nb(IV) species **14**. This is subsequently reduced irreversibly at −2.39 V. We formulate **14** as a neutral THF adduct, consistent with the reversible nature of its production. The major mechanistic question centers around the identity of intermediate **13**. As depicted in eq 5, we propose that this species arises from labilization of a niobium−oxygen bond upon reduction; whether this involves an aryloxide *cis* or *trans* to the chloride is unknown. Note that loss of chloride from **5**⁻ would have generated **14**, a species known to reduce at −2.39 V; we have carried out the reduction of **5** (eq 5) past this potential and see no evidence for this wave, suggesting that the chemical process does *not* involve chloride loss (i.e., **14** is not present). While the chemical process converting **5**⁻ to **13** could involve labilization of the Nb−N bond, we believe that that the facile reduction of **13** is more consistent with loss of the anionic aryloxide ligand (rather than the neutral amine).

We interpret the voltammetric data for **5** and **6** in terms of labilization of an aryloxide ligand, a process that should depend on the size of the metal atom and the chelate ring; specifically, the chelate ring (and associated ring strain) is thought to favor this process over the more common chloride labilization. To test for this possibility, we have looked at the analogous titanium compound, CpTi(**1**) (**7**), in which there is no chloride. Indeed, this compound also exhibits a quasi-

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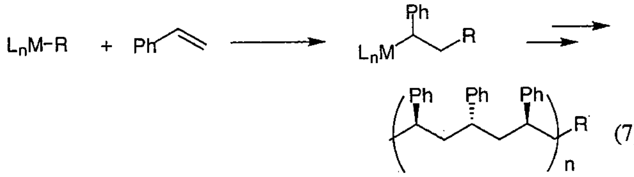
[30] Carl, R. T.; Doig, S. J.; Geiger, W. E.; Hemond, R. C.; Hughes, R. P.; Kelly, R. S.; Samkoff, D. E. *Organometallics* **1987**, *6*, 611−616.

reversible reduction with a potential of −1.66 V; the reduction is partially reversible at a scan rate of 100 mV/s, but becomes increasingly reversible at 500 mV/s. Moreover, the analogue CpTi(**2**) (**8**) exhibits a reduction wave at ca. −1.85 V, and this process is wholly irreversible. This confirms that chloride loss is not required as an explanation for irreversible reduction, since these titanium analogues have no chloride co-ligand. Again, one would not expect such a significant difference for the chloride loss process when comparing complexes of ligands **1** and **2**. Conversely, ligand scission is a reasonable consequence of the structural changes encountered in going from **1** to **2**, since the latter (with a six-membered chelate ring) is expected to exhibit more strain; this is increasingly important with the smaller titanium center.

Polymerizations of Styrene. As a means of correlating the structural and synthetic data discussed above with reaction chemistry, we sought to determine the activity of the compounds in styrene polymerization. In 1986 Ishihara reported the preparation of syndiotactic polystyrene (sPS) and noted that this material differed considerably from the known atactic and isotactic polystyrenes.[31] Specifically, sPS proved to be highly crystalline and exhibited a high melting point (ca. 270 °C) and enhanced chemical resistance. This work involved the use of methylaluminoxane (MAO) cocatalyst and catalytic quantities of either $TiCl_4$, $Ti(OEt)_4$, or $CpTiCl_3$; of these, $CpTiCl_3$/MAO proved to exhibit the best combination of activity and stereospecificity.[32] Since that time, there has been considerable industrial interest in the synthesis and potential applications of sPS.[33]

Mechanistic work with Cp^*TiR_3/MAO or $Cp^*TiR_3/B(C_6F_5)_3$ has led to the conclusion that the active catalyst is a Ti(III) species such as $[Cp^*TiR]^+$ and that the formation of this reduced compound is enhanced in the presence of added styrene.[34] Moreover, the use of ^{13}C-labeled catalysts and end-group analysis suggests that polymerization results from a 2° insertion process (eq 7) in which the substituted styrene terminus is α to the metal center.[35,36] It has further been deduced that



(7)

β-hydride elimination constitutes the major termination event and that the resulting metal hydrides are also capable of inducing polymerization via 2° insertion.[36] Rausch and Chien have reported several studies of the effect of catalyst structure on polymerization activity and stereospecificity.[37−40] These results have shown that (a) many catalysts, e.g., $CpTiCl_3$/MAO, lose stereospecificity at high temperatures, but the indenyl derivative (η^5-Ind)$TiCl_3$ does not, (b) the presence of electron donor substituents on the cyclopentadienyl rings of $CpTiX_3$ derivatives increases activity, and (c) more highly annulated systems such as (η^5-benzindenyl)TiX_3 constitute particularly active catalysts for sPS formation. Others have focused on variations in the remaining titanium-bound ligands, and both Cp^*TiF_3[41] and $Cp^*Ti(OCH_2CH_2)_3N$[26] have exhibited high activity for sPS formation.

In view of the structural similarities with other sPS catalysts, the compounds discussed herein were screened for catalyst activity. This was done in toluene solution with MAO cocatalyst ratios (Al/M) ranging from 500 to 2000 and polymerization temperatures ranging from 50 to 90 °C. Our initial prediction was that the niobium and tantalum compounds would be highly active because they contained either a chloride or THF co-ligand that would be easily removed, leaving an open coordination site for incoming styrene. In fact, none of these compounds proved active in styrene polymerization; it should be noted that Ishihara surveyed a few group V alkoxides, and these also proved to be poor catalysts.[32] However, the titanium analogues **7** and **8** did lead to catalytic activity, and the data are summarized in Table 4.

A number of observations result from the polymerization data. First, it is clear that CpTi(**1**) (**7**) shows reasonable catalytic activity and is slightly more reactive than is CpTi(**2**) (**8**) under comparable conditions. At polymerization temperatures of 75−80 °C and Al/Ti ratios of 1000, **7** shows an activity of 6.4×10^6 (units throughout are (g PS)/(mol of Ti)(mol of styrene)(h)) and **8** shows a reduced activity of ca. 2×10^6. Indeed, under the conditions of 2000:1 MAO:Ti and 50 °C, **7** exhibits reasonably high activity (3.1×10^6) and excellent stereospecificity (98.1%). This may be compared with the (η^5-indenyl)$TiCl_3$/MAO system, for which Rausch and Chien report an activity of 3.7×10^7 and a stereospecificity of 98.2%.[38] Similarly, Do and co-workers have studied the catalyst $Cp^*Ti(OCH_2CH_2)_3N$/MMAO and report activities of ca. $(2-4) \times 10^7$ and stereospecificities of 98−99%.[26] Hence, while **7** can exhibit a stereospecificity comparable to both of these, its activity is reduced by a factor of 10. It should also be noted that both of these previous studies report more consistent stereospecificities for a range of experimental conditions and greater stability at higher reaction temperatures. At an Al/Ti ratio of 500 catalyst **7** shows a loss of stereospecificity with increasing temperature, with only 68% sPS resulting at a polymerization tem-

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perature of 90 °C. $CpTiCl_3$/MAO has exhibited acitivities comparable to that of **7**, but the stereospecificities range from ca. 60 to 90%;[40] Do reports that the use of $CpTi(OCH_2CH_2)_3N$ leads to low activities (2.4×10^5 at 50 °C) and poor selectivities (73% sPS).[26] Hence, we conclude there is considerable promise for complexes of ligand **1** in polystyrene catalysis, and we are pursuing the use of other derivatives with different π-complexed co-ligands in this chemistry. Conversely, **8** is less reactive than is **7** *and* less stereospecific; we have attained only ca. 80% sPS with **8**, and many reactions show considerably lower values.

In studies of sPS formation by $Cp^*TiMe_3/B(C_6F_5)_3$, Grassi has shown ESR evidence for the production of Ti(III) species and noted that this reduction process is enhanced by the presence of styrene.[42] The observation of two ESR active species was taken as evidence for the presence of two species in solution, Cp^*TiR^+ and $Cp^*Ti(R)(\mu\text{-}R)BAr_3$. We have studied the reaction of CpTi(**1**) (**7**) with MAO and styrene by ESR and also see evidence for the presence of Ti(III) species. These studies were done at 50 °C so as to simulate polymerization conditions. A reaction of **7** with excess MAO in toluene leads to the prompt production of two ESR signals at $g = 1.992$ and 1.988. Also in evidence is some hyperfine structure, attributed to the presence of the ^{47}Ti and ^{49}Ti isotopes; these isotopes have spins of 5/2 and 7/2, respectively, and abundances of 7.75 and 5.51%. It is impossible to resolve the hyperfine pattern, which appears to contain contributions from both major species and both titanium isotopes. A similar experiment was subsequently done with added styrene, and the relative concentrations of **7**, MAO, and styrene were chosen to match the polymerization reactions; this led to the generation of two ESR signals which were reminiscent of those seen by Grassi.[42] Hence, it appears quite likely that **7** is reduced by MAO and that Ti(III) species are important in the polymerization.

The catalytic results suggest some interesting correlations between structure and polymerization activity, many of which differ from those reported in earlier studies on catalysts with different structures. The redox data discussed earlier suggest that reduction can lead to chelate ring opening, particularly with ligand **2**, and it is reasonable to assume that the presence of excess aluminum in the polymerization solutions will serve to facilitate this. The Nb and Ta analogues may provide a nice model for the reactions occurring at titanium, even though the group V metals do not support polymerization. These structures exhibit octahedral coordination geometries in which a chloride ligand accompanies the chelating aryloxides in the coordination sphere, and it is likely that titanium can do the same despite its smaller size. This would provide a site for a Ti−alkyl, but a Ti−O bond must also labilize in order to accommodate an incoming styrene molecule. This points out the importance of chelate ring opening in reduction and is consistent with the ESR result implicating titanium reduction in the polymerization process. However, it is clear that other factors are at play here as well. The redox data cited above show that compounds containing ligand **2** are more prone to chelate ring opening than are those of ligand **1**, yet CpTi(**1**) (**7**) is a more efficient catalyst for sPS formation than is CpTi(**2**) (**8**) under comparable conditions. This does not reflect any inherent difficulty in producing Ti(III), since we have examined the reaction of **8** with MAO and see clear ESR evidence for reduction (two signals with $g = 1.992$ and 1.988); in this sense **8** is similar to **7**. However, it is clear that ligand electronic effects play a complex role in styrene polymerization. Rausch and Chien have shown that polymerization is enhanced by the presence of electron donor substituents on the arene ring[39] and $Cp^*Ti(OCH_2CH_2)_3N$ is much more active than is the Cp analogue.[26] However, it appears that the inclusion of electron acceptors in the co-ligand set can have beneficial consequences; Kaminsky has shown that Cp^*TiF_3 is considerably more active than is Cp^*TiCl_3 under similar conditions.[41] This trend is apparent from the series of cyclopentadienyltitanium compounds studied thus far, since complexes of **1** are more active than are those of **2** or triethanolamine.[26] Clearly, then, while chelate ring opening is undoubtedly required for styrene polymerization, the rate of this process is not a determining factor in the catalysis. Ring opening may be essentially irreversible in the presence of excess MAO, whereupon the electronic properties of the remaining bound ligands dictate the rate of catalysis.

It is possible that the ligands **1** and **2** leave the coordination sphere completely, in which case the very different polymerization reactivities of **7**, **8**, and $CpTi(OCH_2CH_2)_3N$ would be the result of ion pair formation.[26] However, Feher has reported related data on ethylene polymerization by vanadium silsesquioxanes and trialkylaluminum.[43] In that study, an oxovanadium moiety constituted a vertex of the silsesquioxane framework, meaning that the vanadium center was also bound to three siloxides. Upon treatment with the aluminum cocatalyst, two of the original V−O links were labilized so as to accommodate two new alkyl ligands. This species then polymerized ethylene readily, and there is no reason to believe that the vanadium center left the silsesquioxane moiety. In a similar way, we suspect that added MAO serves to labilize one or two of the aryloxide arms in **7** and **8** and that this coordinatively unsaturated species constitutes the active catalyst for sytrene polymerization.

Summary

The aryloxides **1** and **2** constitute excellent ligands for early transition metals, as would be expected for hard base chelates interacting with hard acid metal centers. It is nonetheless reasonable to consider the possibility that chelate ring strain would serve to weaken the metal−oxygen bonds, and the X-ray data for **3** show some evidence for this; the Nb−O bond lengths are at the high end of the range expected for such bonds. However, the apparent weakness in the individual bonds is compensated by the benefit derived from chelation effects. At the same time, the compounds exhibit interesting solution chemistry, especially upon reduction. Electrochemical studies show that complexes of **1** exhibit reversible or quasi-reversible reduction

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reactions, while those of **2** are largely irreversible. We have used a combination of synthetic and electrochemical approaches to probe this phenomenon, and the resulting data are consistent with a process involving chelate opening and not chloride labilization. We have eliminated the possibility that Nb−Cl or Ta−Cl bonds are labilized upon reduction; consistent with this is the observation that the titanium compound **8** (which has no chloride co-ligand) also exhibits irreversible reduction. In an attempt to correlate these electrochemical data with solution reactivities, we have studied the compounds in styrene polymerization. Since titanium(IV) compounds serve as precatalysts in a process leading to syndiotactic polystyrene, we were surprised to learn that the isoelectronic niobium and tantalum compounds are ineffective in the catalysis. However, titanium complexes **7** and **8** did prove to be active; under the right conditions, **7** exhibits reasonable acitivity and high selectivity for sPS. ESR studies of the reacting polymerization solution are consistent with the production of Ti(III) species. It appears that the electron-donating substituents on the chelated ligand lead to diminished catalytic activity, but there is no apparent correlation between the tendency toward chelate ring opening and catalytic efficiency. Future mechanistic studies will be devoted to a closer look at the reactions of the transition metal compounds with electrophilic cocatalysts, in an attempt to ascertain the structure of the Ti(III) species and the role of ligand dynamics in polymerization and other solution reactions.

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Supporting Information Available: A listing of crystallographic data, including atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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