Cationic Group 4 Metal Alkyl Compounds Containing *o*-Arylphenoxide Ligation

Matthew G. Thorn, Zac C. Etheridge, Phillip E. Fanwick, and Ian P. Rothwell*

Department of Chemistry, 1393 Brown Building, Purdue University,
West Lafayette, Indiana 47907-1393

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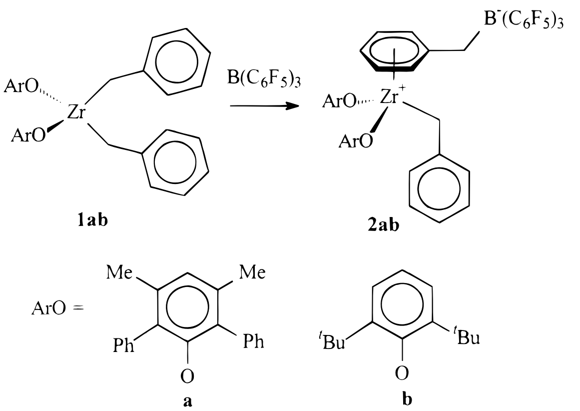
Summary: Treatment of the dibenzyl compounds $[(ArO)_2M(CH_2Ph)_2]$ (ArO = 2,6-diphenyl-3,5-dimethylphenoxide, M = Ti, Zr; ArO = 2,6-diphenylphenoxide, M = Ti) with $[B(C_6F_5)_3]$ gave the corresponding zwitterionic species $[(ArO)_2M^+(CH_2Ph)(\eta^6\text{-}C_6H_5CH_2B^-(C_6F_5)_3)]$. Addition of $[B(C_6F_5)_3]$ to the titanium dimethyl compounds $[(ArO)_2TiMe_2]$ gave unstable species which polymerize ethene and propene.

The great success of group 4 metallocene olefin polymerization catalysts[1] has stimulated interest in the development of related homogeneous catalysts supported by non-Cp ancillary ligation.[2,3] We report here on the synthesis and reactivity of cationic alkyl derivatives of Zr and Ti that contain *o*-phenyl phenoxide ligation.

Scheme 1



Addition of $[B(C_6F_5)_3]$[4] to benzene solutions of the zirconium and titanium dibenzyl compounds **1** and **3**[5] leads to the rapid (^{1}H NMR) formation of the corresponding zwitterionic species **2** and **4** (Schemes 1 and 2).[6] The molecular structures of **2a** and **4a** (Figure 1)[7] show a three-legged piano-stool geometry about the metal center with the titanium benzyl ligand η^1-bound. The M−O(aryloxide) distances in **2a** and **4a** are among the shortest for aryloxide ligands bound to these metals.[8] In solution NMR data show no evidence for displacement of the η^6-bound anion by the *o*-phenyl substituents of the aryloxide ligands.[6] Indeed, at ambient temperatures there is evidence in the ^{1}H NMR spectrum for restricted rotation of the η^6-bound arene ring in **4b.** Specifically, the resonances for the protons

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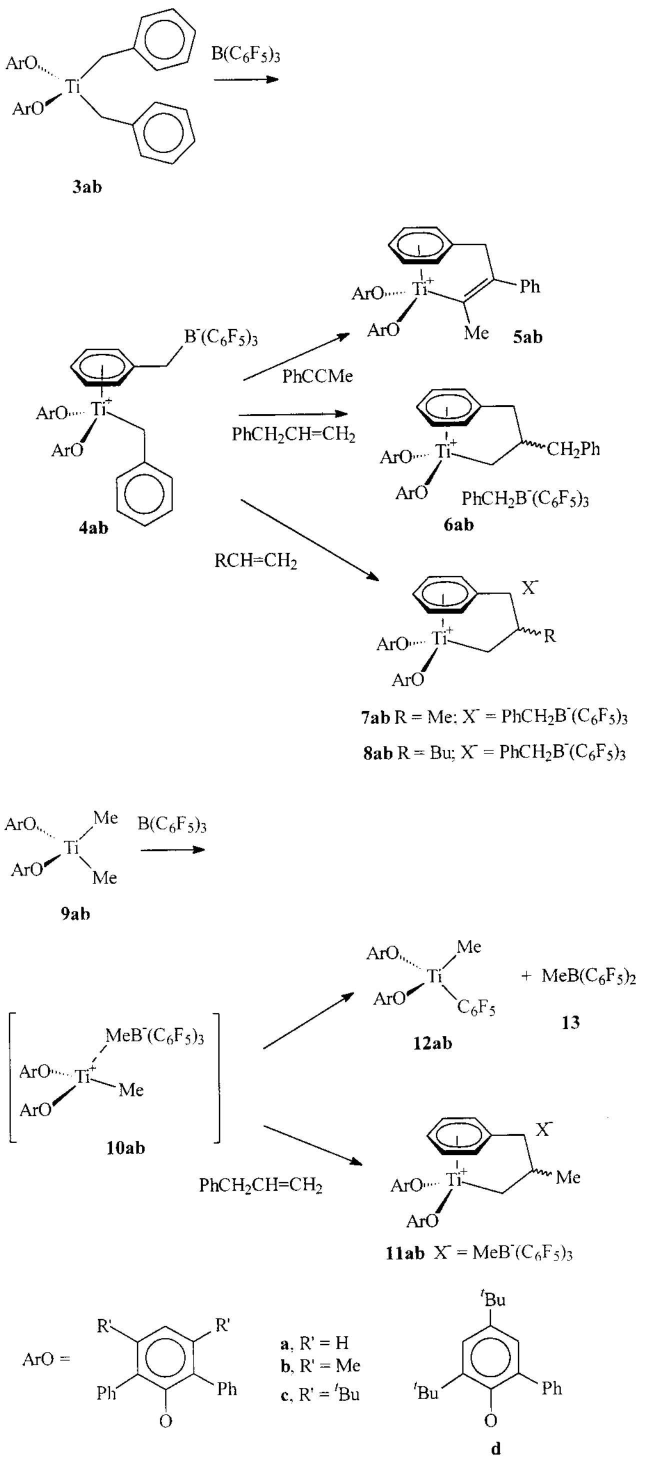
[6] Full experimental details and product characterization are contained in the Supporting Information. Representative synthesis of a zwiterionic species, $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**4a**): a sample of $[Ti(OC_6H_3Ph_2\text{-}2, 6)_2(CH_2Ph)_2]$ (**3a**; 1.00 g, 1.39 mmol) was placed in a solvent-sealed flask along with 1.3 equiv of tris(pentafluorophenyl)boron (0.92 g, 1.80 mmol) and 5 mL of benzene. The reaction solution immediately turned red. The flask was left undisturbed for 12 h, and then the solution was evacuated to dryness. The resulting red solid was redissolved in a minimum of benzene and layered with hexane, affording $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)][\eta^6\text{-}C_6H_5\text{-}CH_2B(C_6F_5)_3]$ (**4a**) as dark red crystals in 63% yield (1.07 g). Anal. Calcd for $C_{68}H_{40}BF_{15}O_2Ti$: C, 66.26; H, 3.27. Found: C, 66.32; H, 3.28. ^{1}H NMR (C_6D_6, 30 °C): δ 6.75−7.30 (aromatics); 6.65 [d, $^3J(^1H-^1H) = 7.0$ Hz, *ortho* Ti−CH_2Ph]; 6.07 [d, $^3J(^1H-^1H) = 6.7$ Hz, *ortho* Ti−η^6-C_6H_5]; 4.78 [t, $^3J(^1H-^1H) = 7.5$ Hz, *meta* Ti−η^6-C_6H_5]; 4.43 [t, $^3J(^1H-^1H) = 7.3$ Hz, *para* Ti-η^6-C_6H_5]; 2.77 (br, B−CH_2); 2.12 (s, Ti−CH_2). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 161.9 (Ti−O−C); 151.0 (br, B−CH_2); 146.2 (*ipso* BCH_2−Ph); 101.2 (TiCH_2). Synthesis of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2\text{-}(C\{CH_3\}C\{Ph\}CH_2\{\eta^6\text{-}C_6H_5\})][PhCH_2B(C_6F_5)_3]$ (**5a**): A sample of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(CH_2Ph)][\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3]$ (**4a**; 130 mg, 0.105 mmol) was dissolved in 2 mL of benzene in a round-bottomed flask. To this solution was added 1.0 equiv of 1-phenylpropyne (13.2 μL, 0.105 mmol). The color of this solution slowly turned from red to orange over the course of 1 h. This orange solution was evacuated to dryness, affording $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(C\{CH_3\}C\{Ph\}CH_2\{\eta^6\text{-}C_6H_5\})][B(C_6F_5)_3(CH_2\text{-}Ph)]$ (**5a**) as a red glassy solid in 64% yield (90 mg). ^{1}H NMR (C_6D_6, 30 °C): δ 6.60−7.40 (aromatics); 6.29 [t, $^3J(^1H-^1H) = 7.6$ Hz, *meta* Ti−η^6-C_6H_5]; 5.82 [d, $^3J(^1H-^1H) = 7.4$ Hz, *ortho* Ti−η^6-C_6H_5]; 4.29 [t, $^3J(^1H-^1H) = 7.4$ Hz, *para* Ti−η^6-C_6H_5]; 3.22 (s, CH_2); 3.17 (s, B−CH_2); 1.87 (s, CH_3). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 231.6 (Ti−C$\{CH_3\}$); 163.8 (Ti−O−C); 45.7 (CH_2); 34.3 (Ti−C$\{CH_3\}$). Attempts to isolate **5a** as a crystalline solid have thus far been unsuccessful.

S0276-7333(98)00287-8 CCC: $15.00

Scheme 2



attached to the η^6-bound arene ring in **4b** are broadened considerably compared to those of **4a**. Further evidence for restricted rotation is given in the ^1H NMR of **2b**, where five distinct signals for the protons of the η^6-bound arene ring are observed. This implies that bulkier aryloxides restrict rotation of the η^6-bound arene ring on the metal center with 2,6-di-*tert*-butyl phenoxide (**2b**) completely locking the arene ring into one conformation with nonequivalent ortho and meta protons.

The zirconium complexes **2** are stable in solution in the presence of propene and phenylpropyne. In contrast, the titanium compounds **4** react with 1 equiv of phenylpropyne or allylbenzene to produce salts **5** and **6** (Scheme 2).[6] The spectroscopic data for these compounds are consistent with insertion of 1 equiv of substrate into the Ti−benzyl bond being followed by chelation via η^6 binding to the benzyl arene ring. In the ^1H NMR spectra of **5** and **6** the free anion $[PhCH_2B^-(C_6F_5)_3]$ was observed. Furthermore, the η^6-arene ring gives rise to three and five multiplets upfield of the normal aromatic region for **5** and **6**, respectively. Although not conclusive, the regiochemistry of phenylpropyne insertion is assigned as shown (Scheme 2) on the basis of the upfield shift of the methyl resonance from δ 1.87 for **5a** to δ 1.03 in **5b**. Previous work has shown that the introduction of *m*-methyl substituents increases the upfield shifting of adjacent groups by the diamagnetic anisotropy of the *o*-phenyl rings.[9] The 1,2-insertion of α-olefins is unequivocal from the NMR data. Attempts to crystallize these insertion products led only to the formation of hexane- or pentane-insoluble oils that dried to glassy solids. The addition of propene or 1-hexene to solutions of **4** initially led to the analogous insertion products **7** and **8**, identified by ^1H NMR

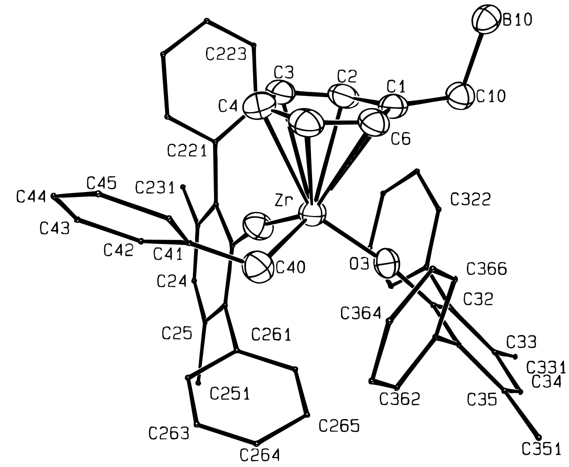


Figure 1. Molecular structure of **2a** showing the atomic numbering scheme. The three C_6F_5 groups attached to boron have been omitted for clarity. The titanium compound **4a** is isostructural, with an identical numbering scheme. Selected bond lengths (Å) and angles (deg) for **2** {**4a**}: M−O(2), 1.893(3) {1.761(5)}; M−O(3), 1.900(3) {1.795(4)}; M−C(40), 2.230(4) {2.159(9)}; M−C(1), 2.821(4) {2.627(6)}; M−C(2), 2.653(4) {2.555(6)}; M−C(3), 2.662(4) {2.543(7)}; M−C(4), 2.681(5) {2.566(7)}; M−C(5), 2.694(4) {2.538(7)}; M−C(6), 2.764(4) {2.558(7)}; O(2)−M−O(3), 113.6(1) {110.0(2)}; O(2)−M−C(40), 99.4(2) {96.6(3)}; O(3)−M−C(40), 99.6(1) {97.8(3)}; M−O(2)−C(21), 165.3(3) {158.9(5)}; M−O(3)−C(31), 158.8(4) {170.5(3)}; M−C(40)−C(41), 117.4(3) {120.6(6)}.

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(7) Crystallographic data for **2a** at 203 K: $ZrF_{15}O_2C_{84}BH_{55}$, M_r = 1483.38, space group $P\bar{1}$ (No. 2), a = 13.358(2) Å, b = 14.722(4) Å, c = 20.596(7) Å, α = 71.45(2)°, β = 77.55(2)°, γ = 72.18(2)°, V = 3624(2) Å^3, d_{calc} = 1.359 g cm^{-3}, Z = 2. Of the 9594 unique reflections collected ($5.14 \leq 2\theta \leq 45.34°$) with Mo Kα ($\lambda$ = 0.710 73 Å), 9594 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.055 and $R_w(F_o^2)$ = 0.160. Crystallographic Data for **4a** at 295 K: $TiF_{15}O_2C_{68}BH_{40}$, M_w = 1232.76, space group $P\bar{1}$ (No. 2), a = 12.917(2) Å, b = 13.045(2) Å, c = 19.600(2) Å, α = 84.757(12)°, β = 77.580(12)°, γ = 61.871(13)°, V = 2844.0(8) Å^3, d_{calc} = 1.444 g cm^{-3}, Z = 2. Of the 7524 unique reflections collected ($5.78 \leq 2\theta\_ \leq 45.34°$) with Mo Kα ($\lambda$ = 0.710 73 Å), the 7523 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.069 and $R_w(F_o^2)$ = 0.178.

(8) Based upon analysis of the Cambridge Structural Database.

(9) Vilardo, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3353.

(Scheme 2). These species carry out the very slow oligomerization of propene and isomerization of 1-hexene into 2-hexene and 3-hexene.

The dimethyl compounds **9**[5b] also react rapidly (^{1}H NMR) with 1 equiv of [B(C_6F_5)$_3$] in C_6D_6 to initially produce a solution containing the single component **10** (Scheme 2). The spectroscopic data for **10** are consistent with the anion being bound to the cationic metal center, as observed for related methyl species. Within 1 h at ambient temperatures this solution converts to a mixture of [(ArO)$_2$Ti(Me)(C_6F_5)] (**12**), [MeB(C_6F_5)$_2$] (**13**),[4a] and a small amount of [(ArO)$_3$TiMe],[5b] as identified by ^{1}H NMR. This type of decomposition has precedence in Zr−Cp chemistry.[4a] The Ti−Me resonance for **12** appears as a sharp triplet; $^5J(^{19}F-^1H) = 1.5$ Hz. Although broad, the B−Me resonance for **13** can be resolved as a pentet; $^5J(^{19}F-^1H) = 1.8$ Hz. The addition of allylbenzene to the initially formed solution of **10** generated the salt **11**, which contains the same cation obtained by addition of propene to **4** (Scheme 2).

Solutions of **10** will catalyze the polymerization of ethene and propene (Table 1). Analysis of the polypropylene by NMR showed an atactic polymer with predominantly vinylidene end groups consistent with 1,2-insertion/β-hydrogen elimination pathways. It can be seen (Table 1) that the molecular weight of both polymers is strongly dependent on the nature of the aryloxide. Although it is not possible at present to rule out electronic effects, previously we have shown that the most important influence of introducing meta substituents onto the 2,6-diphenylphenoxide nucleus is to increase the steric properties of the ligand.[9] This is a consequence of a decrease in conformational flexibility imposed upon the *o*-phenyl rings. Hence, the data in Table 1 can be interpreted as a correlation between ligand bulk and polymer molecular weight.

Table 1. Polyethylene and Polypropylene Properties and Catalyst Activities[a]

cat. precursor	$10^{-3}M_n$	$10^{-3}M_w$	M_w/M_n	10^{-3}(activity), g mol^{-1} h^{-1} atm^{-1}
		Polyethylene		
9a	2.59	5.64	2.2	3
9b	2.61	4.91	1.9	4
9c	8.23	11.8	1.4	3
9d	12.5	23.5	1.9	2
		Polypropylene		
9a	1.53	1.97	1.3	6
9b	1.72	2.17	1.3	5
9c	3.45	4.65	1.4	3
9d	14.5	28.98	2.0	2

[a] Conditions: 0.089 mmol of **9**; 0.097 mmol of B(C_6F_5)$_3$; 3 mL of toluene; 0 °C; 1 atm; 15 min reaction time.

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Supporting Information Available: Figures giving NMR spectra for **3a**,**b** and **5a**, text giving experimental details and product characterization, an ORTEP view of **4a**, text giving a description of the experimental procedures for X-ray diffraction studies, and tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and mutiplicities for **2a** and **4a** (55 pages). Ordering information is given on any current masthead page.

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