

Al-, Nb-, and Ta-Based Perfluoroaryloxo Anions as Cocatalysts for Metallocene-Mediated Ziegler–Natta Olefin Polymerization

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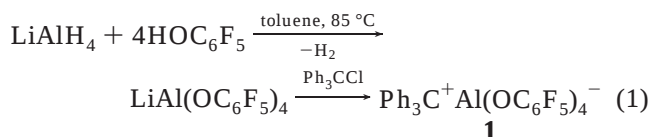
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Summary: Perfluoroaryloxo salts of the formula $\text{Ph}_3\text{C}^+\text{Al}(\text{OC}_6\text{F}_5)_4^-$ and $\text{Ph}_3\text{C}^+\text{M}(\text{OC}_6\text{F}_5)_6^-$ ($\text{M} = \text{Nb}, \text{Ta}$) have been synthesized and characterized. In combination with sterically encumbered zirconocene dimethyl complexes, they yield active ethylene polymerization catalysts.

Current generation abstractors/cocatalysts for homogeneous single-site olefin polymerization¹ are typically group 13-based and contain metal/metalloid–carbon bonds, e.g., methylalumoxane (MAO),² $\text{MAR}_x^+\text{Ar}_{3-x}^-$,³ $\text{M}(\text{C}_6\text{F}_4\text{-2-C}_6\text{F}_5)_3$,⁴ MAR_4^+ ($\text{M} = \text{B}, \text{Al}$),⁵ Due to their structurally well-defined chemical nature and high cocatalytic activity, the perfluoroarylboranes, -borates, and -aluminates are of considerable current scientific and technological interest. Results to date reveal that many of the properties of such catalyst systems are intimately connected with the nature of the cation–anion interaction in ways that are not well-understood. The size, shape, electronic structure, and ligational characteristics of the anion can have a profound effect on catalyst activity, thermal stability, chain transfer characteristics, stereoselection, etc.^{2a,3a–c,4,5a,6} The num-

ber of available cocatalysts is, however, limited and has so far impeded a broad, systematic study of anion effects. We communicate here the synthesis, characterization, and cocatalytic features of a new series of sterically encumbered metalloid and transition metal cocatalysts/counteranions based on the pentafluorophenoxide group, $\text{C}_6\text{F}_5\text{O}^-$. We report that effective cocatalysts need not contain metalloid/metal–carbon bonds and that the properties of the resulting metallocenium cation–anion pairs are sensitive to both the counteranion core structure and the metallocene ancillary ligation.⁷

Reaction of LiAlH_4 with HOC_6F_5 affords $\text{Li}^+\text{Al}(\text{OC}_6\text{F}_5)_4^-$,⁸ and subsequent metathesis with Ph_3CCl yields the corresponding trityl tetrakis(pentafluorophenoxy)-aluminate, $\text{Ph}_3\text{C}^+\text{Al}(\text{OC}_6\text{F}_5)_4^-$ (**1**) (eq 1).⁹ All new com-

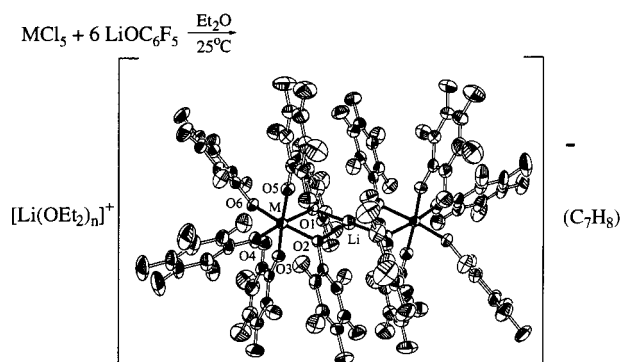


pounds were characterized by conventional spectroscopic and analytical methodology.⁹ Compound **1** is thermally stable at 25 °C in CD_2Cl_2 solution for days without noticeable decomposition. The pentachlorides MCl_5 ($\text{M} = \text{Nb}, \text{Ta}$) readily undergo reaction with LiOC_6F_5 in Et_2O at 25 °C to afford crystalline $[\text{Li}(\text{OEt})_2]^+[\text{M}(\text{OC}_6\text{F}_5)_4(\mu_2\text{-OC}_6\text{F}_5)_2]_2\text{Li}^+\cdot\text{C}_7\text{H}_8$ (Scheme 1; $\text{M} = \text{Nb}$, $n = 4$ (**2a**); $\text{M} = \text{Ta}$, $n = 3$ (**2b**)) salts.^{9,10} Diffraction results for **2a** reveal the quasi-octahedral

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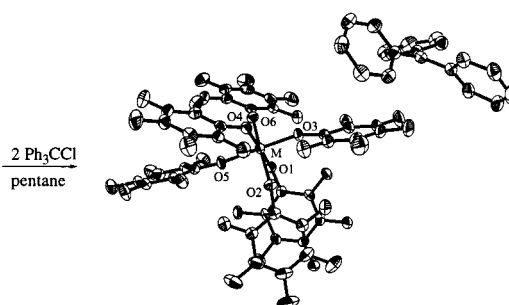
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Scheme 1. Preparation of Complexes 2 and 3



M = Nb (**2a**), yellow crystals. Important distances (Å) and angles (°): avg. Nb–μO = 2.029(3); avg. Nb–terminal O = 1.907(3); avg. Li–O 2.038(3); O1–Nb–O2 = 80.03(10); O1–Li–O2 = 79.62(10); O3–Nb–O5 = 176.70(13); O4–Nb–O6 = 94.78(12); avg. cis O–Nb–O = 89.93(13).

M = Ta (**2b**), colorless crystals. Important distances (Å) and angles (°): avg. Ta–μO = 2.0320(18); avg. Ta–terminal O = 1.910(2); avg. Li–O 2.038(2); O1–Ta–O2 = 79.95(7); O1–Li–O2 = 79.66(7); O3–Ta–O5 = 176.19(9); O4–Ta–O6 = 95.38(9); avg. cis O–Ta–O = 89.91(9).



M = Nb (**3a**), red crystals. Important distances (Å) and angles (°): avg. Nb–O = 1.955(2); avg. cis O–Nb–O = 90.08(8); avg. trans O–Nb–O = 173.60(8).

M = Ta (**3b**), red crystals. Important distances (Å) and angles (°): avg. Ta–O = 1.952(3); avg. cis O–Ta–O = 89.9(1); avg. trans O–Ta–O = 174.0(1).

nature of the group 5 centers and square-planar Li⁺ coordination (Scheme 1). Compounds **2** are cleanly converted with Ph₃CCl to the corresponding mononuclear, thermally stable Ph₃C⁺M(OC₆F₅)₆[−] (M = Nb, (**3a**); M = Ta (**3b**)) salts^{9,10} in high yield. Diffraction analysis reveals six-coordinate metal centers with pronounced nonlinearity of the M–O–C₆F₅ linkages and dispersion in Nb–O distances. For example, the Nb–O–C(aryl) angle ranges from 135.3(2)° to 170.6(2)° and the Nb–O distance from 1.913(2) to 2.009(2) Å.

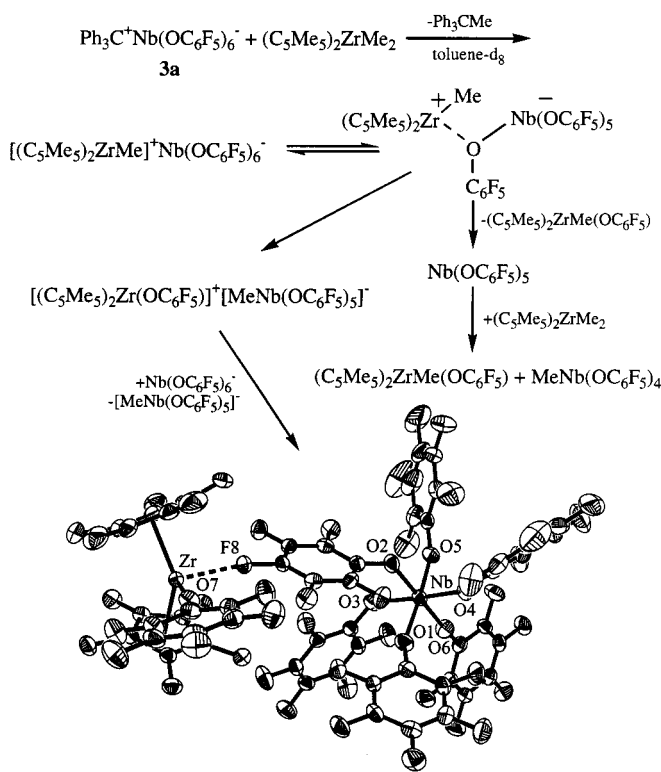
The reactivity and cocatalytic characteristics of **3** were investigated with respect to a series of metallocene dimethyls. At room temperature, facile C₆F₅O[−] transfer from Nb/Ta to Zr/Ti is observed for coordinatively more open complexes such as (C₅H₅)₂ZrMe₂, which reacts readily to form, as assessed by ¹H/¹⁹F NMR spectral comparison with authentic samples,¹¹ (C₅H₅)₂Zr(OC₆F₅)₂, Ph₃CCH₃, and presumably MeNb(OC₆F₅)₄, as well as unidentified minor byproducts.¹¹ Reaction of **3a** with 1.0 equiv of *rac*-Me₂Si(Ind)₂ZrMe₂ proceeds in a similar fashion with formation of *rac*-Me₂Si(Ind)₂ZrMe(OC₆F₅).⁹ In contrast, the behavior toward sterically encumbered

metallocenes, e.g., (C₅Me₄H)₂ZrMe₂ and (C₅Me₅)₂ZrMe₂, is significantly different. Thus, reaction of **3a** with 1.0 equiv of each of these metallocenes in toluene-*d*₈ initially results in red oily products, typical of more ionic (more loosely ion-paired) species,^{5a} as well as (C₅Me₄H)₂ZrMe(OC₆F₅) or (C₅Me₅)₂ZrMe(OC₆F₅), respectively, with the latter assignments confirmed by NMR spectral comparison with authentic samples generated by C₆F₅OH addition to the neutral dimethyl complexes.⁹ On standing at −20 °C, the oily material slowly converts to the metallocenium ion pair [(C₅Me₅)₂ZrOC₆F₅]⁺Nb(OC₆F₅)₆[−] (**4**; Scheme 2), characterized by diffraction and featuring both unexceptional (C₅Me₅)₂ZrR⁺ metrical parameters^{3f} and a relatively short Zr⁺⋯F–C(aryloxide) contact (2.342(2) Å) and a correspondingly elongated F–C bond distance (1.383(4) vs 1.345(4) Å (av)).^{2e,f,5c,12} This result argues for the intermediacy of [(C₅Me₅)₂ZrMe]⁺Nb(OC₆F₅)₆[−], as does observation of [(C₅Me₅)₂ZrMe(THF-*d*₈)]⁺Nb(OC₆F₅)₆[−] (**5**)¹³ in reaction of **3a** with (C₅Me₅)₂ZrMe₂ in THF-*d*₈ and the olefin polymerization activity (vide infra). The instability of [(C₅Me₅)₂ZrMe]⁺Nb(OC₆F₅)₆[−] may reflect the aforementioned deformability of the Nb–O–C₆F₅ linkages, which would facilitate Nb–O–C₆F₅ interaction with, and subsequent C₆F₅O[−] transfer to, the electrophilic Zr center.

The above results imply that phenoxide transfer from **3** is facile for sterically open metallocenium systems, explaining why such preactivated catalysts are inactive toward olefin polymerization. However, spectroscopic

(12) For some related M⁺⋯F–C examples, see: (a) Sun, Y.; Spence, R. E. v. H.; Piers, W. E.; Parvez, M.; Yap, G. P. A. *J. Am. Chem. Soc.* **1997**, *119*, 5132–5143. (b) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80–83. (c) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910–3918.

(13) ¹H and ¹⁹F NMR for **5** (THF-*d*₈, 23 °C): δ 2.01 (s, 30 H, C₅Me₅), 0.40 (s, 3 H, Zr–Me). ¹⁹F NMR (THF-*d*₈, 23 °C): δ −157.26 (d, 2 F, *o*-F, J_{F–F} = 18.1 Hz), −165.38 (tr, 2 F, *p*-F, J_{F–F} = 20.6 Hz), −169.14 (tr, 1 F, *m*-F, J_{F–F} = 22.9 Hz).

Scheme 2. Proposed Reactivity Pattern of $(C_5Me_5)_2ZrMe_2$ with Cocatalyst **3a**

$[(C_5Me_5)_2Zr(OC_6F_5)]^+[Nb(OC_6F_5)_6]^-$ (**4**) Important distances (Å) and angles (°):
 Zr-F8 = 2.343(2); Zr-O7 = 1.984(2); F8-C10 = 1.383(4); avg. C-F = 1.345(4); avg. Nb-O = 1.946(3);
 avg. Zr-Cp(centroid) = 2.219; Cp(centroid)-Zr-Cp(centroid) = 137.8; F8-Zr-O7 = 94.28(9);
 Zr-F8-C10 = 167.7(2); avg. cis O-Nb-O = 89.98(11), avg. trans O-Nb-O = 176.76(11).

Table 1. Ethylene Polymerization Activities and Polymer Properties^a

entry	precursor	cocatalyst	μ mol of cat.	rxn, time (s)	polymer yield (g)	activity g PE/atm·mol·h	M_n^b	M_w/M_n	T_m^c (°C)
1	$(C_5Me_5)_2ZrMe_2$	$Ph_3C^+Al(OC_6F_5)_4^-$ (1)	13.5	30	0.441	3.9×10^6	62 200	2.77	139.8
2	$(C_5Me_5)_2ZrMe_2$	$Ph_3C^+Nb(OC_6F_5)_6^-$ (3a)	1.27	30	0.498	6.0×10^6	45 800	3.32	138.7
3	$(C_5Me_5)_2ZrMe_2$	$Ph_3C^+Ta(OC_6F_5)_6^-$ (3b)	1.32	30	0.561	6.5×10^6	79 800	2.48	136.9
4	$(C_5Me_5)_2ZrMe_2$	$Ph_3C^+B(C_6F_5)_4^-$	1.76	30	0.636	4.3×10^6	88 200	2.15	137.9
5	$(C_5Me_4H)_2ZrMe_2$	$Ph_3C^+Al(OC_6F_5)_4^-$ (1)	1.81	30	0.471	3.1×10^6	127 000	1.91	137.2
6	$(C_5Me_4H)_2ZrMe_2$	$Ph_3C^+Nb(OC_6F_5)_6^-$ (3a)	1.73	30	0.549	4.1×10^6	106 000	3.30	136.8
7	$(C_5Me_4H)_2ZrMe_2$	$Ph_3C^+Ta(OC_6F_5)_6^-$ (3b)	1.75	30	0.739	5.0×10^6	62 500	4.03	136.5
8	$(C_5Me_4H)_2ZrMe_2$	$Ph_3C^+B(C_6F_5)_4^-$	1.73	30	0.729	5.1×10^6	33 200	7.60	135.9

^a Carried out at 1.0 atm of ethylene pressure in 100 mL of toluene on a high-vacuum line at 25 °C. See Supporting Information and ref 4a for polymerization procedures. ^b GPC relative to polystyrene standards. ^c DSC trace from the second scan.

observation of ion pair **5** prompted studies of in situ $(C_5Me_5)_2ZrMe_2$ and $(C_5Me_4H)_2ZrMe_2$ activation in the presence of olefin (as is commonly performed for unstable $B(C_6F_5)_4^-$ -based catalysts).⁵ Under such conditions, reaction of **1** and **3** with $(C_5Me_5)_2ZrMe_2$ and $(C_5Me_4H)_2ZrMe_2$ at 25 °C affords efficient ethylene polymerization catalysts (Table 1; procedure of refs 3c, 4a), with activities and product polymer properties comparable to those of $Ph_3C^+B(C_6F_5)_4^-$ -activated systems under identical polymerization conditions.⁵ One striking and unprecedented feature of the present catalysts is that high ethylene polymerization activity is *not* paralleled by propylene polymerization activity. To our knowledge, this is the first report of such an anion-modulated metallocene reactivity pattern.^{1,6} However, propylene incorporation in ethylene + propylene copolymerizations is observed. The ability of the present catalyst system to differentiate $CH_2=CH_2$ and $CH_2=CHCH_3$ at the activa-

tion step may be related to secondary interactions of the anion phenoxide ligands with the cationic metallocene centers. These results demonstrate that neither group 13 elements nor metal/metalloid–C bonds are necessary for effective metallocene olefin polymerization cocatalysts. Additional steric and electronic modifications are the subject of continuing research.

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Supporting Information Available: Experimental procedures and X-ray structural data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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