

Supporting Information

Synthesis and characterization of phosphine-(thio)phenolate-based half-zirconocenes and their application in ethylene (co-)polymerization

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Table S1. Crystal data and structure refinements of complexes **2a-b** and **2d**.

	2a	2b	2d
Empirical formula	C ₃₈ H ₄₁ Cl ₂ O ₂ PZr	C ₃₆ H ₄₅ Cl ₂ O ₂ PZr	C ₃₉ H ₅₃ Cl ₂ O ₃ PSiZr
Formula weight	722.80	702.81	790.99
Crystal system	monoclinic	triclinic	triclinic
Space group	P2 ₁ /n	P-1	P-1
a (Å)	13.8359(7)	8.5278(5)	10.2467(5)
b (Å)	17.5334(9)	11.6963(7)	12.3347(6)
c (Å)	14.0252(7)	19.2212(12)	17.2140(8)
α (°)	90.00	91.3190(10)	106.1290(10)
β (°)	97.1520(10)	95.4530(10)	91.0240(10)
γ (°)	90.00	110.6890(10)	111.5860(10)
V (Å ³), Z	3375.9(3), 4	1782.14(19), 2	1925.82(16), 2
Density _{calcd} (Mg/m ³)	1.422	1.310	1.364
Absorption coefficient (mm ⁻¹)	0.564	0.532	0.532
F (000)	1496	732	828
Crystal size (mm)	0.28×0.21×0.14	0.28×0.20×0.13	0.32×0.24×0.13
θ range for data collection (°)	1.87 to 26.02	1.86 to 26.04	1.86 to 26.04
Reflections collected	21388	9814	10513
Independent reflections	6657 (R _{int} = 0.0414)	6871 (R _{int} = 0.0209)	7405 (R _{int} = 0.0159)
Data/restraints/ parameters	6657/15/402	6871/0/387	7405/23/424
Goodness-of-fit on F ²	1.043	1.055	1.047
Final R indices [I>2σ (I)]: R1, wR2	0.0455, 0.1055	0.0428, 0.1043	0.0409, 0.1066
Largest diff. Peak and hole (e Å ⁻³)	0.739 and -0.643	0.606 and -0.312	0.881 and -0.434

Table S2. Ethylene polymerization by **2a-e**/MMAO and **3b-e**/MMAO catalytic systems. ^a

Entry	Catalyst (μmol)	Al/Zr (molar ratio)	Temp. ($^{\circ}\text{C}$)	Yield (mg)	Activity ($\text{kg/mol}_{\text{Zr}}\cdot\text{h}$)	M_{w}^b (10^{-4})	$M_{\text{w}}/M_{\text{n}}^b$
1	2a (2)	2000	75	410	1230	40.1	2.1
2	2b (2)	2000	75	480	1440	65.1	2.6
3	2c (2)	2000	75	220	660	53.6	1.8
	2c (2)	2000	75	220	660	53.1	1.9
4	2d (2)	2000	75	1340	4020	42.7	2.2
	2d (2)	2000	75	1310	3930	40.6	2.1
5	2e (2)	2000	75	860	2580	54.4	2.1
	2e (2)	2000	75	850	2550	53.8	2.1
6	2d (2)	3000	75	570	1710	34.6	2.4
7	2d (2)	2000	100	820	2460	32.4	2.5
8	3b (1)	2000	75	1340	8040	25.8	2.3
	3b (1)	2000	75	1300	7800	25.7	2.2
9	3c (1)	2000	75	2690	16140	17.2	2.0
	3c (1)	2000	75	2650	15900	17.5	2.1
10	3d (1)	2000	75	1390	8340	20.0	2.1
11	3e (2)	2000	75	420	1260	33.6	2.2
	3e (2)	2000	75	410	1230	32.0	2.1
12	3c (1)	3000	75	2930	17580	19.6	2.0
13	3c (1)	2000	100	1080	6480	14.8	2.2
14	4 (1)	2000	75	1920	11520	5.7	3.3

^a Conditions: MMAO as cocatalyst, 10 min, ethylene 4 atm, $V_{\text{total}} = 80$ mL. ^b Weight-average molecular weights and polydispersity indexes determined by high temperature GPC at 150 $^{\circ}\text{C}$ in 1,2,4- $\text{C}_6\text{Cl}_3\text{H}_3$ vs. narrow polystyrene standards.