Supporting Information

Efficient copolymerization of ethylene with norbornene or its derivatives using half-metallocenezirconium(IV) catalysts

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

	2a	**2d**
Formula	$C_{30}H_{41}O_2PZrCl_2$	$C_{70}H_{84}Cl_4F_2O_4P_2Zr_2$
Formula weight	626.72	596.16
Crystal system	orthorhombic	monoclinic
Space group	P_{bc}/n	P_{21}/c
a (Å)	20.3736(16)	18.2887(9)
b (Å)	21.5156(16)	27.7326(14)
c (Å)	13.6999(10)	15.9855(8)
α (°)	90.00	90.00
β (°)	90.00	108.4900(10)
γ (°)	90.00	90.00
V (Å^3), Z	6005.4(8), 8	7689.2(7), 4
Density(Mg/m^3)	1.386	1.221
Absorpt. Coeff. (mm^{-1})	0.622	0.497
F (000)	2608	2928
θ range (°)	1.38 to 28.31	1.38 to 25.03
Reflect. collected	34222	38035
Independ. Reflect.	7269(R_{int} = 0.0579)	13552 (R_{int} = 0.0500)
Data/restraints/ parameters	7269/0/325	13552/2/769
Goof on F^2	1.092	0.995
R_1, wR_2	0.0934, 0.1288	0.0552, 0.1524
diff. Peak/hole (e Å^{-3})	1.29/-0.39	2.517/-0.624

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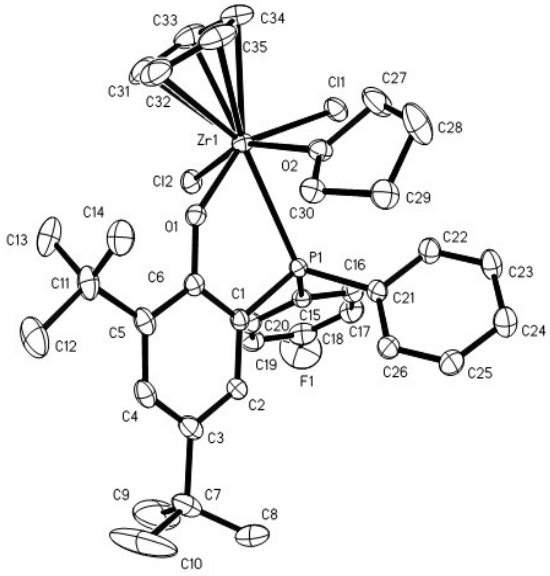

Fig. S1 Molecular structure of **2d** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

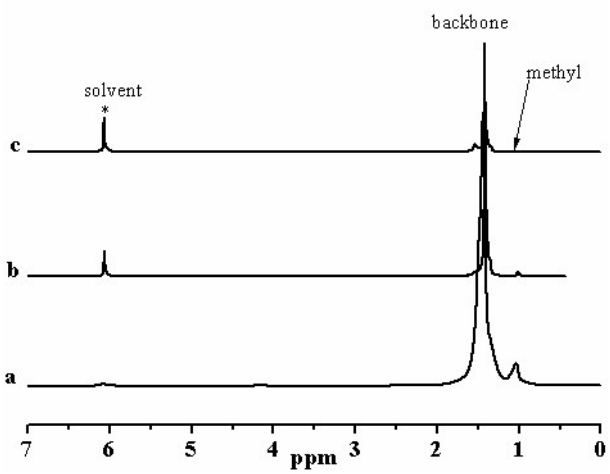

Fig. S2 ^{1}H NMR spectra of ethylene polymers in CD_2Cl_4 (a, run 2; b, run 4; c, run 3 in Table 2).[1]

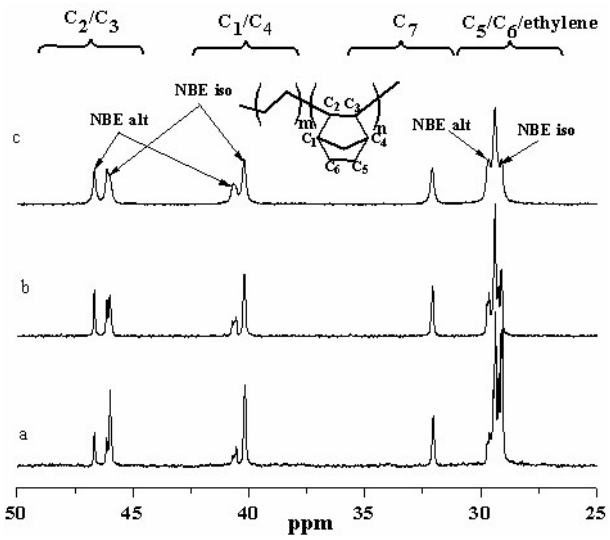

Fig. S3 ^{13}C spectra of ethylene/NBE copolymers produced by catalyst **2b** with different NBE contents in $CDCl_3$. (a: run 13, 28.1%; b: run 8, 37.4%; c: run 1, 39.3% in Table 4).

DFT calculations for catalysts 2a-d

Comonomers coordinate with the vacant in the active species from the opposite place of THF, coordinating on the Zr atom. Therefore the coordination space for catalyst **2a**, **2c** and **2d** is comparable due to the planar structure of Phenyl (Fig. S4, left), which is bigger than that of catalyst **2b** with extra methyl on the *tert*-butyl group taking some incorporation space.

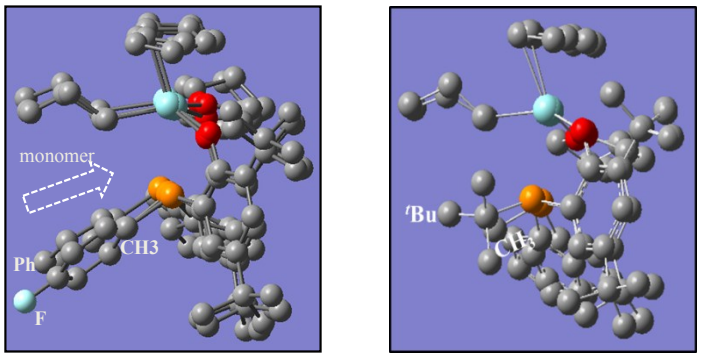

Fig. S4 (a) left. The overlay of the active species of catalyst **2a**, **2c** and **2d**; (b) right. The overlay of the active species of catalyst **2a** and **2b**.

As shown in the Fig. S5, the angle of <1,2,3>, distance of $D_{3,4}$ and $d_{Zr\text{-}P}$ can be used to measure the coordination space and electronic factor quantitatively. The larger angle of <1,2,3> and shorter distance of $D_{3,4}$ together means bigger coordination space and the steric hindrance is decreased in the order: **2a** > **2c** ~ **2d** >> **2b**. Shorter distance of $d_{Zr\text{-}P}$ hints much stronger coordination ability of P atom to Zr atom, reflecting the more electron donating property of P moiety. Therefore, the electron withdrawing ability is decreased in the order: **2d** > **2c** > **2a** > **2b**. It is worthy to note that catalysts **2a-d** only show a slightly degree of divergence in electronic factor, because of unobvious

disparities in $d_{Zr\text{-}P}$. In all, the DFT calculations are in accordance with our experimental analysis.

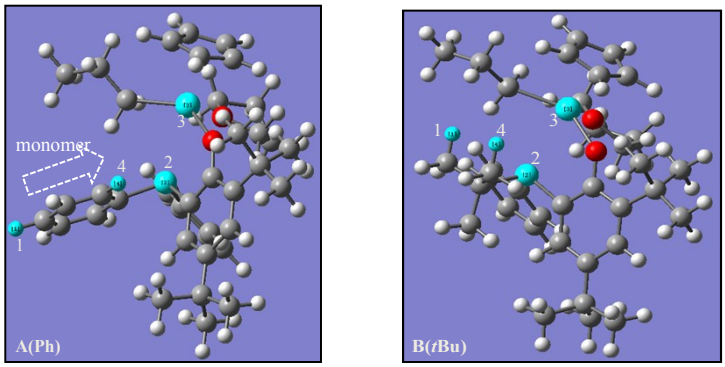

Fig. S5 (a), left. The active species of catalyst **2c**. (b), right. the active species of catalyst **2b**. (To catalyst **2a**: <1,2,3> = 124.4° $D_{3,4}$ = 4.32 Å $d_{Zr\text{-}P}$ = 2.89 Å; catalyst **2b**: <1,2,3> = 109.4° $D_{3,4}$= 3.57 Å $d_{Zr\text{-}P}$ = 2.88 Å; catalyst **2c**: <1,2,3> = 121.0° $D_{3,4}$ = 4.21 Å $d_{Zr\text{-}P}$ = 2.90 Å; catalyst **2d**: <1,2,3> = 123.3° $D_{3,4}$ = 4.14 Å $d_{Zr\text{-}P}$ = 2.92 Å. <1,2,3> is the angle between the three atoms, $D_{3,4}$ is the distance between atom 3 and atom 4, $d_{Zr\text{-}P}$ is the distance between atom P and Zr).

Reference

1 W. Thomas, V. Gregor, T. Alexandra, R. Philipp, G. S. Inigo and M. Stefan, *J. Am. Chem. Soc.*, 2014, **136**, 2078-2085.