Supporting information

Synthesis, cyclization and migration insertion oligomerization of $CpFe(CO)_2(CH_2)_3PPh_2$ in solution

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Table S1. Summary of Crystal Data and Structure Refinement of FpP, (1) and (2)

	FpP	(1)	(2)
Empirical Formula	$C_{22}H_{21}O_2PFe$	$C_{21}H_{21}OPFe$	$C_{22}H_{21}O_2PFe$
Formula Weight	404.21	376.20 g/mol	404.21 g/mol
Temperature	296(2) K	200(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$\boldsymbol{P2_1/c}$	$\boldsymbol{P2_1/c}$	$\boldsymbol{P2_1/c}$
A	8.6898(2) Å	16.2810(8) Å	10.3890(4) Å
B	24.7491(7) Å	7.8128(4) Å	12.5243(3) Å
C	10.1917(3) Å	15.0261(7) Å	14.4003(4) Å
A	90º	90°	90°
B	110.519(2) º	110.433(2)°	94.592(2)°
Γ	90º	90°	90°
Volume	2052.81(10) $Å^3$	1791.06(15) $Å^3$	1867.68(10) $Å^3$
Z, calculated Density	4, 1.308 g/cm^3	4, 1.395 g/cm^3	4, 1.438 g/cm^3
Absorption Coefficient	0.824 mm^{-1}	0.935 mm^{-1}	0.906 mm^{-1}
F(000)	840	784	840
θ range for data collection	2.29 to 28.00 º	1.33 to 28.00°	1.97 to 28.00°
Reflections collected /unique	34800/4972[R(int)=0.0648]	38882/4310[$R_{(int)}$= 0.0201]	20942/4424[$R_{(int)}$= 0.0211]
Completeness to θ = 28.00	100.0 %	99.7 %	98.1 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4972 / 0 / 235	4310 / 0 / 217	4424 / 0 / 236
Goodness-of-fit on F^2	1.054	1.065	1.306
Final R indices [I>2σ(I)]	R1=0.0436,wR2= 0.0787	R1=0.0219, wR2 = 0.0576	R1=0.0248,wR2=0.0674
R indices (all data)	R1= 0.0938, wR2 = 0.0950	R1= 0.0249, wR2 = 0.0621	R1 =0.0309, wR2 = 0.0799
Largest diff. peak and hole	0.334 and -0.182 e.$Å^{-3}$	0.307 and -0.199 e.$Å^{-3}$	0.282 and -0.199 e.$Å^{-3}$

Table S2. Comparison of bond angles and distances between FpP and other Fp derivative

Bond angles and distances	FpP	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2(CH_2)_4$
C(6)-Fe-C(7)	93.64°	95°
C(6)-Fe-C(8)	85.84°	86°
C(7)-Fe-C(8)	87.29°	88°
Fe-C8	2.066	2.08
C8-C9	1.52	1.54

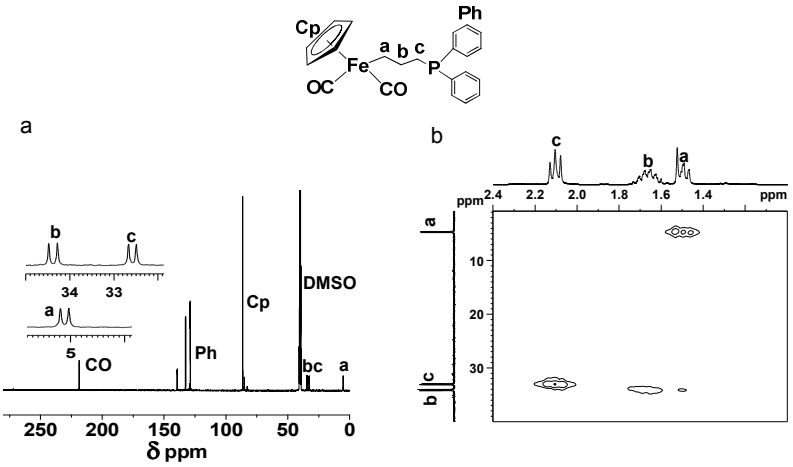

Figure S1 ^{13}C NMR of FpP in DMSO-d_6 (a) and ^{13}C- ^{1}H HMQC 2D NMR of FpP in C_6D_6 (b)

Table S3. Selected torsion angles for (1)

Number	Atom1	Atom2	Atom3	Atom4	Torsion angle
1	C8	Fe1	P1	C10	-16.28(6)
2	P1	Fe1	C8	C9	39.4(1)
3	Fe1	P1	C10	C9	-6.6(1)
4	Fe1	C8	C9	C10	-54.2(1)
5	C8	C9	C10	P1	35.8(1)

Table S4. Selected torsion angles for (2)

Number	Atom1	Atom2	Atom3	Atom4	Torsion angle
1	P13	Fe1	C1	C2	55.6(1)
2	C1	Fe1	P13	C4	-47.54(8)
3	Fe1	C1	C2	C3	-69.4(2)
4	C1	C2	C3	C4	65.6(2)
5	C2	C3	C4	P13	-61.7(2)
6	C3	C4	P13	Fe1	58.5(1)

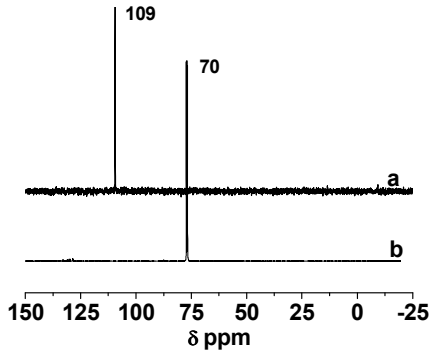

Figure S2. ^{31}P NMR spectra for (1) (a) and (2) (b) in $CDCl_3$

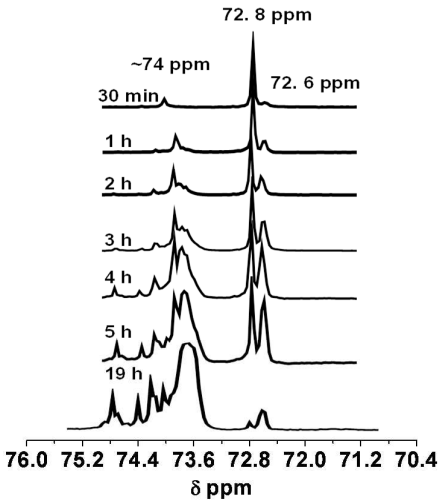

Figure S3. ^{31}PNMR of the main chain coordinated phosphorus in THF

The peaks appearing at 73.4-75.0 ppm are attributed to main chain coordinated phosphorus. The intensity for these peaks improved during the polymerization suggesting the growth of PFpP chains. The multiple peaks probably are caused by PFpP with different DP or different repeat units in the same PFpP chains. This result suggests that the chemical shifts for these phosphorus are sensitive to the length of PFpP and their positions in the same polymers when THF is used as solvent.