(Revised)

Supplementary Material Available

The *ansa*-Cyclopentadienyl-Phenoxy Titanium(IV) Complexes (PHENICS) : Synthesis, Characterization and Catalytic Behavior in Olefin Polymerization

Masaaki Nabika,[†] Hiroaki Katayama,[†] Tsuyoshi Watanabe,[†]
Hiroshi Kawamura-Kuribayashi,[†] Kazunori Yanagi,[‡] and Akio Imai[†]

[†]*Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 2-1 Kitasode, Sodegaura, Chiba 299-0295, Japan.*

[‡]*Genomic Science Laboratories, Dainippon Sumitomo Pharma Co., Ltd., 3-1-98, Kasugadenaka, Konohana-ku, Osaka 554-0022, Japan.*

Table S1. Summary of Crystallographic Data of **1b**

Empirical Formula	$C_{19}H_{24}OCl_2Ti$
Formula Weight	387.20
Crystal Dimensions	0.1 × 0.2 × 0.2 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 18.437(4) Å
	b = 10.675(2) Å
	c = 10.002(3) Å
	β = 96.80(2)°
	V = 1954.7(8) Å^3
Space Group	$P2_1/a$ (#14)
Z value	4
D_{calc}	1.316 g/cm^3
F_{000}	808.00
μ(MoKα)	7.123 cm^{-1}
Diffractometer	CAD4
Radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
Temperature	23.0°C
Scan Type	ω-2θ
$2\theta_{max}$	54.9°
Refinement	Full-matrix least-squares on F^2
Refinement program	SHELX-97
No. of Reflections Measured	4580
No. Observations (All reflections)	4444
No. Variables	233
Reflection/Parameter Ratio	19.07
Residuals: R1 (I>2σ(I))	0.0593
Residuals: R (All reflections)	0.1070
Residuals: wR2 (All reflections)	0.1789
Goodness of Fit Indicator	1.015
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.46 e$^-$/Å^3
Minimum peak in Final Diff. Map	-1.01 e$^-$/Å^3

Table S2. Positional and Isotropic Thermal Parameters of **1b**.

atom	x	y	z	B_{eq}
Ti(1)	0.28965(3)	0.51647(5)	0.17134(5)	3.23(2)
CL(1)	0.18196(6)	0.4245(1)	0.0921(1)	6.11(2)
CL(2)	0.35202(6)	0.5279(1)	-0.01006(8)	5.83(2)
O(1)	0.3359(1)	0.3978(2)	0.2763(2)	3.02(3)
C(1)	0.3481(1)	0.4327(2)	0.5157(2)	2.50(4)
C(2)	0.3702(1)	0.3705(2)	0.4036(2)	2.55(4)
C(3)	0.4261(1)	0.2787(2)	0.4145(2)	2.91(4)
C(4)	0.4572(2)	0.2506(2)	0.5464(2)	3.19(4)
C(5)	0.4368(2)	0.3089(2)	0.6597(2)	3.24(4)
C(6)	0.3829(2)	0.4008(2)	0.6431(2)	2.89(4)
C(7)	0.4713(2)	0.2742(3)	0.8003(3)	4.54(6)
C(8)	0.4541(2)	0.2178(2)	0.2905(3)	3.49(5)
C(9)	0.3919(2)	0.1502(3)	0.2014(4)	5.33(8)
C(10)	0.4880(2)	0.3181(3)	0.2084(3)	4.72(6)
C(11)	0.5137(2)	0.1207(3)	0.3321(4)	5.92(9)
C(12)	0.2117(2)	0.4529(3)	0.4971(3)	3.71(5)
C(13)	0.2877(2)	0.6173(3)	0.6244(2)	3.74(5)
C(14)	0.2838(1)	0.6088(2)	0.3785(2)	2.69(4)
C(15)	0.3462(2)	0.6580(2)	0.3267(2)	3.15(4)
C(16)	0.3228(2)	0.7281(3)	0.2091(3)	4.09(6)
C(17)	0.2462(2)	0.7215(3)	0.1879(3)	4.44(7)
C(18)	0.2219(2)	0.6493(2)	0.2921(3)	3.63(5)
C(19)	0.2839(2)	0.5267(2)	0.5030(2)	2.69(4)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S2. Positional and Isotropic Thermal Parameters of **1b** (continued).

atom	x	y	z	B_{eq}
H(4)	0.496(2)	0.191(3)	0.554(3)	3.2(6)
H(6)	0.371(2)	0.451(3)	0.722(3)	3.2(6)
H(7A)	0.5072	0.2099	0.7944	5.45
H(7B)	0.4342	0.2440	0.8519	5.45
H(7C)	0.4942	0.3467	0.8434	5.45
H(9A)	0.3707	0.0875	0.2536	6.40
H(9B)	0.4113	0.1111	0.1267	6.40
H(9C)	0.3551	0.2099	0.1684	6.40
H(10A)	0.5052	0.2802	0.1311	5.66
H(10B)	0.5281	0.3569	0.2630	5.66
H(10C)	0.4519	0.3803	0.1795	5.66
H(11A)	0.4943	0.0559	0.3841	7.11
H(11B)	0.5540	0.1606	0.3853	7.11
H(11C)	0.5302	0.0849	0.2531	7.11
H(12A)	0.2124	0.4016	0.5760	4.46
H(12B)	0.2063	0.4007	0.4184	4.46
H(12C)	0.1715	0.5104	0.4933	4.46
H(13A)	0.2881	0.5699	0.7060	4.49
H(13B)	0.2460	0.6717	0.6142	4.49
H(13C)	0.3315	0.6665	0.6282	4.49
H(15)	0.392(2)	0.644(2)	0.358(3)	2.6(5)
H(16)	0.354(2)	0.773(3)	0.155(3)	3.7(6)
H(17)	0.219(2)	0.754(4)	0.125(4)	5.9(9)
H(18)	0.170(2)	0.621(3)	0.302(3)	5.2(8)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S3. Anisotropic Displacement Parameters of **1b**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.0579(3)	0.0405(3)	0.0224(2)	0.0123(2)	-0.0033(2)	-0.0021(2)
CL(1)	0.0754(6)	0.0831(7)	0.0660(6)	0.0017(5)	-0.0233(4)	-0.0251(5)
CL(2)	0.1101(8)	0.0839(7)	0.0304(4)	0.0254(5)	0.0198(4)	0.0043(4)
O(1)	0.055(1)	0.0333(9)	0.0248(8)	0.0088(8)	-0.0029(7)	-0.0047(7)
C(1)	0.042(1)	0.027(1)	0.026(1)	0.000(1)	0.0020(9)	0.0002(9)
C(2)	0.042(1)	0.028(1)	0.026(1)	0.0003(9)	-0.0016(9)	0.0006(9)
C(3)	0.047(1)	0.033(1)	0.031(1)	0.003(1)	0.004(1)	0.000(1)
C(4)	0.042(1)	0.038(1)	0.041(2)	0.006(1)	0.001(1)	0.008(1)
C(5)	0.046(1)	0.042(2)	0.032(1)	-0.002(1)	-0.004(1)	0.006(1)
C(6)	0.047(1)	0.036(1)	0.026(1)	-0.002(1)	0.002(1)	0.000(1)
C(7)	0.064(2)	0.071(2)	0.035(2)	0.010(2)	-0.007(1)	0.010(2)
C(8)	0.056(2)	0.041(2)	0.037(1)	0.013(1)	0.011(1)	0.000(1)
C(9)	0.086(2)	0.059(2)	0.059(2)	0.000(2)	0.016(2)	-0.029(2)
C(10)	0.065(2)	0.063(2)	0.054(2)	0.006(2)	0.020(2)	0.007(2)
C(11)	0.097(2)	0.069(2)	0.064(2)	0.043(2)	0.028(2)	0.006(2)
C(12)	0.050(2)	0.040(2)	0.053(2)	0.002(1)	0.010(1)	0.005(1)
C(13)	0.073(2)	0.042(2)	0.027(1)	0.014(4)	0.005(1)	-0.005(1)
C(14)	0.051(2)	0.026(1)	0.025(1)	0.008(1)	0.004(1)	-0.0031(9)
C(15)	0.055(2)	0.032(1)	0.033(1)	0.000(1)	0.005(1)	0.000(1)
C(16)	0.079(2)	0.039(2)	0.039(2)	0.005(2)	0.013(2)	0.007(1)
C(17)	0.087(2)	0.044(2)	0.037(2)	0.025(2)	0.003(1)	0.007(1)
C(18)	0.059(2)	0.043(2)	0.036(1)	0.016(1)	0.002(1)	0.000(1)
C(19)	0.046(1)	0.029(1)	0.028(1)	0.002(1)	0.004(1)	-0.0004(9)

The general temperature factor expression:

$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S4. Bond Distances of **1b** in Å.

atom	atom	distance	atom	atom	distance
Ti(1)	CL(1)	2.272(1)	Ti(1)	CL(2)	2.263(1)
Ti(1)	O(1)	1.795(2)	Ti(1)	C(14)	2.309(2)
Ti(1)	C(15)	2.324(2)	Ti(1)	C(16)	2.359(3)
Ti(1)	C(17)	2.343(3)	Ti(1)	C(18)	2.321(3)
O(1)	C(2)	1.384(2)	C(1)	C(2)	1.404(3)
C(1)	C(6)	1.399(3)	C(1)	C(19)	1.546(3)
C(2)	C(3)	1.417(3)	C(3)	C(4)	1.407(3)
C(3)	C(8)	1.542(4)	C(4)	C(5)	1.383(4)
C(5)	C(6)	1.393(3)	C(5)	C(7)	1.519(4)
C(8)	C(9)	1.545(4)	C(8)	C(10)	1.528(5)
C(8)	C(11)	1.532(5)	C(12)	C(19)	1.541(4)
C(13)	C(19)	1.548(3)	C(14)	C(15)	1.416(4)
C(14)	C(18)	1.416(3)	C(14)	C(19)	1.522(3)
C(15)	C(16)	1.418(4)	C(16)	C(17)	1.404(5)
C(17)	C(18)	1.411(4)			

Table S4. Bond Distances of **1b** in Å (continued).

atom	atom	distance	atom	atom	distance
C(4)	H(4)	0.95(3)	C(6)	H(6)	1.00(3)
C(7)	H(7A)	0.960	C(7)	H(7B)	0.960
C(7)	H(7C)	0.960	C(9)	H(9A)	0.960
C(9)	H(9B)	0.960	C(9)	H(9C)	0.960
C(10)	H(10A)	0.960	C(10)	H(10B)	0.960
C(10)	H(10C)	0.960	C(11)	H(11A)	0.960
C(11)	H(11B)	0.960	C(11)	H(11C)	0.960
C(12)	H(12A)	0.960	C(12)	H(12B)	0.960
C(12)	H(12C)	0.960	C(13)	H(13A)	0.960
C(13)	H(13B)	0.960	C(13)	H(13C)	0.960
C(15)	H(15)	0.88(2)	C(16)	H(16)	0.96(3)
C(17)	H(17)	0.83(3)	C(18)	H(18)	1.01(3)

Table S5. Bond Angles of **1b** in Degrees.

atom	atom	atom	angle	atom	atom	atom	angle
CL(1)	Ti(1)	CL(2)	104.46(4)	CL(1)	Ti(1)	O(1)	103.51(7)
CL(1)	Ti(1)	C(14)	111.46(7)	CL(1)	Ti(1)	C(15)	144.91(9)
CL(1)	Ti(1)	C(16)	131.97(9)	CL(1)	Ti(1)	C(17)	97.85(9)
CL(1)	Ti(1)	C(18)	86.76(8)	CL(2)	Ti(1)	O(1)	104.82(7)
CL(2)	Ti(1)	C(14)	141.13(7)	CL(2)	Ti(1)	C(15)	105.73(8)
CL(2)	Ti(1)	C(16)	86.00(9)	CL(2)	Ti(1)	C(17)	102.51(9)
CL(2)	Ti(1)	C(18)	137.74(8)	O(1)	Ti(1)	C(14)	81.13(8)
O(1)	Ti(1)	C(15)	85.62(9)	O(1)	Ti(1)	C(16)	119.1(1)
O(1)	Ti(1)	C(17)	139.5(1)	O(1)	Ti(1)	C(18)	111.99(9)
C(14)	Ti(1)	C(15)	35.6(1)	C(14)	Ti(1)	C(16)	59.1(1)
C(14)	Ti(1)	C(17)	59.0(1)	C(14)	Ti(1)	C(18)	35.61(9)
C(15)	Ti(1)	C(16)	35.2(1)	C(15)	Ti(1)	C(17)	58.4(1)
C(15)	Ti(1)	C(18)	58.7(1)	C(16)	Ti(1)	C(17)	34.7(1)
C(16)	Ti(1)	C(18)	58.5(1)	C(17)	Ti(1)	C(18)	35.2(1)
Ti(1)	O(1)	C(2)	145.1(2)	C(2)	C(1)	C(6)	117.9(2)
C(2)	C(1)	C(19)	122.2(2)	C(6)	C(1)	C(19)	119.8(2)
O(1)	C(2)	C(1)	119.4(2)	O(1)	C(2)	C(3)	117.7(2)
C(1)	C(2)	C(3)	122.8(2)	C(2)	C(3)	C(4)	115.6(2)
C(2)	C(3)	C(8)	122.6(2)	C(4)	C(3)	C(8)	121.7(2)
C(3)	C(4)	C(5)	123.5(2)	C(4)	C(5)	C(6)	118.6(2)
C(4)	C(5)	C(7)	121.6(2)	C(6)	C(5)	C(7)	119.8(2)
C(1)	C(6)	C(5)	121.6(2)	C(3)	C(8)	C(9)	111.4(2)
C(3)	C(8)	C(10)	109.5(2)	C(3)	C(8)	C(11)	111.4(2)
C(9)	C(8)	C(10)	109.9(2)	C(9)	C(8)	C(11)	107.5(2)
C(10)	C(8)	C(11)	107.1(2)	Ti(1)	C(14)	C(15)	72.8(2)
Ti(1)	C(14)	C(18)	72.7(2)	Ti(1)	C(14)	C(19)	119.5(2)
C(15)	C(14)	C(18)	107.1(2)	C(15)	C(14)	C(19)	126.2(2)
C(18)	C(14)	C(19)	126.7(2)	Ti(1)	C(15)	C(14)	71.6(2)
Ti(1)	C(15)	C(16)	73.8(2)	C(14)	C(15)	C(16)	108.6(2)
Ti(1)	C(16)	C(15)	71.0(2)	Ti(1)	C(16)	C(17)	72.0(2)
C(15)	C(16)	C(17)	107.5(3)	Ti(1)	C(17)	C(16)	73.3(2)
Ti(1)	C(17)	C(18)	71.5(2)	C(16)	C(17)	C(18)	108.5(2)
Ti(1)	C(18)	C(14)	71.7(2)	Ti(1)	C(18)	C(17)	73.2(2)
C(14)	C(18)	C(17)	108.3(2)	C(1)	C(19)	C(12)	108.7(2)
C(1)	C(19)	C(13)	112.2(2)	C(1)	C(19)	C(14)	111.5(2)
C(12)	C(19)	C(13)	108.0(2)	C(12)	C(19)	C(14)	110.3(2)
C(13)	C(19)	C(14)	106.1(2)				

Table S6. Summary of Crystallographic Data of **1d**.

Empirical Formula	$C_{22}H_{32}OCl_2SiTi$
Formula Weight	459.39
Crystal Dimensions	0.2 × 0.2 × 0.2 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.010(2) Å
	b = 22.969(3) Å
	c = 10.416(1) Å
	β = 96.38(2)°
	V = 2380.0(6) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.282 g/cm^3
F_{000}	968.00
μ(MoKα)	6.437 cm^{-1}
Diffractometer	CAD4
Radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
Temperature	23℃
Scan Type	ω-2θ
$2\theta_{max}$	54.9°
Refinement	Full-matrix least-squares on F^2
Refinement program	SHELX-97
No. of Reflections Measured	5731
No. Observations (All reflections)	5445
No. Variables	253
Reflection/Parameter Ratio	21.52
Residuals: R1 (I>2σ(I))	0.0540
Residuals: R (All reflections)	0.1250
Residuals: wR2 (All reflections)	0.1686
Goodness of Fit Indicator	1.026
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.70 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.52 e$^-$/Å^3

Table S7. Positional and Isotropic Thermal Parameters of **1d**.

atom	x	y	z	B_{eq}
Ti(1)	0.34203(6)	0.16420(3)	0.49414(6)	3.14(2)
CL(1)	0.3587(2)	0.26031(7)	0.4517(1)	7.50(4)
CL(2)	0.5377(1)	0.1279(1)	0.4406(1)	8.51(5)
Si(1)	0.0064(1)	0.13261(5)	0.56577(9)	2.90(2)
O(1)	0.2235(2)	0.1381(1)	0.3665(2)	2.90(4)
C(1)	-0.0062(3)	0.1181(2)	0.3875(3)	2.47(5)
C(2)	0.1005(3)	0.1204(2)	0.3110(3)	2.37(5)
C(3)	0.0841(3)	0.1059(2)	0.1782(3)	2.66(5)
C(4)	-0.0455(3)	0.0929(2)	0.1248(3)	3.18(6)
C(5)	-0.1559(3)	0.0929(2)	0.1946(3)	3.20(6)
C(6)	-0.1329(3)	0.1043(2)	0.3261(3)	2.97(6)
C(7)	-0.2957(4)	0.0818(2)	0.1285(4)	5.0(1)
C(8)	0.2043(3)	0.1023(2)	0.0979(3)	3.58(7)
C(9)	0.2719(5)	0.1619(2)	0.0931(4)	5.7(1)
C(10)	0.3041(4)	0.0571(2)	0.1560(4)	5.1(1)
C(11)	0.1597(5)	0.0847(2)	-0.0417(3)	5.6(1)
C(12)	-0.1003(4)	0.1965(2)	0.5921(4)	5.5(1)
C(13)	-0.0674(4)	0.0698(2)	0.6467(4)	5.5(1)
C(14)	0.1873(3)	0.1424(2)	0.6331(2)	2.57(6)
C(15)	0.2839(3)	0.0964(2)	0.6395(3)	3.19(6)
C(16)	0.4086(4)	0.1183(2)	0.6968(3)	4.07(8)
C(17)	0.3930(3)	0.1772(2)	0.7224(3)	3.72(7)
C(18)	0.2568(3)	0.1923(2)	0.6871(3)	3.39(7)
C(19)	0.2589(5)	0.0350(2)	0.5922(5)	5.3(1)
C(20)	0.5342(5)	0.0831(2)	0.7330(5)	6.9(1)
C(21)	0.5037(5)	0.2180(2)	0.7788(4)	6.5(1)
C(22)	0.1971(5)	0.2510(2)	0.7110(6)	6.2(1)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S7. Positional and Isotropic Thermal Parameters of **1d** (continued).

atom	x	y	z	B_{eq}
H(7A)	-0.3592	0.0833	0.1911	5.95
H(7B)	-0.2988	0.0440	0.0887	5.95
H(7C)	-0.3179	0.1109	0.0636	5.95
H(9A)	0.2075	0.1900	0.0565	6.87
H(9B)	0.3448	0.1595	0.0407	6.87
H(9C)	0.3059	0.1737	0.1790	6.87
H(10A)	0.3337	0.0673	0.2440	6.15
H(10B)	0.3800	0.0559	0.1073	6.15
H(10C)	0.2616	0.0196	0.1535	6.15
H(11A)	0.0962	0.1126	-0.0805	6.67
H(11B)	0.1184	0.0469	-0.0430	6.67
H(11C)	0.2364	0.0834	-0.0893	6.67
H(12A)	-0.0660	0.2301	0.5520	6.54
H(12B)	-0.0993	0.2033	0.6832	6.54
H(12C)	-0.1908	0.1891	0.5550	6.54
H(13A)	-0.0152	0.0355	0.6357	6.63
H(13B)	-0.1582	0.0637	0.6089	6.63
H(13C)	-0.0668	0.0780	0.7372	6.63
H(19A)	0.1664	0.0309	0.5578	6.41
H(19B)	0.2790	0.0084	0.6627	6.41
H(19C)	0.3155	0.0267	0.5259	6.41
H(20A)	0.5194	0.0437	0.7044	8.32
H(20B)	0.5560	0.0837	0.8251	8.32
H(20C)	0.6071	0.0996	0.6925	8.32
H(21A)	0.4673	0.2563	0.7873	7.75
H(21B)	0.5733	0.2195	0.7225	7.75
H(21C)	0.5404	0.2041	0.8622	7.75
H(22A)	0.1034	0.2510	0.6789	7.39
H(22B)	0.2429	0.2804	0.6674	7.39
H(22C)	0.2069	0.2588	0.8021	7.39
H(4)	-0.058(3)	0.083(1)	0.036(3)	2.3(6)
H(6)	-0.211(3)	0.101(2)	0.373(3)	2.6(7)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table S8. Anisotropic Displacement Parameters of **1d**.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.0309(3)	0.0603(4)	0.0283(3)	-0.0125(3)	0.0044(2)	-0.0034(3)
CL(1)	0.136(1)	0.079(1)	0.0666(8)	-0.0529(9)	-0.0030(8)	0.0173(7)
CL(2)	0.0373(5)	0.220(2)	0.0672(8)	0.0146(8)	0.0135(5)	-0.030(1)
Si(1)	0.0305(4)	0.0523(6)	0.0283(4)	-0.0040(4)	0.0077(3)	-0.0049(4)
O(1)	0.032(1)	0.052(2)	0.027(1)	-0.007(1)	0.0065(9)	-0.004(1)
C(1)	0.028(2)	0.038(2)	0.029(2)	0.001(1)	0.004(1)	-0.004(1)
C(2)	0.030(2)	0.034(2)	0.025(2)	-0.001(1)	0.002(1)	0.000(1)
C(3)	0.037(2)	0.038(2)	0.026(2)	-0.003(2)	0.004(1)	-0.001(1)
C(4)	0.046(2)	0.049(2)	0.024(2)	-0.003(2)	-0.004(1)	-0.002(2)
C(5)	0.036(2)	0.045(2)	0.039(2)	0.000(2)	-0.005(2)	-0.005(2)
C(6)	0.028(2)	0.048(2)	0.037(2)	0.001(2)	0.005(1)	-0.003(2)
C(7)	0.040(2)	0.092(3)	0.052(2)	-0.003(2)	-0.014(2)	-0.012(2)
C(8)	0.048(2)	0.063(2)	0.027(2)	-0.010(2)	0.011(2)	-0.006(2)
C(9)	0.090(3)	0.082(3)	0.051(2)	-0.036(2)	0.029(2)	-0.000(2)
C(10)	0.053(2)	0.087(3)	0.057(2)	0.014(2)	0.016(2)	-0.016(2)
C(11)	0.070(3)	0.111(4)	0.032(2)	-0.018(2)	0.014(2)	-0.018(2)
C(12)	0.054(2)	0.092(3)	0.061(2)	0.019(2)	0.008(2)	-0.028(2)
C(13)	0.059(2)	0.109(4)	0.040(2)	-0.044(2)	0.002(2)	0.012(2)
C(14)	0.033(2)	0.045(2)	0.021(2)	-0.005(1)	0.008(1)	0.000(1)
C(15)	0.044(2)	0.040(2)	0.038(2)	-0.001(2)	0.003(2)	0.004(2)
C(16)	0.041(2)	0.070(3)	0.042(2)	0.006(2)	-0.002(2)	0.005(2)
C(17)	0.043(2)	0.067(3)	0.030(2)	-0.014(2)	0.000(2)	-0.008(2)
C(18)	0.044(2)	0.050(2)	0.037(2)	-0.009(2)	0.009(2)	-0.012(2)
C(19)	0.074(3)	0.045(2)	0.085(3)	0.007(2)	0.011(2)	0.001(2)
C(20)	0.059(3)	0.105(4)	0.094(4)	0.018(3)	-0.016(2)	0.016(3)
C(21)	0.064(3)	0.123(4)	0.058(2)	-0.041(3)	0.003(2)	-0.033(3)
C(22)	0.075(3)	0.056(3)	0.107(4)	-0.017(2)	0.027(3)	-0.035(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S9. Bond Distances of **1d** in Å.

atom	atom	distance	atom	atom	distance
Ti(1)	CL(1)	2.261(2)	Ti(1)	CL(2)	2.255(2)
Ti(1)	O(1)	1.784(2)	Ti(1)	C(14)	2.290(3)
Ti(1)	C(15)	2.292(3)	Ti(1)	C(16)	2.387(4)
Ti(1)	C(17)	2.394(3)	Ti(1)	C(18)	2.359(3)
Si(1)	C(1)	1.877(3)	Si(1)	C(12)	1.852(5)
Si(1)	C(13)	1.863(5)	Si(1)	C(14)	1.881(3)
O(1)	C(2)	1.363(3)	C(1)	C(2)	1.403(4)
C(1)	C(6)	1.392(4)	C(2)	C(3)	1.414(4)
C(3)	C(4)	1.386(4)	C(3)	C(8)	1.542(5)
C(4)	C(5)	1.389(5)	C(5)	C(6)	1.387(5)
C(5)	C(7)	1.512(5)	C(8)	C(9)	1.530(6)
C(8)	C(10)	1.519(6)	C(8)	C(11)	1.528(5)
C(14)	C(15)	1.429(5)	C(14)	C(18)	1.424(5)
C(15)	C(16)	1.414(5)	C(15)	C(19)	1.505(6)
C(16)	C(17)	1.391(6)	C(16)	C(20)	1.507(6)
C(17)	C(18)	1.415(5)	C(17)	C(21)	1.519(6)
C(18)	C(22)	1.506(6)			

Table S9. Bond Distances of **1d** in Å (continued).

atom	atom	distance	atom	atom	distance
C(4)	H(4)	0.95(3)	C(6)	H(6)	0.96(3)
C(7)	H(7A)	0.960	C(7)	H(7B)	0.960
C(7)	H(7C)	0.960	C(9)	H(9A)	0.960
C(9)	H(9B)	0.960	C(9)	H(9C)	0.960
C(10)	H(10A)	0.960	C(10)	H(10B)	0.960
C(10)	H(10C)	0.960	C(11)	H(11A)	0.960
C(11)	H(11B)	0.960	C(11)	H(11C)	0.960
C(12)	H(12A)	0.960	C(12)	H(12B)	0.960
C(12)	H(12C)	0.960	C(13)	H(13A)	0.960
C(13)	H(13B)	0.960	C(13)	H(13C)	0.960
C(19)	H(19A)	0.960	C(19)	H(19B)	0.960
C(19)	H(19C)	0.960	C(20)	H(20A)	0.960
C(20)	H(20B)	0.960	C(20)	H(20C)	0.960
C(21)	H(21A)	0.960	C(21)	H(21B)	0.960
C(21)	H(21C)	0.960	C(22)	H(22A)	0.960
C(22)	H(22B)	0.960	C(22)	H(22C)	0.960

Table S10. Bond Angles of **1b** in Degrees.

atom	atom	atom	angle	atom	atom	atom	angle
CL(1)	Ti(1)	CL(2)	103.15(7)	CL(1)	Ti(1)	O(1)	103.86(9)
CL(1)	Ti(1)	C(14)	114.0(1)	CL(1)	Ti(1)	C(15)	145.30(1)
CL(1)	Ti(1)	C(16)	125.8(1)	CL(1)	Ti(1)	C(17)	93.5(1)
CL(1)	Ti(1)	C(18)	86.6(1)	CL(2)	Ti(1)	O(1)	102.46(9)
CL(2)	Ti(1)	C(14)	138.0(1)	CL(2)	Ti(1)	C(15)	101.8(1)
CL(2)	Ti(1)	C(16)	83.7(1)	CL(2)	Ti(1)	C(17)	101.3(1)
CL(2)	Ti(1)	C(18)	135.90(9)	O(1)	Ti(1)	C(14)	87.5(1)
O(1)	Ti(1)	C(15)	93.9(1)	O(1)	Ti(1)	C(16)	127.4(1)
O(1)	Ti(1)	C(17)	146.3(1)	O(1)	Ti(1)	C(18)	116.9(1)
C(14)	Ti(1)	C(15)	36.4(1)	C(14)	Ti(1)	C(16)	59.1(1)
C(14)	Ti(1)	C(17)	58.9(1)	C(14)	Ti(1)	C(18)	35.6(1)
C(15)	Ti(1)	C(16)	35.1(1)	C(15)	Ti(1)	C(17)	58.0(1)
C(15)	Ti(1)	C(18)	58.7(1)	C(16)	Ti(1)	C(17)	33.8(2)
C(16)	Ti(1)	C(18)	57.3(1)	C(17)	Ti(1)	C(18)	34.6(1)
C(1)	Si(1)	C(12)	108.1(2)	C(1)	Si(1)	C(13)	108.9(2)
C(1)	Si(1)	C(14)	110.2(1)	C(12)	Si(1)	C(13)	106.4(2)
C(12)	Si(1)	C(14)	113.4(2)	C(13)	Si(1)	C(14)	109.7(2)
Ti(1)	O(1)	C(2)	155.7(2)	Si(1)	C(1)	C(2)	125.7(2)
Si(1)	C(1)	C(6)	116.9(2)	C(2)	C(1)	C(6)	117.4(2)
O(1)	C(2)	C(1)	118.6(2)	O(1)	C(2)	C(3)	119.1(2)
C(1)	C(2)	C(3)	122.2(2)	C(2)	C(3)	C(4)	116.4(3)
C(2)	C(3)	C(8)	122.0(2)	C(4)	C(3)	C(8)	121.5(2)
C(3)	C(4)	C(5)	123.6(3)	C(4)	C(5)	C(6)	117.5(3)
C(4)	C(5)	C(7)	120.8(3)	C(6)	C(5)	C(7)	121.7(3)
C(1)	C(6)	C(5)	122.6(3)	C(3)	C(8)	C(9)	110.1(3)
C(3)	C(8)	C(10)	109.8(3)	C(3)	C(8)	C(11)	111.6(3)
C(9)	C(8)	C(10)	110.5(3)	C(9)	C(8)	C(11)	106.8(3)
C(10)	C(8)	C(11)	107.9(3)	Ti(1)	C(14)	Si(1)	118.8(1)
Ti(1)	C(14)	C(15)	71.9(2)	Ti(1)	C(14)	C(18)	74.8(2)
Si(1)	C(14)	C(15)	123.2(2)	Si(1)	C(14)	C(18)	130.7(2)
C(15)	C(14)	C(18)	106.1(2)	Ti(1)	C(15)	C(14)	71.7(2)
Ti(1)	C(15)	C(16)	76.1(2)	Ti(1)	C(15)	C(19)	117.7(2)
C(14)	C(15)	C(16)	108.5(3)	C(14)	C(15)	C(19)	126.2(3)
C(16)	C(15)	C(19)	125.3(3)	Ti(1)	C(16)	C(15)	68.8(2)
Ti(1)	C(16)	C(17)	73.4(2)	Ti(1)	C(16)	C(20)	127.0(3)
C(15)	C(16)	C(17)	108.3(3)	C(15)	C(16)	C(20)	126.0(4)
C(17)	C(16)	C(20)	125.6(3)	Ti(1)	C(17)	C(16)	72.8(2)
Ti(1)	C(17)	C(18)	71.3(2)	Ti(1)	C(17)	C(21)	121.8(2)
C(16)	C(17)	C(18)	108.3(3)	C(16)	C(17)	C(21)	125.6(3)
C(18)	C(17)	C(21)	126.1(4)	Ti(1)	C(18)	C(14)	69.5(2)
Ti(1)	C(18)	C(17)	74.1(2)	Ti(1)	C(18)	C(22)	125.0(3)
C(14)	C(18)	C(17)	108.7(3)	C(14)	C(18)	C(22)	126.9(3)
C(17)	C(18)	C(22)	124.4(3)				

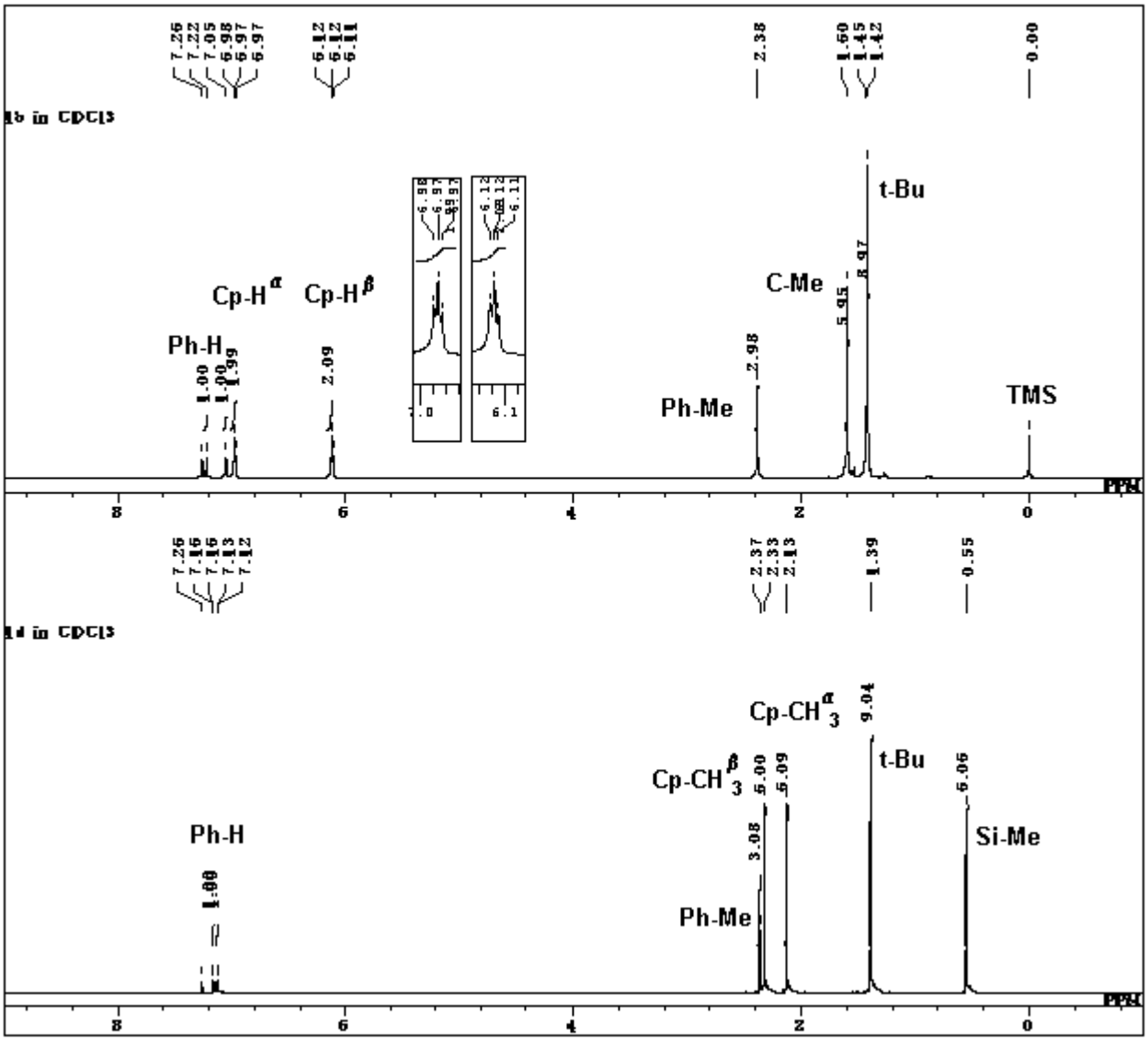

Figure S1. ^{1}H NMR spectra of complex **1b** (upper) and complex **1d** (lower) in $CDCl_3$ at room temperature.