Supporting Information (33 pages) for

Synthesis and Reactivities of Neutral and Cationic Titanium (1-Pyridinio)Imido Complexes. Reductive N-N Bond Cleavage and Catalytic Activity in Olefin Polymerisation Reactions

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Table 1. Atomic coordinates and B(eq) values for $CpTiCl_2NNC_5H_5$ (**3a**)

atom	x	y	z	B_{eq}
Ti(1)	0.26508(5)	0.19155(7)	-0.07933(3)	2.77(1)
Cl(1)	0.12606(8)	0.42200(9)	-0.10605(5)	3.74(2)
Cl(2)	0.33958(9)	0.1740(1)	0.08402(5)	5.46(2)
N(1)	0.4159(2)	0.2572(3)	-0.1009(1)	3.04(6)
N(2)	0.5261(2)	0.2770(3)	-0.1341(1)	2.60(5)
C(1)	0.6345(3)	0.3709(3)	-0.0860(2)	3.13(7)
C(2)	0.7466(3)	0.3933(4)	-0.1177(2)	3.75(8)
C(3)	0.7483(3)	0.3230(4)	-0.1995(2)	3.68(8)
C(4)	0.6367(3)	0.2289(4)	-0.2479(2)	3.85(8)
C(5)	0.5270(3)	0.2055(4)	-0.2145(2)	3.60(7)
C(6)	0.2626(4)	-0.0743(5)	-0.1226(4)	7.9(1)
C(7)	0.2048(6)	0.0132(6)	-0.2052(3)	7.4(2)
C(8)	0.0800(4)	0.0754(4)	-0.2025(3)	5.5(1)
C(9)	0.0581(4)	0.0280(4)	-0.1231(3)	5.1(1)
C(10)	0.1664(5)	-0.0637(5)	-0.0743(3)	6.4(1)
H(1)	0.6333	0.4219	-0.0299	3.6943
H(2)	0.8237	0.4581	-0.0828	4.1273
H(3)	0.8253	0.3393	-0.2222	4.2142
H(4)	0.6357	0.1796	-0.3050	4.3896
H(5)	0.4506	0.1385	-0.2480	4.0990
H(6)	0.3501	-0.1299	-0.1034	8.8370
H(7)	0.2446	0.0269	-0.2541	7.9084
H(8)	0.0185	0.1417	-0.2494	6.2722
H(9)	-0.0212	0.0551	-0.1047	5.7336
H(10)	0.1760	-0.1136	-0.0158	7.6817

Table 2. Anisotropic displacement parameters for $CpTiCl_2NNC_5H_5$ (**3a**)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.0342(3)	0.0417(3)	0.0312(3)	-0.0014(3)	0.0132(2)	-0.0006(3)
Cl(1)	0.0456(5)	0.0467(5)	0.0491(5)	0.0051(4)	0.0143(4)	0.0011(4)
Cl(2)	0.0801(6)	0.0940(7)	0.0336(4)	0.0159(6)	0.0188(4)	0.0088(5)
N(1)	0.032(1)	0.045(2)	0.042(1)	-0.005(1)	0.016(1)	-0.006(1)
N(2)	0.031(1)	0.033(1)	0.035(1)	0.001(1)	0.013(1)	0.001(1)
C(1)	0.039(2)	0.044(2)	0.035(2)	-0.009(1)	0.011(1)	-0.003(1)
C(2)	0.039(2)	0.056(2)	0.049(2)	-0.015(2)	0.015(2)	0.000(2)
C(3)	0.041(2)	0.051(2)	0.056(2)	0.003(2)	0.026(2)	0.006(2)
C(4)	0.054(2)	0.047(2)	0.055(2)	0.001(2)	0.032(2)	-0.011(2)
C(5)	0.045(2)	0.044(2)	0.050(2)	-0.008(2)	0.019(1)	-0.016(2)
C(6)	0.050(2)	0.050(3)	0.188(6)	0.006(2)	0.021(3)	-0.047(3)
C(7)	0.122(4)	0.099(4)	0.094(3)	-0.076(3)	0.082(3)	-0.069(3)
C(8)	0.082(3)	0.056(3)	0.051(2)	-0.022(2)	-0.004(2)	-0.005(2)
C(9)	0.050(2)	0.059(3)	0.090(3)	-0.017(2)	0.030(2)	-0.011(2)
C(10)	0.094(3)	0.048(2)	0.089(3)	-0.015(2)	0.014(3)	0.023(2)

Table 3. Bond lengths (Å) for nonhydrogen atoms for $CpTiCl_2NNC_5H_5$ (**3a**)

atom	atom	distance	atom	atom	distance
Ti(1)	Cl(1)	2.339(1)	Ti(1)	Cl(2)	2.3261(9)
Ti(1)	N(1)	1.734(2)	Ti(1)	C(6)	2.322(4)
Ti(1)	C(7)	2.332(4)	Ti(1)	C(8)	2.360(3)
Ti(1)	C(9)	2.391(3)	Ti(1)	C(10)	2.370(4)
N(1)	N(2)	1.363(3)	N(2)	C(1)	1.345(3)
N(2)	C(5)	1.352(3)	C(1)	C(2)	1.368(4)
C(2)	C(3)	1.368(4)	C(3)	C(4)	1.367(4)
C(4)	C(5)	1.363(4)	C(6)	C(7)	1.395(6)
C(6)	C(10)	1.385(6)	C(7)	C(8)	1.367(5)
C(8)	C(9)	1.342(5)	C(9)	C(10)	1.336(4)

Table 4. Bond angles (deg) for nonhydrogen atoms for $CpTiCl_2NNC_5H_5$ (**3a**)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Ti(1)	Cl(2)	101.59(4)	Cl(1)	Ti(1)	N(1)	102.17(8)
Cl(1)	Ti(1)	C(6)	142.6(1)	Cl(1)	Ti(1)	C(7)	114.2(2)
Cl(1)	Ti(1)	C(8)	86.3(1)	Cl(1)	Ti(1)	C(9)	90.8(1)
Cl(1)	Ti(1)	C(10)	121.4(1)	Cl(2)	Ti(1)	N(1)	102.64(7)
Cl(2)	Ti(1)	C(6)	101.9(2)	Cl(2)	Ti(1)	C(7)	136.4(1)
Cl(2)	Ti(1)	C(8)	134.5(1)	Cl(2)	Ti(1)	C(9)	101.8(1)
Cl(2)	Ti(1)	C(10)	84.4(1)	N(1)	Ti(1)	C(6)	100.6(1)
N(1)	Ti(1)	C(7)	93.6(1)	N(1)	Ti(1)	C(8)	119.6(1)
N(1)	Ti(1)	C(9)	149.3(1)	N(1)	Ti(1)	C(10)	133.7(2)
C(6)	Ti(1)	C(7)	34.9(1)	C(6)	Ti(1)	C(8)	56.6(1)
C(6)	Ti(1)	C(9)	56.1(1)	C(6)	Ti(1)	C(10)	34.3(1)
C(7)	Ti(1)	C(8)	33.9(1)	C(7)	Ti(1)	C(9)	55.8(1)
C(7)	Ti(1)	C(10)	56.3(1)	C(8)	Ti(1)	C(9)	32.8(1)
C(8)	Ti(1)	C(10)	54.8(1)	C(9)	Ti(1)	C(10)	32.6(1)
Ti(1)	N(1)	N(2)	165.1(2)	N(1)	N(2)	C(1)	118.8(2)
N(1)	N(2)	C(5)	121.1(2)	C(1)	N(2)	C(5)	120.1(2)
N(2)	C(1)	C(2)	120.2(3)	C(1)	C(2)	C(3)	120.4(3)
C(2)	C(3)	C(4)	118.7(3)	C(3)	C(4)	C(5)	120.3(3)
N(2)	C(5)	C(4)	120.4(3)	Ti(1)	C(6)	C(7)	73.0(2)
Ti(1)	C(6)	C(10)	74.7(2)	C(7)	C(6)	C(10)	106.0(4)
Ti(1)	C(7)	C(6)	72.1(2)	Ti(1)	C(7)	C(8)	74.2(2)
C(6)	C(7)	C(8)	106.9(4)	Ti(1)	C(8)	C(7)	72.0(2)
Ti(1)	C(8)	C(9)	74.9(2)	C(7)	C(8)	C(9)	109.3(4)
Ti(1)	C(9)	C(8)	72.3(2)	Ti(1)	C(9)	C(10)	72.8(2)

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	C(9)	C(10)	108.6(4)	Ti(1)	C(10)	C(6)	70.9(2)
Ti(1)	C(10)	C(9)	74.6(2)	C(6)	C(10)	C(9)	109.1(4)

Table 5. Atomic coordinates and B(eq) values for $[CpTiCl_2NNC_5H_3Me_2\text{-}2,6]$ (**3b**)

atom	x	y	z	B_{eq}
Ti(1)	0.25823(7)	0.62435(3)	-0.11375(4)	2.72(2)
Ti(2)	0.22892(6)	0.14965(3)	0.11927(4)	2.65(1)
Cl(1)	0.1416(1)	0.72717(5)	-0.11394(7)	4.74(3)
Cl(2)	0.4191(1)	0.62442(6)	0.03978(7)	5.10(3)
Cl(3)	0.13183(10)	0.13882(6)	-0.04719(7)	5.10(3)
Cl(4)	0.38128(10)	0.05736(5)	0.15015(8)	4.29(3)
N(1)	0.3613(3)	0.6411(1)	-0.1885(2)	2.63(7)
N(2)	0.4189(3)	0.6363(1)	-0.2626(2)	2.57(7)
N(3)	0.0958(3)	0.1220(1)	0.1648(2)	2.57(7)
N(4)	-0.0152(3)	0.1120(1)	0.1997(2)	2.68(7)
C(1)	0.0519(6)	0.5702(3)	-0.2064(4)	6.5(2)
C(2)	0.1655(8)	0.5311(4)	-0.2109(5)	8.5(2)
C(3)	0.2279(5)	0.5072(2)	-0.1204(6)	8.0(2)
C(4)	0.1519(6)	0.5286(3)	-0.0629(3)	5.9(2)
C(5)	0.0460(5)	0.5671(2)	-0.1141(4)	5.2(1)
C(6)	0.3564(4)	0.6713(2)	-0.3463(3)	2.94(9)
C(7)	0.4155(4)	0.6659(2)	-0.4210(2)	4.0(1)
C(8)	0.5345(4)	0.6286(2)	-0.4108(3)	4.3(1)
C(9)	0.5978(4)	0.5962(2)	-0.3251(3)	3.9(1)
C(10)	0.5400(4)	0.5999(2)	-0.2498(3)	3.00(9)
C(11)	0.2315(4)	0.7127(2)	-0.3501(2)	4.2(1)
C(12)	0.6016(4)	0.5662(2)	-0.1556(3)	4.2(1)
C(13)	0.2469(5)	0.2540(2)	0.1992(3)	4.7(1)
C(14)	0.2262(4)	0.2686(2)	0.1034(3)	4.6(1)

atom	x	y	z	B_{eq}
C(15)	0.3445(5)	0.2486(2)	0.0777(3)	5.0(1)
C(16)	0.4376(4)	0.2196(2)	0.1569(4)	5.3(1)
C(17)	0.3765(5)	0.2213(2)	0.2333(3)	5.2(1)
C(18)	-0.0071(4)	0.1286(2)	0.2928(3)	3.6(1)
C(19)	-0.1252(5)	0.1189(2)	0.3234(3)	5.1(1)
C(20)	-0.2452(5)	0.0934(2)	0.2622(4)	5.9(2)
C(21)	-0.2498(4)	0.0753(2)	0.1714(3)	4.8(1)
C(22)	-0.1339(4)	0.0835(2)	0.1385(3)	3.20(10)
C(23)	0.1253(5)	0.1573(2)	0.3569(3)	5.4(1)
C(24)	-0.1293(4)	0.0624(2)	0.0425(3)	4.6(1)
H(1)	-0.0103	0.5945	-0.2581	7.8133
H(2)	0.1943	0.5226	-0.2667	10.3306
H(3)	0.3105	0.4802	-0.1011	9.8548
H(4)	0.1709	0.5178	0.0035	7.1106
H(5)	-0.0220	0.5887	-0.0900	6.2866
H(6)	0.3726	0.6883	-0.4804	4.7599
H(7)	0.5735	0.6251	-0.4630	5.1317
H(8)	0.6818	0.5712	-0.3177	4.7311
H(9)	0.2552	0.7465	-0.3011	5.0561
H(10)	0.1987	0.7341	-0.4114	5.0561
H(11)	0.1600	0.6841	-0.3403	5.0561
H(12)	0.5363	0.5345	-0.1443	4.9920
H(13)	0.6849	0.5430	-0.1561	4.9920
H(14)	0.6231	0.5995	-0.1059	4.9920

atom	x	y	z	B_{eq}
H(15)	0.1844	0.2642	0.2356	5.5832
H(16)	0.1447	0.2891	0.0615	5.5142
H(17)	0.3581	0.2541	0.0161	6.0330
H(18)	0.5271	0.2015	0.1599	6.3900
H(19)	0.4163	0.2036	0.2963	6.2254
H(20)	-0.1220	0.1301	0.3876	6.1003
H(21)	-0.3262	0.0884	0.2832	7.0949
H(22)	-0.3336	0.0568	0.1296	5.7157
H(23)	0.1991	0.1255	0.3629	6.4759
H(24)	0.1469	0.1985	0.3300	6.4759
H(25)	0.1145	0.1662	0.4186	6.4759
H(26)	-0.2176	0.0440	0.0073	5.4806
H(27)	-0.1086	0.1007	0.0091	5.4806
H(28)	-0.0587	0.0288	0.0488	5.4998

Table 6. Anisotropic displacement parameters for [$CpTiCl_2NNC_5H_3Me_2$-2,6] (**3b**)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.0375(4)	0.0360(4)	0.0314(4)	-0.0026(4)	0.0128(3)	-0.0037(4)
Ti(2)	0.0270(3)	0.0369(4)	0.0358(4)	-0.0020(3)	0.0077(3)	0.0000(4)
Cl(1)	0.0617(7)	0.0519(7)	0.0687(8)	0.0142(6)	0.0223(6)	-0.0113(6)
Cl(2)	0.0643(7)	0.0875(9)	0.0356(6)	-0.0082(7)	0.0045(5)	-0.0009(6)
Cl(3)	0.0449(6)	0.111(1)	0.0360(6)	-0.0062(7)	0.0094(5)	-0.0021(6)
Cl(4)	0.0411(6)	0.0448(7)	0.0791(8)	0.0076(5)	0.0205(5)	0.0042(6)
N(1)	0.034(2)	0.036(2)	0.031(2)	-0.002(1)	0.013(1)	0.000(1)
N(2)	0.035(2)	0.028(2)	0.037(2)	-0.006(1)	0.014(1)	-0.004(1)
N(3)	0.026(2)	0.037(2)	0.036(2)	-0.006(1)	0.010(1)	-0.004(1)
N(4)	0.037(2)	0.025(2)	0.043(2)	0.001(1)	0.017(2)	0.003(1)
C(1)	0.081(4)	0.079(4)	0.060(4)	-0.046(3)	-0.020(3)	0.015(3)
C(2)	0.162(7)	0.101(6)	0.097(5)	-0.097(5)	0.094(5)	-0.074(4)
C(3)	0.062(4)	0.033(3)	0.220(8)	-0.009(3)	0.056(5)	-0.021(5)
C(4)	0.084(4)	0.071(4)	0.063(3)	-0.034(3)	0.010(3)	0.022(3)
C(5)	0.051(3)	0.066(4)	0.092(4)	-0.019(3)	0.036(3)	-0.016(3)
C(6)	0.037(2)	0.038(2)	0.035(2)	-0.006(2)	0.008(2)	-0.002(2)
C(7)	0.058(3)	0.061(3)	0.035(2)	-0.012(2)	0.020(2)	0.003(2)
C(8)	0.063(3)	0.061(3)	0.053(3)	-0.011(3)	0.039(2)	-0.013(2)
C(9)	0.045(3)	0.045(3)	0.069(3)	-0.003(2)	0.032(2)	-0.007(2)
C(10)	0.035(2)	0.033(2)	0.046(3)	-0.004(2)	0.013(2)	0.000(2)
C(11)	0.054(3)	0.063(3)	0.042(2)	0.012(2)	0.012(2)	0.012(2)
C(12)	0.042(2)	0.047(3)	0.068(3)	0.013(2)	0.016(2)	0.009(2)
C(13)	0.088(4)	0.034(3)	0.064(3)	-0.012(3)	0.036(3)	-0.003(2)
C(14)	0.066(3)	0.038(3)	0.075(3)	0.005(2)	0.028(3)	0.017(2)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(15)	0.068(3)	0.046(3)	0.089(4)	-0.008(3)	0.043(3)	0.007(3)
C(16)	0.037(3)	0.044(3)	0.115(4)	-0.018(2)	0.014(3)	-0.007(3)
C(17)	0.077(4)	0.041(3)	0.057(3)	-0.026(3)	-0.013(3)	-0.001(2)
C(18)	0.074(3)	0.026(2)	0.045(3)	0.010(2)	0.029(2)	0.003(2)
C(19)	0.092(4)	0.051(3)	0.072(3)	0.021(3)	0.060(3)	0.018(3)
C(20)	0.067(3)	0.073(4)	0.107(5)	0.023(3)	0.062(3)	0.040(3)
C(21)	0.038(3)	0.054(3)	0.094(4)	-0.001(2)	0.028(3)	0.021(3)
C(22)	0.033(2)	0.031(2)	0.059(3)	0.003(2)	0.015(2)	0.006(2)
C(23)	0.111(4)	0.055(3)	0.044(3)	-0.017(3)	0.030(3)	-0.009(2)
C(24)	0.037(2)	0.062(3)	0.067(3)	-0.011(2)	0.003(2)	-0.013(3)

Table 7. Bond lengths (Å) for nonhydrogen atoms for $[CpTiCl_2NNC_5H_3Me_2\text{-}2,6]$ (**3b**)

atom	atom	distance	atom	atom	distance
Ti(1)	Cl(1)	2.329(1)	Ti(1)	Cl(2)	2.332(1)
Ti(1)	N(1)	1.732(3)	Ti(1)	C(1)	2.357(4)
Ti(1)	C(2)	2.330(5)	Ti(1)	C(3)	2.317(5)
Ti(1)	C(4)	2.381(4)	Ti(1)	C(5)	2.397(4)
Ti(2)	Cl(3)	2.333(1)	Ti(2)	Cl(4)	2.322(1)
Ti(2)	N(3)	1.736(3)	Ti(2)	C(13)	2.334(4)
Ti(2)	C(14)	2.346(4)	Ti(2)	C(15)	2.424(4)
Ti(2)	C(16)	2.419(4)	Ti(2)	C(17)	2.336(4)
N(1)	N(2)	1.364(3)	N(2)	C(6)	1.375(4)
N(2)	C(10)	1.369(4)	N(3)	N(4)	1.361(3)
N(4)	C(18)	1.370(4)	N(4)	C(22)	1.374(4)
C(1)	C(2)	1.387(7)	C(1)	C(5)	1.360(6)
C(2)	C(3)	1.361(7)	C(3)	C(4)	1.349(7)
C(4)	C(5)	1.334(6)	C(6)	C(7)	1.383(4)
C(6)	C(11)	1.476(4)	C(7)	C(8)	1.365(5)
C(8)	C(9)	1.374(5)	C(9)	C(10)	1.379(4)
C(10)	C(12)	1.481(4)	C(13)	C(14)	1.374(5)
C(13)	C(17)	1.398(5)	C(14)	C(15)	1.395(5)
C(15)	C(16)	1.371(5)	C(16)	C(17)	1.415(6)
C(18)	C(19)	1.390(5)	C(18)	C(23)	1.485(5)
C(19)	C(20)	1.359(6)	C(20)	C(21)	1.353(6)
C(21)	C(22)	1.384(4)	C(22)	C(24)	1.468(5)

Table 8. Bond angles (deg) for nonhydrogen atoms for [$CpTiCl_2NNC_5H_3Me_2$-2,6] (**3b**)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Ti(1)	Cl(2)	101.78(5)	Cl(1)	Ti(1)	N(1)	102.96(10)
Cl(1)	Ti(1)	C(1)	92.1(2)	Cl(1)	Ti(1)	C(2)	124.8(2)
Cl(1)	Ti(1)	C(3)	143.1(1)	Cl(1)	Ti(1)	C(4)	114.6(2)
Cl(1)	Ti(1)	C(5)	88.0(1)	Cl(2)	Ti(1)	N(1)	103.25(9)
Cl(2)	Ti(1)	C(1)	141.8(1)	Cl(2)	Ti(1)	C(2)	128.2(2)
Cl(2)	Ti(1)	C(3)	94.9(2)	Cl(2)	Ti(1)	C(4)	87.1(1)
Cl(2)	Ti(1)	C(5)	111.2(2)	N(1)	Ti(1)	C(1)	108.0(2)
N(1)	Ti(1)	C(2)	88.5(2)	N(1)	Ti(1)	C(3)	104.9(2)
N(1)	Ti(1)	C(4)	138.2(2)	N(1)	Ti(1)	C(5)	140.8(2)
C(1)	Ti(1)	C(2)	34.4(2)	C(1)	Ti(1)	C(3)	56.4(2)
C(1)	Ti(1)	C(4)	55.0(2)	C(1)	Ti(1)	C(5)	33.2(1)
C(2)	Ti(1)	C(3)	34.1(2)	C(2)	Ti(1)	C(4)	55.5(2)
C(2)	Ti(1)	C(5)	55.7(2)	C(3)	Ti(1)	C(4)	33.3(2)
C(3)	Ti(1)	C(5)	55.3(2)	C(4)	Ti(1)	C(5)	32.4(1)
Cl(3)	Ti(2)	Cl(4)	100.25(5)	Cl(3)	Ti(2)	N(3)	103.56(9)
Cl(3)	Ti(2)	C(13)	122.8(1)	Cl(3)	Ti(2)	C(14)	90.0(1)
Cl(3)	Ti(2)	C(15)	84.2(1)	Cl(3)	Ti(2)	C(16)	110.7(1)
Cl(3)	Ti(2)	C(17)	140.5(1)	Cl(4)	Ti(2)	N(3)	102.38(10)
Cl(4)	Ti(2)	C(13)	129.6(1)	Cl(4)	Ti(2)	C(14)	141.5(1)
Cl(4)	Ti(2)	C(15)	109.9(1)	Cl(4)	Ti(2)	C(16)	85.8(1)
Cl(4)	Ti(2)	C(17)	95.3(1)	N(3)	Ti(2)	C(13)	92.3(1)
N(3)	Ti(2)	C(14)	111.1(1)	N(3)	Ti(2)	C(15)	144.9(1)
N(3)	Ti(2)	C(16)	142.8(2)	N(3)	Ti(2)	C(17)	108.2(2)
C(13)	Ti(2)	C(14)	34.2(1)	C(13)	Ti(2)	C(15)	56.5(1)

atom	atom	atom	angle	atom	atom	atom	angle
C(13)	Ti(2)	C(16)	57.0(1)	C(13)	Ti(2)	C(17)	34.8(1)
C(14)	Ti(2)	C(15)	34.0(1)	C(14)	Ti(2)	C(16)	56.1(1)
C(14)	Ti(2)	C(17)	57.1(1)	C(15)	Ti(2)	C(16)	32.9(1)
C(15)	Ti(2)	C(17)	56.4(1)	C(16)	Ti(2)	C(17)	34.6(1)
Ti(1)	N(1)	N(2)	161.2(2)	N(1)	N(2)	C(6)	118.4(3)
N(1)	N(2)	C(10)	119.3(3)	C(6)	N(2)	C(10)	122.2(3)
Ti(2)	N(3)	N(4)	170.0(2)	N(3)	N(4)	C(18)	121.0(3)
N(3)	N(4)	C(22)	117.4(3)	C(18)	N(4)	C(22)	121.6(3)
Ti(1)	C(1)	C(2)	71.7(3)	Ti(1)	C(1)	C(5)	75.0(3)
C(2)	C(1)	C(5)	107.2(5)	Ti(1)	C(2)	C(1)	73.8(3)
Ti(1)	C(2)	C(3)	72.4(3)	C(1)	C(2)	C(3)	107.0(5)
Ti(1)	C(3)	C(2)	73.5(3)	Ti(1)	C(3)	C(4)	75.9(3)
C(2)	C(3)	C(4)	108.0(6)	Ti(1)	C(4)	C(3)	70.7(3)
Ti(1)	C(4)	C(5)	74.5(3)	C(3)	C(4)	C(5)	109.2(5)
Ti(1)	C(5)	C(1)	71.7(3)	Ti(1)	C(5)	C(4)	73.1(3)
C(1)	C(5)	C(4)	108.5(4)	N(2)	C(6)	C(7)	117.8(3)
N(2)	C(6)	C(11)	117.9(3)	C(7)	C(6)	C(11)	124.3(4)
C(6)	C(7)	C(8)	121.0(4)	C(7)	C(8)	C(9)	120.0(3)
C(8)	C(9)	C(10)	120.3(3)	N(2)	C(10)	C(9)	118.6(3)
N(2)	C(10)	C(12)	117.9(3)	C(9)	C(10)	C(12)	123.5(3)
Ti(2)	C(13)	C(14)	73.4(2)	Ti(2)	C(13)	C(17)	72.6(2)
C(14)	C(13)	C(17)	107.6(4)	Ti(2)	C(14)	C(13)	72.5(2)
Ti(2)	C(14)	C(15)	76.1(2)	C(13)	C(14)	C(15)	108.9(4)
Ti(2)	C(15)	C(14)	69.9(2)	Ti(2)	C(15)	C(16)	73.4(2)

atom	atom	atom	angle	atom	atom	atom	angle
C(14)	C(15)	C(16)	108.1(4)	Ti(2)	C(16)	C(15)	73.7(2)
Ti(2)	C(16)	C(17)	69.5(2)	C(15)	C(16)	C(17)	107.7(4)
Ti(2)	C(17)	C(13)	72.5(2)	Ti(2)	C(17)	C(16)	76.0(2)
C(13)	C(17)	C(16)	107.5(4)	N(4)	C(18)	C(19)	118.2(4)
N(4)	C(18)	C(23)	119.4(3)	C(19)	C(18)	C(23)	122.3(4)
C(18)	C(19)	C(20)	120.6(4)	C(19)	C(20)	C(21)	120.3(4)
C(20)	C(21)	C(22)	120.9(4)	N(4)	C(22)	C(21)	118.3(4)
N(4)	C(22)	C(24)	117.8(3)	C(21)	C(22)	C(24)	123.9(4)

Table 9. Atomic coordinates and B(eq) values for $[Cp^*TiCl_2NNC_5H_3Me_2\text{-}2,6]$ (**3c**)

atom	x	y	z	B_{eq}
Ti(1)	0.28614(7)	0.0564(1)	0.73641(7)	3.13(3)
Cl(1)	0.3622(1)	0.0232(2)	0.64179(9)	4.67(4)
Cl(2)	0.2549(1)	0.3301(2)	0.7228(1)	5.41(5)
N(1)	0.1680(3)	-0.0226(5)	0.6721(2)	2.9(1)
N(2)	0.0759(3)	-0.0885(5)	0.6232(3)	3.0(1)
C(1)	0.0117(4)	0.1119(7)	0.6913(4)	5.4(2)
C(2)	-0.0069(5)	-0.0209(7)	0.6273(4)	3.8(2)
C(3)	-0.0998(5)	-0.0804(9)	0.5715(4)	5.1(2)
C(4)	-0.1119(5)	-0.2026(9)	0.5141(4)	5.6(2)
C(5)	-0.0288(5)	-0.2689(7)	0.5114(4)	4.6(2)
C(6)	0.0663(4)	-0.2149(7)	0.5670(4)	3.4(2)
C(7)	0.1592(4)	-0.2810(7)	0.5688(4)	4.8(2)
C(8)	0.3146(5)	-0.1170(9)	0.8547(4)	4.2(2)
C(9)	0.3963(5)	-0.1319(7)	0.8364(4)	3.5(2)
C(10)	0.4503(4)	0.0104(9)	0.8609(4)	4.4(2)
C(11)	0.3993(6)	0.1133(8)	0.8917(4)	5.7(2)
C(12)	0.3140(6)	0.037(1)	0.8865(4)	5.6(2)
C(13)	0.2426(5)	-0.2529(9)	0.8453(4)	8.8(3)
C(14)	0.4275(5)	-0.2810(8)	0.8031(4)	7.0(2)
C(15)	0.5475(4)	0.0411(9)	0.8556(4)	9.2(2)
C(16)	0.4365(6)	0.2783(9)	0.9293(4)	12.9(3)
C(17)	0.2402(6)	0.099(1)	0.9178(4)	13.4(3)
H(1)	0.0535	0.0763	0.7504	6.4890
H(2)	0.0437	0.1971	0.6764	6.4890

atom	x	y	z	B_{eq}
H(3)	-0.0500	0.1483	0.6881	6.4890
H(4)	-0.1571	-0.0347	0.5732	6.1440
H(5)	-0.1768	-0.2419	0.4762	6.7342
H(6)	-0.0370	-0.3532	0.4706	5.4992
H(7)	0.2014	-0.3192	0.6274	5.8142
H(8)	0.1431	-0.3664	0.5271	5.8142
H(9)	0.1931	-0.2001	0.5531	5.8142
H(10)	0.1929	-0.2165	0.8619	10.5312
H(11)	0.2114	-0.2887	0.7848	10.5312
H(12)	0.2783	-0.3388	0.8833	10.5312
H(13)	0.3791	-0.3624	0.7917	8.4017
H(14)	0.4323	-0.2573	0.7493	8.4017
H(15)	0.4905	-0.3166	0.8474	8.4017
H(16)	0.5967	-0.0326	0.8930	11.0977
H(17)	0.5374	0.0284	0.7953	11.0977
H(18)	0.5696	0.1466	0.8750	11.0977
H(19)	0.4993	0.2699	0.9805	15.4901
H(20)	0.4431	0.3417	0.8850	15.4901
H(21)	0.3898	0.3272	0.9462	15.4901
H(22)	0.2556	0.2064	0.9368	16.1336
H(23)	0.1746	0.0933	0.8699	16.1336
H(24)	0.2435	0.0357	0.9665	16.1336

Table 10. Anisotropic displacement parameters for [Cp*$TiCl_2NNC_5H_3Me_2$-2,6] (**3c**)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.0380(7)	0.0363(7)	0.0371(6)	-0.0005(6)	0.0100(5)	-0.0008(7)
Cl(1)	0.055(1)	0.073(1)	0.055(1)	-0.0076(10)	0.0299(9)	0.002(1)
Cl(2)	0.070(1)	0.036(1)	0.070(1)	0.0013(9)	0.005(1)	-0.0005(10)
N(1)	0.033(3)	0.033(3)	0.037(3)	-0.003(2)	0.008(2)	-0.004(2)
N(2)	0.040(3)	0.039(3)	0.035(3)	-0.002(3)	0.015(3)	0.005(3)
C(1)	0.059(5)	0.070(5)	0.089(5)	0.021(4)	0.044(4)	0.008(4)
C(2)	0.047(4)	0.052(5)	0.050(4)	0.009(4)	0.027(4)	0.010(4)
C(3)	0.040(4)	0.081(6)	0.064(5)	-0.005(5)	0.015(4)	0.028(5)
C(4)	0.045(5)	0.080(6)	0.066(6)	-0.016(5)	0.004(4)	0.024(5)
C(5)	0.065(5)	0.052(5)	0.035(4)	-0.024(4)	0.002(4)	0.001(3)
C(6)	0.056(5)	0.036(4)	0.033(4)	-0.002(4)	0.016(4)	0.004(3)
C(7)	0.064(5)	0.056(5)	0.063(5)	-0.003(4)	0.029(4)	-0.019(4)
C(8)	0.043(5)	0.076(6)	0.039(4)	-0.005(4)	0.016(4)	0.019(4)
C(9)	0.050(5)	0.044(4)	0.033(4)	0.007(4)	0.014(4)	0.006(3)
C(10)	0.041(4)	0.058(5)	0.041(4)	-0.004(4)	-0.007(4)	0.016(4)
C(11)	0.097(7)	0.049(5)	0.023(4)	0.019(5)	-0.015(4)	-0.007(4)
C(12)	0.074(6)	0.098(7)	0.034(4)	0.037(6)	0.017(4)	-0.003(5)
C(13)	0.072(6)	0.161(9)	0.093(6)	-0.022(6)	0.030(5)	0.057(6)
C(14)	0.104(6)	0.070(5)	0.086(6)	0.030(5)	0.037(5)	0.013(5)
C(15)	0.039(5)	0.146(8)	0.123(6)	-0.014(5)	-0.002(4)	0.063(6)
C(16)	0.22(1)	0.065(6)	0.071(6)	0.016(7)	-0.053(6)	-0.022(5)
C(17)	0.158(8)	0.31(1)	0.048(5)	0.160(9)	0.052(5)	0.022(6)

Table 11. Bond lengths (Å) for nonhydrogen atoms for [Cp*$TiCl_2NNC_5H_3Me_2$-2,6] (**3c**)

atom	atom	distance	atom	atom	distance
Ti(1)	Cl(1)	2.331(2)	Ti(1)	Cl(2)	2.334(2)
Ti(1)	N(1)	1.739(4)	Ti(1)	C(8)	2.330(6)
Ti(1)	C(9)	2.354(5)	Ti(1)	C(10)	2.437(5)
Ti(1)	C(11)	2.425(6)	Ti(1)	C(12)	2.347(6)
N(1)	N(2)	1.367(5)	N(2)	C(2)	1.389(6)
N(2)	C(6)	1.379(6)	C(1)	C(2)	1.480(7)
C(2)	C(3)	1.377(7)	C(3)	C(4)	1.358(8)
C(4)	C(5)	1.379(8)	C(5)	C(6)	1.383(7)
C(6)	C(7)	1.482(7)	C(8)	C(9)	1.389(7)
C(8)	C(12)	1.398(8)	C(8)	C(13)	1.527(8)
C(9)	C(10)	1.396(7)	C(9)	C(14)	1.523(7)
C(10)	C(11)	1.391(8)	C(10)	C(15)	1.516(7)
C(11)	C(12)	1.394(9)	C(11)	C(16)	1.518(8)
C(12)	C(17)	1.504(8)			

Table 12. Bond angles (deg) for nonhydrogen atoms for [Cp*$TiCl_2NNC_5H_3Me_2$-2,6] (**3c**)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Ti(1)	Cl(2)	100.87(7)	Cl(1)	Ti(1)	N(1)	101.9(1)
Cl(1)	Ti(1)	C(8)	122.3(2)	Cl(1)	Ti(1)	C(9)	89.9(2)
Cl(1)	Ti(1)	C(10)	86.9(2)	Cl(1)	Ti(1)	C(11)	115.1(2)
Cl(1)	Ti(1)	C(12)	143.2(2)	Cl(2)	Ti(1)	N(1)	102.2(1)
Cl(2)	Ti(1)	C(8)	130.5(2)	Cl(2)	Ti(1)	C(9)	140.9(2)
Cl(2)	Ti(1)	C(10)	108.7(2)	Cl(2)	Ti(1)	C(11)	85.7(2)
Cl(2)	Ti(1)	C(12)	96.0(2)	N(1)	Ti(1)	C(8)	92.0(2)
N(1)	Ti(1)	C(9)	112.3(2)	N(1)	Ti(1)	C(10)	145.7(2)
N(1)	Ti(1)	C(11)	140.1(3)	N(1)	Ti(1)	C(12)	106.2(3)
C(8)	Ti(1)	C(9)	34.5(2)	C(8)	Ti(1)	C(10)	56.4(2)
C(8)	Ti(1)	C(11)	56.2(2)	C(8)	Ti(1)	C(12)	34.8(2)
C(9)	Ti(1)	C(10)	33.8(2)	C(9)	Ti(1)	C(11)	56.1(2)
C(9)	Ti(1)	C(12)	57.6(2)	C(10)	Ti(1)	C(11)	33.3(2)
C(10)	Ti(1)	C(12)	56.6(2)	C(11)	Ti(1)	C(12)	33.9(2)
Ti(1)	N(1)	N(2)	178.3(4)	N(1)	N(2)	C(2)	119.2(5)
N(1)	N(2)	C(6)	119.2(5)	C(2)	N(2)	C(6)	121.4(5)
N(2)	C(2)	C(1)	117.2(5)	N(2)	C(2)	C(3)	118.2(6)
C(1)	C(2)	C(3)	124.7(6)	C(2)	C(3)	C(4)	121.8(7)
C(3)	C(4)	C(5)	119.2(7)	C(4)	C(5)	C(6)	121.3(6)
N(2)	C(6)	C(5)	118.1(6)	N(2)	C(6)	C(7)	117.4(5)
C(5)	C(6)	C(7)	124.5(6)	Ti(1)	C(8)	C(9)	73.7(3)
Ti(1)	C(8)	C(12)	73.3(4)	Ti(1)	C(8)	C(13)	121.6(4)
C(9)	C(8)	C(12)	108.6(6)	C(9)	C(8)	C(13)	123.9(7)
C(12)	C(8)	C(13)	127.4(8)	Ti(1)	C(9)	C(8)	71.8(3)

atom	atom	atom	angle	atom	atom	atom	angle
Ti(1)	C(9)	C(10)	76.4(3)	Ti(1)	C(9)	C(14)	121.7(4)
C(8)	C(9)	C(10)	108.0(6)	C(8)	C(9)	C(14)	126.5(7)
C(10)	C(9)	C(14)	125.3(7)	Ti(1)	C(10)	C(9)	69.8(3)
Ti(1)	C(10)	C(11)	72.9(4)	Ti(1)	C(10)	C(15)	123.5(4)
C(9)	C(10)	C(11)	107.4(6)	C(9)	C(10)	C(15)	124.9(7)
C(11)	C(10)	C(15)	127.7(8)	Ti(1)	C(11)	C(10)	73.8(4)
Ti(1)	C(11)	C(12)	70.0(4)	Ti(1)	C(11)	C(16)	124.9(4)
C(10)	C(11)	C(12)	109.1(7)	C(10)	C(11)	C(16)	123.8(9)
C(12)	C(11)	C(16)	127.0(9)	Ti(1)	C(12)	C(8)	72.0(4)
Ti(1)	C(12)	C(11)	76.1(4)	Ti(1)	C(12)	C(17)	122.2(4)
C(8)	C(12)	C(11)	106.8(7)	C(8)	C(12)	C(17)	125.2(9)
C(11)	C(12)	C(17)	127.6(9)				

Table 13. Atomic coordinates and B(eq) values for $[Cp^*Ti(terpy)NNC_5H_3Me_2\text{-}2,6][OTf]_2$ (**5**)

atom	x	y	z	B_{eq}
Ti(1)	0.3974(1)	0.12366(3)	0.74921(7)	2.86(2)
S(1)	0.5697(2)	0.22931(6)	0.3974(1)	4.95(5)
S(2)	-0.0141(2)	0.05379(6)	0.2511(1)	4.88(5)
F(1)	0.7465(5)	0.1902(2)	0.5342(4)	11.5(2)
F(2)	0.8588(4)	0.2287(1)	0.4344(4)	9.6(2)
F(3)	0.7640(5)	0.1727(1)	0.3779(4)	9.8(2)
F(4)	0.1870(5)	0.1071(1)	0.3290(3)	9.6(2)
F(5)	0.1521(6)	0.1052(1)	0.1669(3)	11.0(2)
F(6)	0.2767(5)	0.0579(2)	0.2498(5)	12.7(2)
O(1)	0.5641(5)	0.2618(2)	0.4696(4)	8.8(2)
O(2)	0.5856(6)	0.2434(2)	0.2969(3)	9.2(2)
O(3)	0.4563(5)	0.1991(1)	0.4001(4)	8.3(2)
O(4)	-0.1283(5)	0.0841(1)	0.2495(3)	8.2(2)
O(5)	-0.0215(4)	0.0298(1)	0.1572(3)	5.7(1)
O(6)	0.0141(5)	0.0305(1)	0.3442(3)	7.3(1)
N(1)	0.4125(5)	0.1754(1)	0.7137(3)	3.1(1)
N(2)	0.4429(5)	0.2164(1)	0.7058(3)	3.2(1)
N(3)	0.4365(5)	0.1424(1)	0.9152(3)	3.3(1)
N(4)	0.6021(5)	0.0939(1)	0.8230(3)	3.0(1)
N(5)	0.5331(5)	0.1037(1)	0.6280(3)	3.4(1)
C(1)	0.2024(7)	0.2225(2)	0.5927(5)	5.5(2)
C(2)	0.3386(7)	0.2416(2)	0.6492(5)	4.0(2)
C(3)	0.3693(8)	0.2832(2)	0.6507(5)	5.5(2)
C(4)	0.4995(9)	0.2989(2)	0.7014(6)	6.8(3)

atom	x	y	z	B_{eq}
C(5)	0.6057(7)	0.2731(2)	0.7533(5)	5.3(2)
C(6)	0.5802(7)	0.2315(2)	0.7545(5)	4.1(2)
C(7)	0.6925(7)	0.2020(2)	0.8068(5)	6.2(2)
C(8)	0.2522(7)	0.0656(2)	0.6649(5)	4.0(2)
C(9)	0.2944(6)	0.0537(2)	0.7687(5)	4.1(2)
C(10)	0.2210(7)	0.0809(2)	0.8313(5)	4.4(2)
C(11)	0.1418(6)	0.1107(2)	0.7663(5)	4.1(2)
C(12)	0.1611(6)	0.1005(2)	0.6635(5)	4.1(2)
C(13)	0.2826(7)	0.0401(2)	0.5714(5)	6.7(2)
C(14)	0.3811(7)	0.0157(2)	0.8049(5)	6.5(2)
C(15)	0.2164(8)	0.0747(2)	0.9454(5)	7.7(2)
C(16)	0.0305(7)	0.1415(2)	0.7963(6)	7.3(2)
C(17)	0.0783(7)	0.1197(2)	0.5647(5)	6.8(2)
C(18)	0.3557(7)	0.1718(2)	0.9544(5)	4.2(2)
C(19)	0.3756(8)	0.1821(2)	1.0588(5)	5.2(2)
C(20)	0.4812(8)	0.1611(2)	1.1253(5)	5.3(2)
C(21)	0.5694(7)	0.1316(2)	1.0862(4)	4.5(2)
C(22)	0.5442(6)	0.1226(2)	0.9811(4)	3.5(1)
C(23)	0.6329(6)	0.0933(2)	0.9286(4)	3.4(2)
C(24)	0.7424(7)	0.0674(2)	0.9787(4)	4.4(2)
C(25)	0.8228(7)	0.0427(2)	0.9187(5)	5.1(2)
C(26)	0.7983(6)	0.0445(2)	0.8119(5)	4.3(2)
C(27)	0.6853(6)	0.0707(2)	0.7663(4)	3.3(1)
C(28)	0.6488(6)	0.0773(2)	0.6533(4)	3.2(2)

atom	x	y	z	B_{eq}
C(29)	0.7304(7)	0.0611(2)	0.5806(5)	4.7(2)
C(30)	0.6939(8)	0.0717(2)	0.4768(5)	5.3(2)
C(31)	0.5790(8)	0.0991(2)	0.4508(5)	4.8(2)
C(32)	0.5014(6)	0.1144(2)	0.5271(5)	4.0(2)
C(33)	0.7392(10)	0.2050(3)	0.4379(7)	7.3(3)
C(34)	0.1604(10)	0.0805(3)	0.2518(6)	6.8(3)
H(1)	0.1413	0.2430	0.5559	6.5594
H(2)	0.2316	0.2028	0.5448	6.5594
H(3)	0.1465	0.2092	0.6409	6.5594
H(4)	0.2969	0.3014	0.6150	6.5812
H(5)	0.5173	0.3276	0.7010	8.2020
H(6)	0.6972	0.2840	0.7885	6.3028
H(7)	0.6491	0.1877	0.8597	7.4472
H(8)	0.7201	0.1829	0.7570	7.4472
H(9)	0.7801	0.2164	0.8369	7.4472
H(10)	0.1894	0.0299	0.5369	7.9897
H(11)	0.3298	0.0568	0.5248	7.9897
H(12)	0.3475	0.0179	0.5942	7.9897
H(13)	0.3265	-0.0079	0.7777	7.8528
H(14)	0.4777	0.0162	0.7810	7.8528
H(15)	0.3938	0.0146	0.8789	7.8528
H(16)	0.1604	0.0963	0.9715	9.2304
H(17)	0.1690	0.0492	0.9562	9.2304
H(18)	0.3169	0.0746	0.9808	9.2304

atom	x	y	z	B_{eq}
H(19)	0.0366	0.1425	0.8701	8.7746
H(20)	0.0533	0.1677	0.7705	8.7746
H(21)	-0.0690	0.1336	0.7675	8.7746
H(22)	0.0233	0.1431	0.5826	8.1728
H(23)	0.1499	0.1278	0.5202	8.1728
H(24)	0.0100	0.1003	0.5298	8.1728
H(25)	0.2818	0.1862	0.9086	4.9981
H(26)	0.3170	0.2034	1.0842	6.2596
H(27)	0.4934	0.1669	1.1979	6.3950
H(28)	0.6463	0.1177	1.1307	5.3797
H(29)	0.7617	0.0666	1.0526	5.2222
H(30)	0.8964	0.0242	0.9518	6.1246
H(31)	0.8565	0.0284	0.7705	5.1583
H(32)	0.8115	0.0426	0.6011	5.6686
H(33)	0.7475	0.0602	0.4248	6.3970
H(34)	0.5531	0.1075	0.3805	5.7247
H(35)	0.4215	0.1333	0.5079	4.7851

Table 14. Anisotropic displacement parameters for $[Cp^*Ti(terpy)NNC_5H_3Me_2\text{-}2,6][OTf]_2$ (**5**)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	0.0384(6)	0.0325(6)	0.0361(6)	0.0000(6)	-0.0009(5)	-0.0009(6)
S(1)	0.065(1)	0.063(1)	0.061(1)	0.001(1)	0.013(1)	0.006(1)
S(2)	0.064(1)	0.071(1)	0.048(1)	0.014(1)	-0.0010(9)	-0.001(1)
F(1)	0.152(5)	0.188(6)	0.089(4)	0.010(4)	-0.016(3)	0.048(4)
F(2)	0.078(3)	0.104(4)	0.183(5)	-0.022(3)	0.018(3)	-0.016(4)
F(3)	0.141(4)	0.070(3)	0.168(5)	0.004(3)	0.041(4)	-0.009(3)
F(4)	0.179(5)	0.107(4)	0.076(3)	-0.050(3)	0.005(3)	-0.020(3)
F(5)	0.235(6)	0.106(4)	0.088(4)	-0.028(4)	0.068(4)	0.000(3)
F(6)	0.073(3)	0.127(5)	0.283(7)	0.005(3)	0.024(4)	-0.049(5)
O(1)	0.116(4)	0.114(5)	0.107(4)	0.011(4)	0.030(3)	-0.058(4)
O(2)	0.162(5)	0.122(5)	0.069(4)	0.041(4)	0.035(3)	0.041(3)
O(3)	0.062(3)	0.087(4)	0.163(5)	-0.021(3)	-0.006(3)	0.044(4)
O(4)	0.097(4)	0.126(5)	0.085(4)	0.060(3)	-0.003(3)	-0.024(3)
O(5)	0.085(3)	0.072(3)	0.054(3)	0.021(3)	-0.015(3)	-0.017(2)
O(6)	0.126(4)	0.097(4)	0.050(3)	-0.017(3)	-0.007(3)	0.026(3)
N(1)	0.051(3)	0.027(3)	0.040(3)	0.001(2)	0.003(2)	-0.002(2)
N(2)	0.047(3)	0.038(3)	0.038(3)	0.003(3)	0.012(2)	0.000(3)
N(3)	0.047(3)	0.041(3)	0.038(3)	-0.001(2)	0.004(2)	-0.004(2)
N(4)	0.038(3)	0.033(3)	0.041(3)	-0.003(2)	0.001(2)	0.003(2)
N(5)	0.054(3)	0.037(3)	0.036(3)	-0.005(3)	0.004(2)	0.003(3)
C(1)	0.070(5)	0.059(5)	0.074(5)	0.019(4)	-0.010(4)	0.011(4)
C(2)	0.055(4)	0.046(4)	0.054(4)	0.015(4)	0.013(3)	0.004(4)
C(3)	0.079(6)	0.037(4)	0.096(6)	0.018(4)	0.024(5)	0.023(4)
C(4)	0.100(7)	0.043(5)	0.122(8)	-0.020(5)	0.034(6)	-0.005(5)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(5)	0.071(5)	0.043(4)	0.086(5)	-0.011(4)	0.010(4)	-0.004(4)
C(6)	0.054(4)	0.048(4)	0.055(4)	-0.007(4)	0.013(3)	-0.005(4)
C(7)	0.055(5)	0.071(5)	0.102(6)	-0.011(4)	-0.020(4)	0.009(4)
C(8)	0.056(4)	0.040(4)	0.053(4)	-0.019(3)	0.001(3)	-0.005(3)
C(9)	0.053(4)	0.042(4)	0.061(5)	-0.011(3)	0.002(4)	0.007(4)
C(10)	0.047(4)	0.071(5)	0.047(4)	-0.031(4)	0.007(3)	0.000(4)
C(11)	0.043(4)	0.049(4)	0.064(5)	-0.006(3)	0.012(3)	-0.012(4)
C(12)	0.045(4)	0.044(4)	0.061(5)	-0.006(3)	-0.011(3)	0.001(4)
C(13)	0.110(6)	0.060(5)	0.084(6)	-0.024(4)	0.014(5)	-0.028(4)
C(14)	0.076(5)	0.045(4)	0.121(6)	-0.012(4)	-0.010(5)	0.029(4)
C(15)	0.101(6)	0.135(7)	0.059(5)	-0.065(5)	0.021(4)	0.000(5)
C(16)	0.054(5)	0.080(6)	0.151(7)	-0.011(4)	0.040(5)	-0.043(5)
C(17)	0.084(5)	0.073(5)	0.089(5)	-0.023(4)	-0.036(4)	0.014(5)
C(18)	0.060(4)	0.049(4)	0.050(4)	0.004(3)	0.008(3)	-0.008(3)
C(19)	0.084(6)	0.059(5)	0.057(5)	-0.002(4)	0.019(4)	-0.015(4)
C(20)	0.093(6)	0.072(6)	0.038(4)	-0.013(4)	0.007(4)	-0.012(4)
C(21)	0.069(5)	0.058(5)	0.039(4)	-0.007(4)	-0.008(3)	0.001(4)
C(22)	0.049(4)	0.044(4)	0.038(4)	-0.008(3)	-0.002(3)	0.002(3)
C(23)	0.042(4)	0.039(4)	0.047(4)	-0.006(3)	-0.003(3)	0.004(3)
C(24)	0.055(4)	0.059(5)	0.047(4)	0.003(4)	-0.011(3)	0.012(4)
C(25)	0.058(5)	0.050(5)	0.080(5)	0.008(4)	-0.012(4)	0.012(4)
C(26)	0.046(4)	0.047(4)	0.071(5)	0.006(3)	0.009(4)	-0.002(4)
C(27)	0.036(4)	0.035(4)	0.053(4)	-0.002(3)	0.005(3)	0.004(3)
C(28)	0.048(4)	0.028(4)	0.050(4)	0.000(3)	0.014(3)	-0.001(3)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(29)	0.064(5)	0.046(4)	0.072(5)	0.001(4)	0.021(4)	-0.001(4)
C(30)	0.097(6)	0.052(5)	0.060(5)	-0.010(4)	0.036(4)	-0.016(4)
C(31)	0.087(6)	0.056(5)	0.042(4)	-0.012(4)	0.022(4)	0.001(4)
C(32)	0.068(4)	0.038(4)	0.046(4)	-0.010(3)	0.008(3)	0.006(3)
C(33)	0.086(7)	0.102(8)	0.090(7)	-0.037(6)	0.013(6)	-0.017(6)
C(34)	0.108(7)	0.098(7)	0.055(5)	-0.002(6)	0.023(5)	0.006(5)

Table 15. Bond lengths (Å) for nonhydrogen atoms for $[Cp^*Ti(terpy)NNC_5H_3Me_2\text{-}2,6][OTf]_2$ (**5**)

atom	atom	distance	atom	atom	distance
Ti(1)	N(1)	1.755(4)	Ti(1)	N(3)	2.216(4)
Ti(1)	N(4)	2.171(4)	Ti(1)	N(5)	2.197(4)
Ti(1)	C(8)	2.465(6)	Ti(1)	C(9)	2.481(6)
Ti(1)	C(10)	2.442(6)	Ti(1)	C(11)	2.350(6)
Ti(1)	C(12)	2.369(5)	S(1)	O(1)	1.416(4)
S(1)	O(2)	1.404(4)	S(1)	O(3)	1.412(4)
S(1)	C(33)	1.723(9)	S(2)	O(4)	1.415(4)
S(2)	O(5)	1.438(4)	S(2)	O(6)	1.418(4)
S(2)	C(34)	1.778(8)	F(1)	C(33)	1.331(9)
F(2)	C(33)	1.320(8)	F(3)	C(33)	1.342(8)
F(4)	C(34)	1.320(8)	F(5)	C(34)	1.357(8)
F(6)	C(34)	1.271(8)	N(1)	N(2)	1.369(5)
N(2)	C(2)	1.376(6)	N(2)	C(6)	1.391(6)
N(3)	C(18)	1.337(6)	N(3)	C(22)	1.359(6)
N(4)	C(23)	1.359(6)	N(4)	C(27)	1.341(6)
N(5)	C(28)	1.347(6)	N(5)	C(32)	1.346(6)
C(1)	C(2)	1.469(7)	C(2)	C(3)	1.384(8)
C(3)	C(4)	1.354(8)	C(4)	C(5)	1.372(8)
C(5)	C(6)	1.372(7)	C(6)	C(7)	1.486(8)
C(8)	C(9)	1.402(7)	C(8)	C(12)	1.395(7)
C(8)	C(13)	1.518(8)	C(9)	C(10)	1.415(8)
C(9)	C(14)	1.501(7)	C(10)	C(11)	1.413(7)
C(10)	C(15)	1.496(8)	C(11)	C(12)	1.403(7)
C(11)	C(16)	1.494(7)	C(12)	C(17)	1.526(7)

atom	atom	distance	atom	atom	distance
C(18)	C(19)	1.382(7)	C(19)	C(20)	1.372(8)
C(20)	C(21)	1.378(8)	C(21)	C(22)	1.380(7)
C(22)	C(23)	1.462(7)	C(23)	C(24)	1.384(7)
C(24)	C(25)	1.380(8)	C(25)	C(26)	1.372(8)
C(26)	C(27)	1.390(7)	C(27)	C(28)	1.472(7)
C(28)	C(29)	1.368(7)	C(29)	C(30)	1.385(8)
C(30)	C(31)	1.365(8)	C(31)	C(32)	1.369(7)

Table 16. Bond angles (deg) for nonhydrogen atoms for [Cp*Ti(terpy)NNC$_5$H$_3$Me$_2$-2,6][OTf]$_2$ (**5**)

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	Ti(1)	N(3)	89.0(2)	N(1)	Ti(1)	N(4)	117.1(2)
N(1)	Ti(1)	N(5)	91.7(2)	N(1)	Ti(1)	C(8)	132.4(2)
N(1)	Ti(1)	C(9)	161.7(2)	N(1)	Ti(1)	C(10)	137.4(2)
N(1)	Ti(1)	C(11)	107.7(2)	N(1)	Ti(1)	C(12)	106.0(2)
N(3)	Ti(1)	N(4)	71.3(2)	N(3)	Ti(1)	N(5)	137.9(2)
N(3)	Ti(1)	C(8)	130.4(2)	N(3)	Ti(1)	C(9)	99.7(2)
N(3)	Ti(1)	C(10)	76.4(2)	N(3)	Ti(1)	C(11)	89.5(2)
N(3)	Ti(1)	C(12)	124.0(2)	N(4)	Ti(1)	N(5)	71.1(2)
N(4)	Ti(1)	C(8)	102.3(2)	N(4)	Ti(1)	C(9)	81.1(2)
N(4)	Ti(1)	C(10)	95.9(2)	N(4)	Ti(1)	C(11)	130.1(2)
N(4)	Ti(1)	C(12)	134.9(2)	N(5)	Ti(1)	C(8)	76.2(2)
N(5)	Ti(1)	C(9)	92.6(2)	N(5)	Ti(1)	C(10)	125.8(2)
N(5)	Ti(1)	C(11)	129.9(2)	N(5)	Ti(1)	C(12)	96.1(2)
C(8)	Ti(1)	C(9)	32.9(2)	C(8)	Ti(1)	C(10)	54.9(2)
C(8)	Ti(1)	C(11)	56.4(2)	C(8)	Ti(1)	C(12)	33.5(2)
C(9)	Ti(1)	C(10)	33.4(2)	C(9)	Ti(1)	C(11)	56.7(2)
C(9)	Ti(1)	C(12)	55.8(2)	C(10)	Ti(1)	C(11)	34.2(2)
C(10)	Ti(1)	C(12)	56.0(2)	C(11)	Ti(1)	C(12)	34.6(2)
O(1)	S(1)	O(2)	112.5(3)	O(1)	S(1)	O(3)	114.6(3)
O(1)	S(1)	C(33)	104.3(4)	O(2)	S(1)	O(3)	114.2(3)
O(2)	S(1)	C(33)	104.1(4)	O(3)	S(1)	C(33)	105.8(4)
O(4)	S(2)	O(5)	114.3(3)	O(4)	S(2)	O(6)	115.7(3)
O(4)	S(2)	C(34)	106.4(4)	O(5)	S(2)	O(6)	114.3(3)
O(5)	S(2)	C(34)	102.4(3)	O(6)	S(2)	C(34)	101.5(3)

atom	atom	atom	angle	atom	atom	atom	angle
Ti(1)	N(1)	N(2)	167.9(4)	N(1)	N(2)	C(2)	119.7(5)
N(1)	N(2)	C(6)	118.9(5)	C(2)	N(2)	C(6)	121.4(5)
Ti(1)	N(3)	C(18)	122.7(4)	Ti(1)	N(3)	C(22)	119.2(4)
C(18)	N(3)	C(22)	118.1(5)	Ti(1)	N(4)	C(23)	119.9(4)
Ti(1)	N(4)	C(27)	120.1(4)	C(23)	N(4)	C(27)	119.2(5)
Ti(1)	N(5)	C(28)	119.1(4)	Ti(1)	N(5)	C(32)	123.5(4)
C(28)	N(5)	C(32)	117.3(5)	N(2)	C(2)	C(1)	117.9(5)
N(2)	C(2)	C(3)	117.3(6)	C(1)	C(2)	C(3)	124.8(6)
C(2)	C(3)	C(4)	122.0(7)	C(3)	C(4)	C(5)	119.8(7)
C(4)	C(5)	C(6)	120.4(7)	N(2)	C(6)	C(5)	118.8(6)
N(2)	C(6)	C(7)	118.4(6)	C(5)	C(6)	C(7)	122.8(6)
Ti(1)	C(8)	C(9)	74.2(3)	Ti(1)	C(8)	C(12)	69.5(3)
Ti(1)	C(8)	C(13)	129.4(4)	C(9)	C(8)	C(12)	108.6(6)
C(9)	C(8)	C(13)	124.1(6)	C(12)	C(8)	C(13)	126.7(6)
Ti(1)	C(9)	C(8)	72.9(3)	Ti(1)	C(9)	C(10)	71.8(3)
Ti(1)	C(9)	C(14)	127.5(4)	C(8)	C(9)	C(10)	106.9(6)
C(8)	C(9)	C(14)	126.1(6)	C(10)	C(9)	C(14)	126.4(6)
Ti(1)	C(10)	C(9)	74.8(3)	Ti(1)	C(10)	C(11)	69.3(3)
Ti(1)	C(10)	C(15)	127.4(4)	C(9)	C(10)	C(11)	108.7(5)
C(9)	C(10)	C(15)	123.6(7)	C(11)	C(10)	C(15)	127.3(7)
Ti(1)	C(11)	C(10)	76.5(3)	Ti(1)	C(11)	C(12)	73.5(3)
Ti(1)	C(11)	C(16)	125.8(4)	C(10)	C(11)	C(12)	106.8(5)
C(10)	C(11)	C(16)	127.0(7)	C(12)	C(11)	C(16)	124.9(6)
Ti(1)	C(12)	C(8)	77.0(3)	Ti(1)	C(12)	C(11)	71.9(3)

atom	atom	atom	angle	atom	atom	atom	angle
Ti(1)	C(12)	C(17)	124.3(4)	C(8)	C(12)	C(11)	108.9(5)
C(8)	C(12)	C(17)	124.2(6)	C(11)	C(12)	C(17)	126.3(6)
N(3)	C(18)	C(19)	122.6(6)	C(18)	C(19)	C(20)	118.9(6)
C(19)	C(20)	C(21)	119.6(6)	C(20)	C(21)	C(22)	118.9(6)
N(3)	C(22)	C(21)	122.0(6)	N(3)	C(22)	C(23)	113.3(5)
C(21)	C(22)	C(23)	124.6(6)	N(4)	C(23)	C(22)	114.0(5)
N(4)	C(23)	C(24)	121.3(6)	C(22)	C(23)	C(24)	124.7(6)
C(23)	C(24)	C(25)	118.3(6)	C(24)	C(25)	C(26)	121.1(6)
C(25)	C(26)	C(27)	117.7(6)	N(4)	C(27)	C(26)	122.2(5)
N(4)	C(27)	C(28)	113.3(5)	C(26)	C(27)	C(28)	124.5(6)
N(5)	C(28)	C(27)	113.5(5)	N(5)	C(28)	C(29)	122.4(6)
C(27)	C(28)	C(29)	124.0(6)	C(28)	C(29)	C(30)	119.5(6)
C(29)	C(30)	C(31)	118.4(6)	C(30)	C(31)	C(32)	119.4(6)
N(5)	C(32)	C(31)	123.0(6)	S(1)	C(33)	F(1)	112.7(6)
S(1)	C(33)	F(2)	113.4(7)	S(1)	C(33)	F(3)	112.7(6)
F(1)	C(33)	F(2)	107.7(7)	F(1)	C(33)	F(3)	105.4(8)
F(2)	C(33)	F(3)	104.2(7)	S(2)	C(34)	F(4)	113.3(6)
S(2)	C(34)	F(5)	109.3(6)	S(2)	C(34)	F(6)	115.4(7)
F(4)	C(34)	F(5)	102.1(7)	F(4)	C(34)	F(6)	109.2(8)
F(5)	C(34)	F(6)	106.6(7)				