Appendix A

Crystallographic data for [TiCp$_2$(Dbf)$_2$] ***2-02.***

Table 1. Fractional atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [TiCp$_2$(Dbf)$_2$].

Atom	x	y	z	U_{eq}
Ti	7485(1)	1706(1)	235(1)	20(1)
Cl	5763(1)	2640(1)	708(1)	36(1)
S(1)	8951(1)	3370(1)	871(1)	26(1)
S(2)	11721(1)	2761(1)	1440(1)	28(1)
C(1)	9282(2)	2608(3)	1637(1)	26(1)
C(2)	8418(2)	2336(3)	2040(1)	29(1)
C(3)	8767(2)	1864(3)	2652(1)	31(1)
C(4)	9978(2)	1651(3)	2870(1)	28(1)
C(5)	10869(2)	1903(3)	2474(1)	24(1)
C(6)	12182(2)	1743(3)	2591(1)	25(1)
C(7)	12906(2)	1190(3)	3122(1)	30(1)
C(8)	14144(2)	1099(3)	3126(1)	39(1)
C(9)	14698(3)	1548(4)	2607(1)	45(1)
C(10)	14012(2)	2083(4)	2074(1)	39(1)
C(11)	12758(2)	2166(3)	2070(1)	27(1)
C(12)	10498(2)	2398(3)	1865(1)	24(1)
C(13)	8627(2)	-562(3)	758(1)	32(1)
C(14)	7481(2)	-559(3)	970(1)	34(1)
C(15)	6612(2)	-980(3)	468(1)	33(1)
C(16)	7225(2)	-1219(3)	-51(1)	30(1)
C(17)	8477(2)	-936(3)	125(1)	29(1)
C(18)	6493(3)	3620(4)	-522(1)	38(1)
C(19)	6692(2)	2050(4)	-810(1)	33(1)
C(20)	7955(2)	1827(3)	-802(1)	29(1)
C(21)	8533(2)	3230(3)	-493(1)	33(1)
C(22)	7621(3)	4321(3)	-314(1)	37(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths [Å] for $[TiCp_2(Dbf)_2]$.

TiA-C(13A)	2.210(4)	TiB-C(13B)	2.218(4)
TiA-C(1A)	2.218(5)	TiB-C(1B)	2.229(4)
TiA-C(27A)	2.335(4)	TiB-C(32B)	2.341(4)
TiA-C(32A)	2.366(4)	TiB-C(26B)	2.360(4)
TiA-C(26A)	2.385(4)	TiB-C(27B)	2.378(4)
TiA-C(31A)	2.392(4)	TiB-C(33B)	2.391(4)
TiA-C(25A)	2.398(5)	TiB-C(31B)	2.392(4)
TiA-C(28A)	2.400(5)	TiB-C(29B)	2.395(5)
TiA-C(29A)	2.404(5)	TiB-C(28B)	2.400(4)
TiA-C(33A)	2.406(5)	TiB-C(25B)	2.402(5)
TiA-C(30A)	2.410(5)	TiB-C(34B)	2.405(4)
TiA-C(34A)	2.418(5)	TiB-C(30B)	2.419(4)
O(1A)-C(11A)	1.398(5)	O(1B)-C(11B)	1.393(5)
O(1A)-C(12A)	1.405(5)	O(1B)-C(12B)	1.404(5)
O(2A)-C(23A)	1.388(5)	O(2B)-C(23B)	1.397(5)
O(2A)-C(24A)	1.418(4)	O(2B)-C(24B)	1.400(5)
C(1A)-C(12A)	1.410(6)	C(1B)-C(2B)	1.406(6)
C(1A)-C(2A)	1.415(6)	C(1B)-C(12B)	1.401(6)
C(2A)-C(3A)	1.422(6)	C(2B)-C(3B)	1.397(6)
C(3A)-C(4A)	1.382(7)	C(3B)-C(4B)	1.386(6)
C(4A)-C(5A)	1.393(7)	C(4B)-C(5B)	1.387(6)
C(5A)-C(12A)	1.410(6)	C(5B)-C(12B)	1.407(6)
C(5A)-C(6A)	1.450(7)	C(5B)-C(6B)	1.470(6)
C(6A)-C(11A)	1.395(6)	C(6B)-C(11B)	1.388(6)
C(6A)-C(7A)	1.422(7)	C(6B)-C(7B)	1.400(6)
C(7A)-C(8A)	1.372(8)	C(7B)-C(8B)	1.407(7)
C(8A)-C(9A)	1.363(8)	C(8B)-C(9B)	1.370(7)
C(9A)-C(10A)	1.400(7)	C(9B)-C(10B)	1.384(6)
C(10A)-C(11A)	1.375(7)	C(10B)-C(11B)	1.384(6)
C(13A)-C(24A)	1.391(5)	C(13B)-C(14B)	1.404(6)
C(13A)-C(14A)	1.422(5)	C(13B)-C(24B)	1.408(6)
C(14A)-C(15A)	1.390(6)	C(14B)-C(15B)	1.408(6)
C(15A)-C(16A)	1.383(6)	C(15B)-C(16B)	1.390(6)
C(16A)-C(17A)	1.391(6)	C(16B)-C(17B)	1.388(7)
C(17A)-C(24A)	1.404(5)	C(17B)-C(24B)	1.397(6)
C(17A)-C(18A)	1.459(6)	C(17B)-C(18B)	1.452(6)
C(18A)-C(19A)	1.392(6)	C(18B)-C(23B)	1.387(7)
C(18A)-C(23A)	1.398(6)	C(18B)-C(19B)	1.410(6)
C(19A)-C(20A)	1.372(6)	C(19B)-C(20B)	1.374(8)
C(20A)-C(21A)	1.392(7)	C(20B)-C(21B)	1.398(8)
C(21A)-C(22A)	1.399(6)	C(21B)-C(22B)	1.403(6)
C(22A)-C(23A)	1.379(6)	C(22B)-C(23B)	1.386(7)
C(25A)-C(26A)	1.384(6)	C(25B)-C(29B)	1.388(6)
C(25A)-C(29A)	1.421(6)	C(25B)-C(26B)	1.410(6)
C(26A)-C(27A)	1.400(6)	C(26B)-C(27B)	1.406(6)
C(27A)-C(28A)	1.397(6)	C(27B)-C(28B)	1.401(6)
C(28A)-C(29A)	1.391(6)	C(28B)-C(29B)	1.410(6)

C(30A)-C(31A)	1.393(6)	C(30B)-C(31B)	1.387(6)
C(30A)-C(34A)	1.420(6)	C(30B)-C(34B)	1.416(6)
C(31A)-C(32A)	1.415(6)	C(31B)-C(32B)	1.421(6)
C(32A)-C(33A)	1.396(6)	C(32B)-C(33B)	1.402(6)
C(33A)-C(34A)	1.397(6)	C(33B)-C(34B)	1.394(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table 3. Bond angles [°] for $[TiCp_2(Dbf)_2]$.

C(13A)-TiA-C(1A)	104.96(16)	C(13B)-TiB-C(1B)	104.01(17)
C(13A)-TiA-C(27A)	97.27(17)	C(13B)-TiB-C(32B)	132.14(15)
C(1A)-TiA-C(27A)	131.74(17)	C(1B)-TiB-C(32B)	95.17(15)
C(13A)-TiA-C(32A)	131.67(16)	C(13B)-TiB-C(26B)	93.10(16)
C(1A)-TiA-C(32A)	96.17(16)	C(1B)-TiB-C(26B)	131.76(16)
C(27A)-TiA-C(32A)	100.07(17)	C(32B)-TiB-C(26B)	106.02(16)
C(13A)-TiA-C(26A)	130.79(17)	C(13B)-TiB-C(27B)	76.91(15)
C(1A)-TiA-C(26A)	106.16(17)	C(1B)-TiB-C(27B)	106.25(17)
C(27A)-TiA-C(26A)	34.49(14)	C(32B)-TiB-C(27B)	138.45(17)
C(32A)-TiA-C(26A)	81.07(17)	C(26B)-TiB-C(27B)	34.53(15)
C(13A)-TiA-C(31A)	107.63(16)	C(13B)-TiB-C(33B)	108.40(16)
C(1A)-TiA-C(31A)	130.25(17)	C(1B)-TiB-C(33B)	77.40(15)
C(27A)-TiA-C(31A)	79.58(17)	C(32B)-TiB-C(33B)	34.45(14)
C(32A)-TiA-C(31A)	34.59(15)	C(26B)-TiB-C(33B)	138.85(16)
C(26A)-TiA-C(31A)	78.92(17)	C(27B)-TiB-C(33B)	172.89(17)
C(13A)-TiA-C(25A)	127.96(17)	C(13B)-TiB-C(31B)	109.09(16)
C(1A)-TiA-C(25A)	76.08(16)	C(1B)-TiB-C(31B)	129.72(15)
C(27A)-TiA-C(25A)	56.70(16)	C(32B)-TiB-C(31B)	34.92(13)
C(32A)-TiA-C(25A)	98.95(18)	C(26B)-TiB-C(31B)	83.25(16)
C(26A)-TiA-C(25A)	33.65(14)	C(27B)-TiB-C(31B)	117.26(17)
C(31A)-TiA-C(25A)	109.78(18)	C(33B)-TiB-C(31B)	56.92(15)
C(13A)-TiA-C(28A)	76.77(16)	C(13B)-TiB-C(29B)	131.37(15)
C(1A)-TiA-C(28A)	111.54(17)	C(1B)-TiB-C(29B)	78.73(17)
C(27A)-TiA-C(28A)	34.28(14)	C(32B)-TiB-C(29B)	94.96(16)
C(32A)-TiA-C(28A)	133.91(16)	C(26B)-TiB-C(29B)	57.04(16)
C(26A)-TiA-C(28A)	56.68(16)	C(27B)-TiB-C(29B)	56.57(15)
C(31A)-TiA-C(28A)	111.79(17)	C(33B)-TiB-C(29B)	119.27(16)
C(25A)-TiA-C(28A)	56.41(17)	C(31B)-TiB-C(29B)	104.54(17)
C(13A)-TiA-C(29A)	93.72(17)	C(13B)-TiB-C(28B)	98.36(16)
C(1A)-TiA-C(29A)	79.21(17)	C(1B)-TiB-C(28B)	75.56(16)
C(27A)-TiA-C(29A)	56.79(15)	C(32B)-TiB-C(28B)	129.01(17)
C(32A) TiA-C(29A)	133.19(18)	C(26B)-TiB-C(28B)	57.30(17)
C(26A) TiA-C(29A)	56.68(16)	C(27B)-TiB-C(28B)	34.09(15)
C(31A) TiA-C(29A)	133.66(16)	C(33B)-TiB-C(28B)	145.70(17)
C(25A) TiA-C(29A)	34.44(15)	C(31B)-TiB-C(28B)	133.02(17)
C(28A) TiA-C(29A)	33.67(15)	C(29B)-TiB-C(28B)	34.20(15)
C(13A) TiA-C(33A)	109.75(17)	C(13B)-TiB-C(25B)	127.38(15)
C(1A)-TiA-C(33A)	77.69(16)	C(1B)-TiB-C(25B)	110.97(16)
C(27A)-TiA-C(33A)	133.21(16)	C(32B)-TiB-C(25B)	82.77(16)
C(32A)-TiA-C(33A)	34.00(15)	C(26B)-TiB-C(25B)	34.44(14)
C(26A)-TiA-C(33A)	113.47(17)	C(27B)-TiB-C(25B)	56.54(15)
C(31A)-TiA-C(33A)	56.44(16)	C(33B)-TiB-C(25B)	116.59(16)
C(25A)-TiA-C(33A)	120.78(18)	C(31B)-TiB-C(25B)	76.65(16)
C(28A)-TiA-C(33A)	167.48(16)	C(29B)-TiB-C(25B)	33.64(14)
C(29A)-TiA-C(33A)	150.52(18)	C(28B)-TiB-C(25B)	56.45(17)
C(13A)-TiA-C(30A)	76.60(16)	C(13B)-TiB-C(34B)	77.17(15)
C(1A)-TiA-C(30A)	130.16(18)	C(1B)-TiB-C(34B)	97.13(17)

C(27A)-TiA-C(30A)	96.24(18)	C(32B)-TiB-C(34B)	56.98(15)
C(32A)-TiA-C(30A)	56.96(16)	C(26B)-TiB-C(34B)	130.83(17)
C(26A)-TiA-C(30A)	109.12(17)	C(27B)-TiB-C(34B)	148.51(17)
C(31A)-TiA-C(30A)	33.73(15)	C(33B)-TiB-C(34B)	33.80(14)
C(25A)-TiA-C(30A)	142.25(18)	C(31B)-TiB-C(34B)	56.49(16)
C(28A)-TiA-C(30A)	117.00(18)	C(29B)-TiB-C(34B)	151.43(16)
C(29A)-TiA-C(30A)	150.41(18)	C(28B)-TiB-C(34B)	170.42(17)
C(33A)-TiA-C(30A)	56.48(16)	C(25B)-TiB-C(34B)	132.93(16)
C(13A)-TiA-C(34A)	78.00(17)	C(13B)-TiB-C(30B)	77.86(15)
C(1A)-TiA-C(34A)	96.33(17)	C(1B)-TiB-C(30B)	130.62(16)
C(27A)-TiA-C(34A)	130.33(17)	C(32B)-TiB-C(30B)	56.94(14)
C(32A)-TiA-C(34A)	56.55(17)	C(26B)-TiB-C(30B)	96.76(17)
C(26A)-TiA-C(34A)	133.94(16)	C(27B)-TiB-C(30B)	121.67(17)
C(31A)-TiA-C(34A)	56.27(16)	C(33B)-TiB-C(30B)	56.42(15)
C(25A)-TiA-C(34A)	153.93(19)	C(31B)-TiB-C(30B)	33.51(14)
C(28A)-TiA-C(34A)	146.28(18)	C(29B)-TiB-C(30B)	136.80(18)
C(29A)-TiA-C(34A)	169.36(16)	C(28B)-TiB-C(30B)	153.80(17)
C(33A)-TiA-C(34A)	33.67(15)	C(25B)-TiB-C(30B)	105.10(17)
C(30A)-TiA-C(34A)	34.21(16)	C(34B)-TiB-C(30B)	34.14(15)
C(11A)-O(1A)-C(12A)	106.3(4)	C(11B)-O(1B)-C(12B)	106.0(3)
C(23A)-O(2A)-C(24A)	105.9(3)	C(23B)-O(2B)-C(24B)	106.0(3)
C(12A)-C(1A)-C(2A)	110.3(4)	C(2B)-C(1B)-C(12B)	111.1(4)
C(12A)-C(1A)-TiA	126.3(3)	C(2B)-C(1B)-TiB	122.4(3)
C(2A)-C(1A)-TiA	123.3(4)	C(12B)-C(1B)-TiB	126.4(3)
C(1A)-C(2A)-C(3A)	123.9(5)	C(3B)-C(2B)-C(1B)	124.5(4)
C(4A)-C(3A)-C(2A)	121.5(5)	C(4B)-C(3B)-C(2B)	121.4(5)
C(3A)-C(4A)-C(5A)	118.1(5)	C(3B)-C(4B)-C(5B)	117.1(5)
C(4A)-C(5A)-C(12A)	117.9(5)	C(4B)-C(5B)-C(12B)	119.3(4)
C(4A)-C(5A)-C(6A)	135.6(5)	C(4B)-C(5B)-C(6B)	134.7(5)
C(12A)-C(5A)-C(6A)	106.2(4)	C(12B)-C(5B)-C(6B)	106.0(4)
C(11A)-C(6A)-C(7A)	117.4(5)	C(11B)-C(6B)-C(7B)	119.6(4)
C(11A)-C(6A)-C(5A)	106.6(4)	C(11B)-C(6B)-C(5B)	105.7(4)
C(7A)-C(6A)-C(5A)	135.9(5)	C(7B)-C(6B)-C(5B)	134.7(5)
C(8A)-C(7A)-C(6A)	117.8(6)	C(6B)-C(7B)-C(8B)	117.3(5)
C(9A)-C(8A)-C(7A)	123.2(6)	C(9B)-C(8B)-C(7B)	121.4(5)
C(8A)-C(9A)-C(10A)	120.7(6)	C(8B)-C(9B)-C(10B)	121.9(5)
C(11A)-C(10A)-C(9A)	116.2(5)	C(9B)-C(10B)-C(11B)	116.7(5)
C(10A)-C(11A)-O(1A)	124.9(5)	C(10B)-C(11B)-C(6B)	123.1(4)
C(10A)-C(11A)-C(6A)	124.4(5)	C(10B)-C(11B)-O(1B)	125.0(4)
O(1A)-C(11A)-C(6A)	110.7(5)	C(6B)-C(11B)-O(1B)	111.9(4)
C(5A)-C(12A)-O(1A)	110.1(4)	C(1B)-C(12B)-O(1B)	123.2(4)
C(5A)-C(12A)-C(1A)	127.9(4)	C(1B)-C(12B)-C(5B)	126.3(4)
O(1A)-C(12A)-C(1A)	122.0(4)	O(1B)-C(12B)-C(5B)	110.4(4)
C(24A)-C(13A)-C(14A)	110.9(4)	C(14B)-C(13B)-C(24B)	110.8(4)
C(24A)-C(13A)-TiA	126.4(3)	C(14B)-C(13B)-TiB	122.3(3)
C(14A)-C(13A)-TiA	122.6(3)	C(24B)-C(13B)- TiB	126.7(3)
C(15A)-C(14A)-C(13A)	124.3(4)	C(13B)-C(14B)-C(15B)	124.9(5)
C(16A)-C(15A)-C(14A)	121.2(4)	C(16B)-C(15B)-C(14B)	120.7(5)

C(15A)-C(16A)-C(17A)	118.0(4)	C(17B)-C(16B)-C(15B)	117.4(5)
C(16A)-C(17A)-C(24A)	118.4(4)	C(16B)-C(17B)-C(24B)	119.3(5)
C(16A)-C(17A)-C(18A)	135.1(4)	C(16B)-C(17B)-C(18B)	134.2(5)
C(24A)-C(17A)-C(18A)	106.6(4)	C(24B)-C(17B)-C(18B)	106.5(4)
C(19A)-C(18A)-C(23A)	118.8(4)	C(23B)-C(18B)-C(19B)	118.8(5)
C(19A)-C(18A)-C(17A)	135.4(4)	C(23B)-C(18B)-C(17B)	106.2(4)
C(23A)-C(18A)-C(17A)	105.8(4)	C(19B)-C(18B)-C(17B)	135.1(5)
C(20A)-C(19A)-C(18A)	119.2(5)	C(20B)-C(19B)-C(18B)	118.1(5)
C(19A)-C(20A)-C(21A)	120.7(5)	C(19B)-C(20B)-C(21B)	122.1(5)
C(20A)-C(21A)-C(22A)	122.0(5)	C(20B)-C(21B)-C(22B)	120.8(6)
C(23A)-C(22A)-C(21A)	115.6(4)	C(23B)-C(22B)-C(21B)	115.9(5)
C(22A)-C(23A)-O(2A)	124.6(4)	C(18B)-C(23B)-C(22B)	124.2(5)
C(22A)-C(23A)-C(18A)	123.7(4)	C(18B)-C(23B)-O(2B)	111.1(4)
O(2A)-C(23A)-C(18A)	111.8(4)	C(22B)-C(23B)-O(2B)	124.7(5)
C(13A)-C(24A)-C(17A)	127.2(4)	C(17B)-C(24B)-O(2B)	110.3(4)
C(13A)-C(24A)-O(2A)	122.8(4)	C(17B)-C(24B)-C(13B)	126.8(5)
C(17A)-C(24A)-O(2A)	110.0(3)	O(2B)-C(24B)-C(13B)	122.9(4)
C(26A)-C(25A)-C(29A)	108.2(4)	C(29B)-C(25B)-C(26B)	108.4(4)
C(26A)-C(25A)-TiA	72.7(3)	C(29B)-C(25B)-TiB	72.9(3)
C(29A)-C(25A)-TiA	73.0(3)	C(26B)-C(25B)-TiB	71.1(3)
C(25A)-C(26A)-C(27A)	107.7(4)	C(27B)-C(26B)-C(25B)	107.0(4)
C(25A)-C(26A)-TiA	73.7(3)	C(27B)-C(26B)-TiB	73.4(3)
C(27A)-C(26A)-TiA	70.8(2)	C(25B)-C(26B)-TiB	74.4(3)
C(26A)-C(27A)-C(28A)	108.6(4)	C(28B)-C(27B)-C(26B)	108.8(4)
C(26A)-C(27A)-TiA	74.7(3)	C(28B)-C(27B)-TiB	73.8(2)
C(28A)-C(27A)-TiA	75.4(3)	C(26B)-C(27B)-TiB	72.0(2)
C(29A)-C(28A)-C(27A)	107.9(4)	C(27B)-C(28B)-C(29B)	107.2(4)
C(29A)-C(28A)-TiA	73.3(3)	C(27B)-C(28B)-TiB	72.1(2)
C(27A)-C(28A)-TiA	70.3(3)	C(29B)-C(28B)-TiB	72.7(2)
C(28A)-C(29A)-C(25A)	107.5(4)	C(25B)-C(29B)-C(28B)	108.5(4)
C(28A)-C(29A)-TiA	73.0(3)	C(25B)-C(29B)-TiB	73.5(3)
C(25A)-C(29A)-TiA	72.6(3)	C(28B)-C(29B)-TiB	73.1(3)
C(31A)-C(30A)-C(34A)	107.4(4)	C(31B)-C(30B)-(34B)	108.1(4)
C(31A)-C(30A)-TiA	72.4(3)	C(31B)-C(30B)-TiB	72.2(2)
C(34A)-C(30A)-TiA	73.2(3)	C(34B)-C(30B)-TiB	72.4(2)
C(30A)-C(31A)-C(32A)	108.4(4)	C(30B)-C(31B)-(32B)	C107.9(4)
C(30A)-C(31A)-TiA	73.9(3)	C(30B)-C(31B)-TiB	74.3(3)
C(32A)-C(31A)-TiA	71.7(2)	C(32B)-C(31B)-TiB	70.6(2)
C(33A)-C(32A)-C(31A)	107.6(4)	C(33B)-C(32B)-(31B)	107.7(4)
C(33A)-C(32A)-TiA	74.5(3)	C(33B)-C(32B)-TiB	74.7(2)
C(31A)-C(32A)-TiA	73.7(3)	C(31B)-C(32B)-TiB	74.5(2)
C(34A)-C(33A)-C(32A)	108.5(4)	C(34B)-C(33B)-(32B)	108.2(4)
C(34A)-C(33A)-TiA	73.7(3)	C(34B)-C(33B)-TiB	73.6(2)
C(32A)-C(33A)-TiA	71.5(3)	C(32B)-C(33B)-TiB	70.8(2)
C(33A)-C(34A)-C(30A)	107.9(4)	C(33B)-C(34B)-(30B)	108.0(4)
C(33A)-C(34A)-TiA	72.7(3)	C(33B)-C(34B)-TiB	72.6(2)
C(30A)-C(34A)-TiA	72.6(3)	C(30B)-C(34B)-TiB	73.5(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for $[TiCp_2(Dbf)_2]$.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Ti	20(1)	20(1)	20(1)	1(1)	1(1)	1(1)
Cl	27(1)	45(1)	36(1)	-6(1)	8(1)	7(1)
S(1)	31(1)	24(1)	22(1)	3(1)	-3(1)	-4(1)
S(2)	33(1)	33(1)	20(1)	2(1)	4(1)	-2(1)
C(1)	33(1)	22(1)	21(1)	-1(1)	-2(1)	-1(1)
C(2)	27(1)	27(1)	31(2)	0(1)	2(1)	0(1)
C(3)	35(1)	31(1)	27(1)	3(1)	9(1)	-2(1)
C(4)	38(2)	27(1)	19(1)	2(1)	2(1)	2(1)
C(5)	31(1)	19(1)	21(1)	-2(1)	0(1)	-2(1)
C(6)	31(1)	20(1)	22(1)	-2(1)	1(1)	-2(1)
C(7)	38(1)	25(1)	24(1)	-1(1)	-2(1)	-2(1)
C(8)	37(2)	37(2)	39(2)	-1(1)	-9(1)	-2(1)
C(9)	28(2)	54(2)	52(2)	3(2)	-4(1)	-3(1)
C(10)	35(2)	45(2)	38(2)	4(1)	10(1)	-6(1)
C(11)	32(1)	25(1)	24(1)	1(1)	1(1)	-2(1)
C(12)	31(1)	19(1)	21(1)	-2(1)	2(1)	-3(1)
C(13)	36(1)	21(1)	37(2)	4(1)	-6(1)	5(1)
C(14)	52(2)	24(1)	28(2)	5(1)	11(1)	-2(1)
C(15)	35(1)	26(1)	39(2)	0(1)	11(1)	-11(1)
C(16)	33(1)	20(1)	36(2)	-2(1)	3(1)	-2(1)
C(17)	28(1)	20(1)	38(2)	0(1)	5(1)	3(1)
C(18)	42(2)	45(2)	25(1)	9(1)	-1(1)	19(1)
C(19)	32(1)	47(2)	20(1)	0(1)	-3(1)	-2(1)
C(20)	38(2)	29(1)	20(1)	3(1)	7(1)	5(1)
C(21)	35(1)	39(2)	24(1)	16(1)	2(1)	-3(1)
C(22)	65(2)	22(1)	23(1)	7(1)	0(1)	4(1)

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U(11) + ... + 2 h k a^* b^* U(12)]$

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[TiCp_2(Dbf)_2]$.

Atom	x	y	z	U_{eq}
H(2A)	7585	2470	1899	34
H(3A)	8166	1688	2920	37
H(4A)	10203	1337	3285	34
H(7A)	12541	879	3477	35
H(8A)	14627	727	3486	46
H(9A)	15553	1485	2619	54
H(10A)	14385	2384	1720	47
H(13A)	9418	-432	1019	39
H(14A)	7319	-432	1407	41
H(15A)	5733	-1201	491	40
H(16A)	6858	-1649	-459	35
H(17A)	9142	-1146	-136	34
H(18A)	5691	4182	-503	45
H(19A)	6055	1320	-1038	40
H(20A)	8362	907	-1020	34
H(21A)	9419	3482	-453	39
H(22A)	7758	5476	-124	44

Appendix B

*Crystallographic data for [$TiCp_2$(Dbz)Cl] **2-05**.*

Table 1. Fractional atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [$TiCp_2$(Dbz)Cl].

Atom	x/a	y/b	z/c	U_{eq}
Ti	1229(1)	1961(1)	9799(1)	21(1)
Cl	1952(1)	838(1)	10619(1)	31(1)
O(1)	2028(2)	3106(1)	8226(2)	35(1)
C(1)	7618(4)	-1127(2)	3281(2)	51(1)
C(2)	8098(4)	-395(2)	3483(3)	54(1)
O(2)	4402(2)	3185(1)	7529(1)	34(1)
C(3)	9038(4)	-183(2)	4235(3)	49(1)
C(4)	9411(3)	573(2)	4360(2)	35(1)
O(3)	-1151(3)	4258(1)	8588(2)	58(1)
C(5)	10390(4)	748(2)	5150(3)	49(1)
C(6)	10785(4)	1493(2)	5308(3)	55(1)
C(7)	11771(5)	1709(2)	6094(4)	68(1)
C(8)	-739(3)	1180(2)	9250(2)	42(1)
C(9)	-1170(3)	1931(2)	9220(2)	41(1)
C(10)	-589(3)	2321(2)	8592(2)	36(1)
C(11)	189(3)	1793(2)	8235(2)	32(1)
C(12)	114(3)	1096(2)	8648(2)	38(1)
C(13)	506(4)	2732(2)	10858(3)	47(1)
C(14)	822(4)	3215(2)	10205(2)	47(1)
C(15)	2234(4)	3156(2)	10279(2)	38(1)
C(16)	2769(3)	2642(2)	10971(2)	40(1)
C(17)	1694(4)	2404(2)	11325(2)	45(1)
C(18)	2950(3)	2049(1)	9134(2)	22(1)
C(19)	4044(3)	1542(2)	9384(2)	27(1)
C(20)	5194(3)	1567(2)	9014(2)	31(1)
C(21)	5295(3)	2107(2)	8385(2)	28(1)
C(22)	4242(3)	2626(2)	8134(2)	26(1)
C(23)	3090(3)	2589(1)	8490(2)	24(1)
C(24)	3240(3)	3597(2)	7155(2)	29(1)
C(25)	2060(3)	3545(1)	7487(2)	28(1)
C(26)	3276(3)	4080(2)	6448(2)	33(1)
C(27)	2128(3)	4509(2)	6064(2)	37(1)
C(28)	938(3)	4444(2)	6382(2)	37(1)
C(29)	901(3)	3957(2)	7083(2)	33(1)
C(30)	-770(5)	5034(3)	8506(4)	77(1)
C(31)	-2008(5)	5398(2)	7920(3)	61(1)
C(32)	-3136(5)	4968(3)	8141(5)	89(2)
C(33)	-2569(5)	4233(3)	8443(5)	87(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths [Å] for [$TiCp_2$(Dbz)Cl].

Ti-C(18)	2.208(2)	C(7)-C(1)#1	1.439(6)
Ti-C(10)	2.356(3)	C(8)-C(9)	1.394(5)
Ti-C(9)	2.360(3)	C(8)-C(12)	1.406(5)
Ti-C(14)	2.364(3)	C(9)-C(10)	1.417(5)
Ti-C(13)	2.362(3)	C(10)-C(11)	1.408(4)
Ti-Cl	2.3684(7)	C(11)-C(12)	1.395(4)
Ti-C(15)	2.381(3)	C(13)-C(17)	1.365(6)
Ti-C(11)	2.394(3)	C(13)-C(14)	1.408(6)
Ti-C(8)	2.392(3)	C(14)-C(15)	1.397(5)
Ti-C(16)	2.397(3)	C(15)-C(16)	1.404(5)
Ti-C(12)	2.400(3)	C(16)-C(17)	1.383(5)
Ti-C(17)	2.404(3)	C(18)-C(19)	1.397(4)
O(1)-C(25)	1.379(3)	C(18)-C(23)	1.404(3)
O(1)-C(23)	1.389(3)	C(19)-C(20)	1.403(4)
C(1)-C(2)	1.391(5)	C(20)-C(21)	1.376(4)
C(1)-C(7)#1	1.439(6)	C(21)-C(22)	1.383(4)
C(2)-C(3)	1.356(5)	C(22)-C(23)	1.392(3)
O(2)-C(24)	1.378(3)	C(24)-C(26)	1.387(4)
O(2)-C(22)	1.389(3)	C(24)-C(25)	1.397(4)
C(3)-C(5)#1	1.398(5)	C(25)-C(29)	1.387(4)
C(3)-C(4)	1.388(4)	C(26)-C(27)	1.388(4)
C(4)-C(5)	1.400(5)	C(27)-C(28)	1.398(4)
O(3)-C(33)	1.387(6)	C(28)-C(29)	1.383(4)
O(3)-C(30)	1.437(5)	C(30)-C(31)	1.494(7)
C(5)-C(6)	1.380(6)	C(31)-C(32)	1.467(7)
C(5)-C(3)#1	1.398(5)	C(32)-C(33)	1.449(6)
C(6)-C(7)	1.417(7)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table 3. Bond angles [°] for [$TiCp_2$(Dbz)Cl].

C(18)-Ti-C(10)	99.42(10)	C(3)-C(2)-C(1)	125.5(4)
C(18)-Ti-C(9)	131.90(11)	C(24)-O(2)-C(22)	115.7(2)
C(10)-Ti-C(9)	34.98(12)	C(2)-C(3)-C(5)#1	117.9(4)
C(18)-Ti-C(14)	104.94(12)	C(2)-C(3)-C(4)	119.5(3)
C(10)-Ti-C(14)	78.65(12)	C(5)#1-C(3)-C(4)	122.6(3)
C(9)-Ti-C(14)	84.01(13)	C(3)-C(4)-C(5)	116.3(3)
C(18)-Ti-C(13)	132.65(11)	C(33)-O(3)-C(30)	107.5(3)
C(10)-Ti-C(13)	94.38(13)	C(6)-C(5)-C(3)#1	120.5(4)
C(9)-Ti-C(13)	79.56(12)	C(6)-C(5)-C(4)	118.4(3)
C(14)-Ti-C(13)	34.67(14)	C(3)#1-C(5)-C(4)	121.1(3)
C(18)-Ti-Cl	97.42(7)	C(5)-C(6)-C(7)	121.3(4)
C(10)-Ti-Cl	136.53(8)	C(6)-C(7)-C(1)#1	118.4(4)
C(9)-Ti-Cl	109.72(9)	C(9)-C(8)-C(12)	108.2(3)
C(14)-Ti-Cl	134.10(9)	C(9)-C(8)-Ti	71.7(2)
C(13)-Ti-Cl	102.94(11)	C(12)-C(8)-Ti	73.2(2)
C(18)-Ti-C(15)	76.09(10)	C(8)-C(9)-C(10)	108.1(3)
C(10)-Ti-C(15)	101.24(12)	C(8)-C(9)-Ti	74.2(2)
C(9)-Ti-C(15)	117.09(12)	C(10)-C(9)-Ti	72.4(2)
C(14)-Ti-C(15)	34.26(13)	C(11)-C(10)-C(9)	107.2(3)
C(13)-Ti-C(15)	56.79(11)	C(11)-C(10)-Ti	74.3(2)
Cl-Ti-C(15)	121.68(9)	C(9)-C(10)-Ti	72.7(2)
C(18)-Ti-C(11)	75.54(10)	C(12)-C(11)-C(10)	108.3(3)
C(10)-Ti-C(11)	34.47(11)	C(12)-C(11)-Ti	73.3(2)
C(9)-Ti-C(11)	57.16(11)	C(10)-C(11)-Ti	71.3(2)
C(14)-Ti-C(11)	108.55(11)	C(11)-C(12)-C(8)	108.1(3)
C(13)-Ti-C(11)	128.85(13)	C(11)-C(12)-Ti	72.9(2)
Cl-Ti-C(11)	115.69(8)	C(8)-C(12)-Ti	72.6(2)
C(15)-Ti-C(11)	118.11(11)	C(17)-C(13)-C(14)	108.3(3)
C(18)-Ti-C(8)	123.28(11)	C(17)-C(13)-Ti	75.1(2)
C(10)-Ti-C(8)	57.28(12)	C(14)-C(13)-Ti	72.8(2)
C(9)-Ti-C(8)	34.11(13)	C(15)-C(14)-C(13)	107.0(3)
C(14)-Ti-C(8)	117.03(14)	C(15)-C(14)-Ti	73.5(2)
C(13)-Ti-C(8)	102.27(12)	C(13)-C(14)-Ti	72.6(2)
Cl-Ti-C(8)	80.02(9)	C(14)-C(15)-C(16)	108.0(3)
C(15)-Ti-C(8)	150.98(13)	C(14)-C(15)-Ti	72.2(2)
C(11)-Ti-C(8)	56.57(11)	C(16)-C(15)-Ti	73.6(2)
C(18)-Ti-C(16)	82.80(10)	C(17)-C(16)-C(15)	107.4(3)
C(10)-Ti-C(16)	133.93(12)	C(17)-C(16)-Ti	73.6(2)
C(9)-Ti-C(16)	135.35(12)	C(15)-C(16)-Ti	72.3(2)
C(14)-Ti-C(16)	56.82(12)	C(13)-C(17)-C(16)	109.3(3)
C(13)-Ti-C(16)	56.20(12)	C(13)-C(17)-Ti	71.6(2)
Cl-Ti-C(16)	87.75(9)	C(16)-C(17)-Ti	73.0(2)
C(15)-Ti-C(16)	34.17(12)	C(19)-C(18)-C(23)	115.2(2)
C(11)-Ti-C(16)	149.62(12)	C(19)-C(18)-Ti	118.5(2)
C(8)-Ti-C(16)	152.22(12)	C(23)-C(18)-Ti	126.2(2)
C(18)-Ti-C(12)	89.17(10)	C(18)-C(19)-C(20)	122.4(2)

C(10)-Ti-C(12)	57.09(11)	C(21)-C(20)-C(19)	120.7(2)
C(9)-Ti-C(12)	56.89(12)	C(20)-C(21)-C(22)	118.4(2)
C(14)-Ti-C(12)	135.33(12)	C(21)-C(22)-O(2)	117.1(2)
C(13)-Ti-C(12)	134.97(12)	C(21)-C(22)-C(23)	120.7(2)
Cl-Ti-C(12)	83.52(8)	O(2)-C(22)-C(23)	122.2(2)
C(15)-Ti-C(12)	151.82(11)	C(22)-C(23)-O(1)	120.4(2)
C(11)-Ti-C(12)	33.85(11)	C(22)-C(23)-C(18)	122.6(2)
C(8)-Ti-C(12)	34.12(12)	O(1)-C(23)-C(18)	117.1(2)
C(16)-Ti-C(12)	167.29(12)	C(26)-C(24)-O(2)	118.3(2)
C(18)-Ti-C(17)	115.65(11)	C(26)-C(24)-C(25)	120.4(3)
C(10)-Ti-C(17)	127.63(12)	O(2)-C(24)-C(25)	121.3(2)
C(9)-Ti-C(17)	108.53(13)	C(29)-C(25)-O(1)	118.7(2)
C(14)-Ti-C(17)	56.25(12)	C(29)-C(25)-C(24)	119.8(2)
C(13)-Ti-C(17)	33.28(13)	O(1)-C(25)-C(24)	121.5(2)
Cl-Ti-C(17)	78.00(9)	C(24)-C(26)-C(27)	119.6(3)
C(15)-Ti-C(17)	55.97(11)	C(26)-C(27)-C(28)	119.9(3)
C(11)-Ti-C(17)	162.10(12)	C(29)-C(28)-C(27)	120.3(3)
C(8)-Ti-C(17)	118.92(13)	C(25)-C(29)-C(28)	119.9(3)
C(16)-Ti-C(17)	33.47(12)	O(3)-C(30)-C(31)	105.2(4)
C(12)-Ti-C(17)	150.56(12)	C(32)-C(31)-C(30)	102.4(4)
C(25)-O(1)-C(23)	116.3(2)	C(33)-C(32)-C(31)	105.8(4)
C(2)-C(1)-C(7)#1	116.5(4)	O(3)-C(33)-C(32)	109.4(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for [$TiCp_2$(Dbz)Cl].

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Ti	20(1)	20(1)	23(1)	-1(1)	7(1)	-3(1)
Cl	38(1)	27(1)	31(1)	6(1)	12(1)	0(1)
O(1)	34(1)	33(1)	45(1)	16(1)	23(1)	10(1)
C(1)	66(2)	41(2)	46(2)	-5(2)	14(2)	2(2)
C(2)	47(2)	47(2)	62(2)	-10(2)	5(2)	5(2)
O(2)	30(1)	38(1)	40(1)	16(1)	18(1)	4(1)
C(3)	55(2)	39(2)	53(2)	-2(2)	11(2)	3(2)
C(4)	43(2)	24(1)	32(1)	4(1)	-5(1)	0(1)
O(3)	46(2)	38(1)	86(2)	0(1)	9(1)	11(1)
C(5)	47(2)	48(2)	54(2)	9(2)	15(2)	4(1)
C(6)	60(2)	51(2)	57(2)	5(2)	22(2)	10(2)
C(7)	65(3)	38(2)	120(4)	8(2)	57(3)	10(2)
C(8)	37(2)	49(2)	36(2)	2(1)	0(1)	-24(1)
C(9)	18(1)	62(2)	43(2)	-13(1)	9(1)	-5(1)
C(10)	29(1)	36(2)	37(2)	3(1)	-2(1)	4(1)
C(11)	25(1)	42(2)	26(1)	-2(1)	3(1)	-4(1)
C(12)	40(2)	31(2)	36(2)	-9(1)	-5(1)	-3(1)
C(13)	43(2)	47(2)	58(2)	-27(2)	29(2)	-11(1)
C(14)	60(2)	27(1)	47(2)	-15(1)	-2(2)	11(1)
C(15)	52(2)	31(1)	38(2)	-14(1)	21(1)	-19(1)
C(16)	35(2)	43(2)	38(2)	-20(1)	3(1)	-4(1)
C(17)	71(2)	39(2)	30(1)	-10(1)	18(2)	-8(2)
C(18)	21(1)	23(1)	22(1)	-3(1)	7(1)	-3(1)
C(19)	24(1)	24(1)	34(1)	6(1)	7(1)	1(1)
C(20)	25(1)	31(1)	37(1)	5(1)	9(1)	7(1)
C(21)	19(1)	32(1)	35(1)	0(1)	10(1)	-1(1)
C(22)	24(1)	27(1)	27(1)	3(1)	9(1)	-2(1)
C(23)	24(1)	22(1)	28(1)	1(1)	10(1)	2(1)
C(24)	31(1)	24(1)	34(1)	4(1)	14(1)	-1(1)
C(25)	31(1)	23(1)	32(1)	6(1)	11(1)	0(1)
C(26)	39(2)	31(1)	31(1)	3(1)	15(1)	-5(1)
C(27)	47(2)	34(2)	32(1)	6(1)	10(1)	-5(1)
C(28)	37(2)	30(1)	39(2)	5(1)	3(1)	-1(1)
C(29)	28(1)	26(1)	43(2)	4(1)	7(1)	-1(1)
C(30)	64(3)	59(3)	112(4)	-32(3)	29(3)	-10(2)
C(31)	83(3)	38(2)	61(2)	-3(2)	13(2)	-1(2)
C(32)	59(3)	85(4)	118(4)	36(3)	12(3)	25(2)
C(33)	58(3)	76(3)	134(5)	31(3)	38(3)	10(2)

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U(11) + ... + 2 h k a^* b^* U(12)]$

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [$TiCp_2$(Dbz)Cl].

Atom	x	y	z	U_{eq}
H(8)	-939(59)	925(31)	9595(39)	89(17)
H(9)	-1709(39)	2100(20)	9474(27)	41(10)
H(10)	-720(45)	2910(23)	8459(30)	57(11)
H(11)	687(40)	1861(20)	7814(28)	45(10)
H(12)	525(45)	652(24)	8615(29)	56(11)
H(13)	-366(45)	2654(23)	10910(28)	50(11)
H(14)	107(50)	3538(27)	9875(33)	66(14)
H(15)	2764(48)	3289(26)	9936(32)	70(13)
H(16)	3635(35)	2511(19)	11143(23)	31(8)
H(17)	1600(67)	2033(31)	11747(47)	103(21)
H(19)	3969(40)	1167(23)	9786(27)	51(10)
H(20)	5916(44)	1193(25)	9162(27)	57(11)
H(21)	5986(40)	2170(20)	8093(26)	42(9)
H(26)	4094(42)	4119(21)	6236(28)	49(10)
H(27)	2175(38)	4798(21)	5586(26)	42(9)
H(28)	83(37)	4772(21)	6121(24)	42(9)
H(29)	28(38)	3881(20)	7359(24)	41(9)
H(30A)	7(5)	5067(3)	8233(4)	93
H(30B)	-530(5)	5276(3)	9090(4)	93
H(31A)	-2061(5)	5930(2)	8064(3)	73
H(31B)	-2009(5)	5347(2)	7289(3)	73
H(32A)	-3467(5)	5220(3)	8611(5)	107
H(32B)	-3892(5)	4916(3)	7616(5)	107
H(33A)	-2822(5)	4096(3)	8996(5)	104
H(33B)	-2937(5)	3853(3)	7994(5)	104

Appendix C

Crystallographic data for [TiCp$_2$(Dbt)Cl] ***2-16***.

Table 1. Fractional atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [TiCp$_2$(Dbt-S)Cl].

Atom	x	y	z	U_{eq}
Ti	7485(1)	1706(1)	235(1)	20(1)
Cl	5763(1)	2640(1)	708(1)	36(1)
S(1)	8951(1)	3370(1)	871(1)	26(1)
S(2)	11721(1)	2761(1)	1440(1)	28(1)
C(1)	9282(2)	2608(3)	1637(1)	26(1)
C(2)	8418(2)	2336(3)	2040(1)	29(1)
C(3)	8767(2)	1864(3)	2652(1)	31(1)
C(4)	9978(2)	1651(3)	2870(1)	28(1)
C(5)	10869(2)	1903(3)	2474(1)	24(1)
C(6)	12182(2)	1743(3)	2591(1)	25(1)
C(7)	12906(2)	1190(3)	3122(1)	30(1)
C(8)	14144(2)	1099(3)	3126(1)	39(1)
C(9)	14698(3)	1548(4)	2607(1)	45(1)
C(10)	14012(2)	2083(4)	2074(1)	39(1)
C(11)	12758(2)	2166(3)	2070(1)	27(1)
C(12)	10498(2)	2398(3)	1865(1)	24(1)
C(13)	8627(2)	-562(3)	758(1)	32(1)
C(14)	7481(2)	-559(3)	970(1)	34(1)
C(15)	6612(2)	-980(3)	468(1)	33(1)
C(16)	7225(2)	-1219(3)	-51(1)	30(1)
C(17)	8477(2)	-936(3)	125(1)	29(1)
C(18)	6493(3)	3620(4)	-522(1)	38(1)
C(19)	6692(2)	2050(4)	-810(1)	33(1)
C(20)	7955(2)	1827(3)	-802(1)	29(1)
C(21)	8533(2)	3230(3)	-493(1)	33(1)
C(22)	7621(3)	4321(3)	-314(1)	37(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths [A] for [$TiCp_2$(Dbt-S)Cl].

Ti-C(17)	2.368(2)	C(4)-C(5)	1.403(3)
Ti-C(19)	2.378(2)	C(5)-C(12)	1.408(3)
Ti-C(16)	2.382(2)	C(5)-C(6)	1.460(3)
Ti-C(22)	2.387(2)	C(6)-C(7)	1.408(3)
Ti-C(20)	2.393(2)	C(6)-C(11)	1.411(3)
Ti-Cl	2.3948(7)	C(7)-C(8)	1.379(4)
Ti-C(14)	2.398(2)	C(8)-C(9)	1.400(4)
Ti-C(15)	2.395(2)	C(9)-C(10)	1.388(4)
Ti-C(21)	2.398(2)	C(10)-C(11)	1.396(4)
Ti-C(13)	2.398(2)	C(13)-C(17)	1.411(4)
Ti-S(1)	2.4068(7)	C(13)-C(14)	1.407(3)
Ti-C(18)	2.410(3)	C(14)-C(15)	1.420(4)
S(1)-C(1)	1.782(2)	C(15)-C(16)	1.405(4)
S(2)-C(12)	1.757(2)	C(16)-C(17)	1.421(3)
S(2)-C(11)	1.762(2)	C(18)-C(22)	1.399(4)
C(1)-C(2)	1.394(3)	C(18)-C(19)	1.411(4)
C(1)-C(12)	1.400(3)	C(19)-C(20)	1.415(3)
C(2)-C(3)	1.404(4)	C(20)-C(21)	1.407(4)
C(3)-C(4)	1.389(4)	C(21)-C(22)	1.415(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z+1

Table 3. Bond angles [°] for [$TiCp_2$(Dbt-S)Cl].

C(17)-Ti-C(19)	97.31(9)	Cl-Ti-C(18)	77.39(7)
C(17)-Ti-C(16)	34.81(8)	C(14)-Ti-C(18)	152.57(10)
C(19)-Ti-C(16)	80.45(9)	C(15)-Ti-C(18)	121.79(10)
C(17)-Ti-C(22)	129.79(9)	C(21)-Ti-C(18)	56.76(9)
C(19)-Ti-C(22)	56.92(9)	C(13)-Ti-C(18)	165.16(9)
C(16)-Ti-C(22)	134.70(9)	S(1)-Ti-C(18)	106.97(7)
C(17)-Ti-C(20)	77.50(9)	C(1)-S(1)-Ti	114.89(8)
C(19)-Ti-C(20)	34.49(8)	C(12)-S(2)-C(11)	91.06(12)
C(16)-Ti-C(20)	79.69(9)	C(2)-C(1)-C(12)	117.6(2)
C(22)-Ti-C(20)	56.87(9)	C(2)-C(1)-S(1)	124.43(19)
C(17)-Ti-Cl	135.67(7)	C(12)-C(1)-S(1)	117.75(18)
C(19)-Ti-Cl	98.93(7)	C(1)-C(2)-C(3)	120.7(2)
C(16)-Ti-Cl	109.12(6)	C(4)-C(3)-C(2)	120.9(2)
C(22)-Ti-Cl	93.23(7)	C(3)-C(4)-C(5)	119.7(2)
C(20)-Ti-Cl	132.18(6)	C(4)-C(5)-C(12)	118.3(2)
C(17)-Ti-C(14)	57.30(9)	C(4)-C(5)-C(6)	130.0(2)
C(19)-Ti-C(14)	134.76(9)	C(12)-C(5)-C(6)	111.7(2)
C(16)-Ti-C(14)	57.14(9)	C(7)-C(6)-C(11)	118.2(2)
C(22)-Ti-C(14)	168.00(9)	C(7)-C(6)-C(5)	129.7(2)
C(20)-Ti-C(14)	133.36(9)	C(11)-C(6)-C(5)	112.0(2)
Cl-Ti-C(14)	82.59(7)	C(8)-C(7)-C(6)	120.0(2)
C(17)-Ti-C(15)	57.39(9)	C(7)-C(8)-C(9)	120.8(3)
C(19)-Ti-C(15)	100.95(9)	C(10)-C(9)-C(8)	120.7(3)
C(16)-Ti-C(15)	34.20(9)	C(9)-C(10)-C(11)	118.3(3)
C(22)-Ti-C(15)	155.51(9)	C(10)-C(11)-C(6)	122.0(2)
C(20)-Ti-C(15)	112.06(9)	C(10)-C(11)-S(2)	125.7(2)
Cl-Ti-C(15)	79.10(7)	C(6)-C(11)-S(2)	112.36(18)
C(14)-Ti-C(15)	34.48(9)	C(1)-C(12)-C(5)	122.7(2)
C(17)-Ti-C(21)	95.69(9)	C(1)-C(12)-S(2)	124.54(19)
C(19)-Ti-C(21)	57.12(9)	C(5)-C(12)-S(2)	112.75(18)
C(16)-Ti-C(21)	110.89(9)	C(17)-C(13)-C(14)	108.4(2)
C(22)-Ti-C(21)	34.40(9)	C(17)-C(13)-Ti	71.63(13)
C(20)-Ti-C(21)	34.17(9)	C(14)-C(13)-Ti	72.92(14)
Cl-Ti-C(21)	127.59(7)	C(13)-C(14)-C(15)	107.8(2)
C(14)-Ti-C(21)	148.65(9)	C(13)-C(14)-Ti	72.97(14)
C(15)-Ti-C(21)	144.91(9)	C(15)-C(14)-Ti	72.67(14)
C(17)-Ti-C(13)	34.42(9)	C(16)-C(15)-C(14)	108.0(2)
C(19)-Ti-C(13)	131.63(9)	C(16)-C(15)-Ti	72.38(13)
C(16)-Ti-C(13)	57.12(9)	C(14)-C(15)-Ti	72.85(14)
C(22)-Ti-C(13)	144.63(9)	C(15)-C(16)-C(17)	108.1(2)
C(20)-Ti-C(13)	108.88(9)	C(15)-C(16)-Ti	73.42(14)
Cl-Ti-C(13)	115.15(7)	C(17)-C(16)-Ti	72.07(13)
C(14)-Ti-C(13)	34.11(8)	C(13)-C(17)-C(16)	107.6(2)
C(15)-Ti-C(13)	56.93(9)	C(13)-C(17)-Ti	73.95(13)
C(21)-Ti-C(13)	114.55(9)	C(16)-C(17)-Ti	73.12(13)
C(17)-Ti-S(1)	103.77(6)	C(22)-C(18)-C(19)	107.8(2)
C(19)-Ti-S(1)	130.70(7)	C(22)-C(18)-Ti	72.16(14)

C(16)-Ti-S(1)	136.62(6)	C(19)-C(18)-Ti	71.65(14)
C(22)-Ti-S(1)	75.64(7)	C(18)-C(19)-C(20)	107.9(2)
C(20)-Ti-S(1)	108.90(6)	C(18)-C(19)-Ti	74.08(14)
Cl-Ti-S(1)	96.13(3)	C(20)-C(19)-Ti	73.34(14)
C(14)-Ti-S(1)	93.55(7)	C(21)-C(20)-C(19)	108.0(2)
C(15)-Ti-S(1)	127.98(7)	C(21)-C(20)-Ti	73.09(14)
C(21)-Ti-S(1)	76.63(7)	C(19)-C(20)-Ti	72.17(14)
C(13)-Ti-S(1)	80.49(6)	C(20)-C(21)-C(22)	107.5(2)
C(17)-Ti-C(18)	130.92(9)	C(20)-C(21)-Ti	72.75(14)
C(19)-Ti-C(18)	34.27(9)	C(22)-C(21)-Ti	72.39(14)
C(16)-Ti-C(18)	112.52(9)	C(18)-C(22)-C(21)	108.6(2)
C(22)-Ti-C(18)	33.90(9)	C(18)-C(22)-Ti	73.93(15)
C(20)-Ti-C(18)	56.82(9)	C(21)-C(22)-Ti	73.21(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+1

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for [$TiCp_2$(Dbt-S)Cl].

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Ti	20(1)	20(1)	20(1)	1(1)	1(1)	1(1)
Cl	27(1)	45(1)	36(1)	-6(1)	8(1)	7(1)
S(1)	31(1)	24(1)	22(1)	3(1)	-3(1)	-4(1)
S(2)	33(1)	33(1)	20(1)	2(1)	4(1)	-2(1)
C(1)	33(1)	22(1)	21(1)	-1(1)	-2(1)	-1(1)
C(2)	27(1)	27(1)	31(2)	0(1)	2(1)	0(1)
C(3)	35(1)	31(1)	27(1)	3(1)	9(1)	-2(1)
C(4)	38(2)	27(1)	19(1)	2(1)	2(1)	2(1)
C(5)	31(1)	19(1)	21(1)	-2(1)	0(1)	-2(1)
C(6)	31(1)	20(1)	22(1)	-2(1)	1(1)	-2(1)
C(7)	38(1)	25(1)	24(1)	-1(1)	-2(1)	-2(1)
C(8)	37(2)	37(2)	39(2)	-1(1)	-9(1)	-2(1)
C(9)	28(2)	54(2)	52(2)	3(2)	-4(1)	-3(1)
C(10)	35(2)	45(2)	38(2)	4(1)	10(1)	-6(1)
C(11)	32(1)	25(1)	24(1)	1(1)	1(1)	-2(1)
C(12)	31(1)	19(1)	21(1)	-2(1)	2(1)	-3(1)
C(13)	36(1)	21(1)	37(2)	4(1)	-6(1)	5(1)
C(14)	52(2)	24(1)	28(2)	5(1)	11(1)	-2(1)
C(15)	35(1)	26(1)	39(2)	0(1)	11(1)	-11(1)
C(16)	33(1)	20(1)	36(2)	-2(1)	3(1)	-2(1)
C(17)	28(1)	20(1)	38(2)	0(1)	5(1)	3(1)
C(18)	42(2)	45(2)	25(1)	9(1)	-1(1)	19(1)
C(19)	32(1)	47(2)	20(1)	0(1)	-3(1)	-2(1)
C(20)	38(2)	29(1)	20(1)	3(1)	7(1)	5(1)
C(21)	35(1)	39(2)	24(1)	16(1)	2(1)	-3(1)
C(22)	65(2)	22(1)	23(1)	7(1)	0(1)	4(1)

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U(11) + ... + 2 h k a^* b^* U(12)]$

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [$TiCp_2$(Dbt)Cl].

Atom	x	y	z	U_{eq}
H(2A)	7585	2470	1899	34
H(3A)	8166	1688	2920	37
H(4A)	10203	1337	3285	34
H(7A)	12541	879	3477	35
H(8A)	14627	727	3486	46
H(9A)	15553	1485	2619	54
H(10A)	14385	2384	1720	47
H(13A)	9418	-432	1019	39
H(14A)	7319	-432	1407	41
H(15A)	5733	-1201	491	40
H(16A)	6858	-1649	-459	35
H(17A)	9142	-1146	-136	34
H(18A)	5691	4182	-503	45
H(19A)	6055	1320	-1038	40
H(20A)	8362	907	-1020	34
H(21A)	9419	3482	-453	39
H(22A)	7758	5476	-124	44

Appendix D

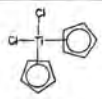
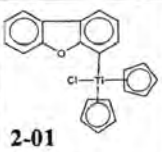
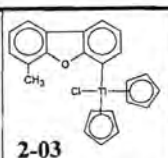
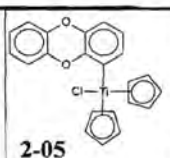
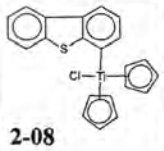
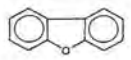
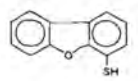
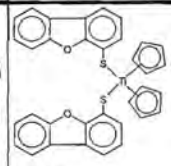
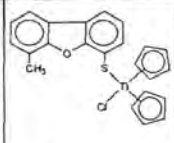
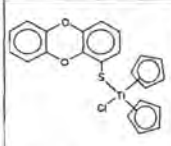
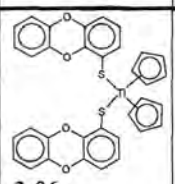
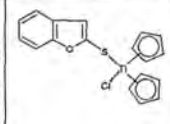
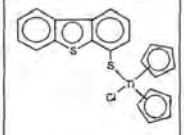
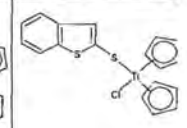
Results of the preclinical tests of the selected complexes on CoLo and HeLa cells

Table 1. Inhibition of HeLa and CoLo cells by **S-01**, **2-08**, **3-09**, **2-05** and **3-05**.

Conc. µg/ml	**S-01**		**2-08**		**3-09**		**2-05**		**3-05**	
	% Cell Growth									
	HeLa	CoLo	HeLa	CoLo	HeLa	CoLo	HeLa	CoLo	HeLa	CoLo
0	100	100	100	100	100	100	100	100	100	100
0.05	100	100	100	100	100	100	96	91	48	69
0.1	100	100	100	100	100	100	87	85	47	50
0.2	100	100	100	100	100	100	75	80	40	49
0.4	100	100	98	100	85	100	48	50	41	40
0.8	100	100	93	100	84	100	40	43	41	45
1.5	100	100	88	100	81	97	-	-	-	-
3	99	98	85	97	68	91	-	-	-	-
6	95	101	70	93	63	89	-	-	-	-
12	78	82	56	78	50	55	-	-	-	-
25	53	57	48	56	42	54	-	-	-	-

Conc. µg/ml	**3-10**		**L2-01**		**L2-03**		**L3-03**	
	% Cell Growth							
	HeLa	CoLo	HeLa	CoLo	HeLa	CoLo	HeLa	CoLo
0	100	100	100	100	100	100	100	100
0.05	100	100	100	100	100	100	96	91
0.1	100	100	100	100	100	100	87	85
0.2	100	100	100	100	100	100	75	80
0.4	100	100	100	100	85	100	48	50
0.8	100	100	100	100	100	100	100	100
1.5	100	99	96	98	95	97	98	99
3	98	97	95	97	94	95	96	98
6	97	95	93	96	92	94	95	97
12	95	93	92	95	90	92	94	96
25	91	90	90	93	88	90	92	95

Table 2. Inhibition of CoLo cells by **S-01**, **2-01**, **2-03**, **2-05**, **2-08**, **2-11**, **L2-06**, **L3-06**, **3-01**, **3-02**, **3-03**, **3-05**, **3-06**, **3-07**, **3-09** and **3-13**.

Conc. µM	 **S-01**	 **2-01**	 **2-03**	 **2-05**	 **2-08**	 **2-11**	 **L2-06**	 **L3-06**
	% Cell Growth							
0	100	100	100	100	100	100	100	100
0.04	100	100	100	100	100	100	100	100
0.08	100	100	100	100	100	100	100	100
0.16	100	100	100	100	100	100	100	100
0.33	100	100	100	100	100	100	100	100
0.75	100	100	100	100	100	100	100	100
1.5	99	95	83	96	97	98	95	97
3	98	83	71	95	94	84	87	98
6	97	75	64	87	92	86	75	97
12	95	55	52	65	87	86	85	91
25	100	43	18	57	84	70	88	100
50	100	8	5	6	8	14	90	96
100	96	5	5	4	5	4	84	100
Conc. µM	 **3-01**	 **3-02**	 **3-03**	 **3-05**	 **3-06**	 **3-07**	 **3-09**	 **3-13**
	% Cell Growth							
0	100	100	100	100	100	100	100	100
0.04	75	100	90	96	100	100	100	100
0.08	46	100	88	95	100	100	100	100
0.16	8	100	86	76	100	100	100	100
0.33	6	100	55	63	100	100	100	100
0.75	4	100	29	11	100	100	100	100
1.5	-	90	100	-	100	83	90	94
3	-	81	-	-	89	72	92	80
6	-	50	-	-	87	66	86	88
12	-	25	-	-	85	54	84	81
25	-	17	-	-	74	22	50	80
50	-	18	-	-	60	8	16	84
100	-	-	-	-	26	2	9	77

Appendix E

Results of the intercalation tests of the selected complexes.

Table 1. Intercalation of ethidium bromide, doxorubicin, propidium iodide, **S-01**, **3-01** and **L2-06**.

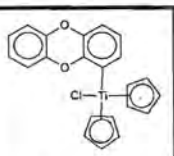
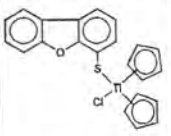
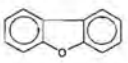
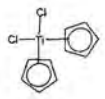
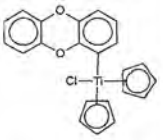
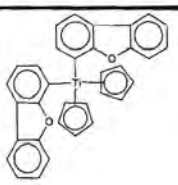
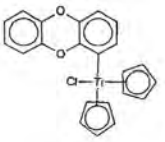
Conc. µg/ml	Ethidium bromide		Doxorubicin		Propidium iodide		 **S-01**		Conc. µg/ml	 **3-01**		 **L2-06**	
	Scattering (Median Channel Number)									Scattering (Median Channel Number)			
	SS	FS	SS	FS	SS	FS	SS	FS		SS	FS	SS	FS
0	0	0	100	100	100	100	0	0	0	0	0	0	0
0.03	1	1	100	100	100	100	1	1	0.3	4	4	7	13
0.06	2	3	100	100	100	100	2	3	0.6	0	2	7	12
0.12	5	6	100	100	100	104	5	6	1.2	3	3	2	12
0.24	10	12	101	101	101	101	10	12	2.4	9	4	0	11
0.49	20	25	102	102	102	102	12	10	4.9	6	3	125	10
0.98	40	50	103	103	103	103	10	8	9.8	9	8	11	11
2	60	55	115	115	103	105	6	7	19.6	10	9	13	8
3.9	110	50	123	115	118	113	5	10	39.1	10	10	11	5
7.8	60	32	115	108	127	105	5	12	59.1	10	10	12	7
15.6	20	28	105	103	100	102	5	8	78.1	8	12	9	3
31.2	3	8	101	100	100	100	5	8	156.2	15	12	13	7
62.5	2	40	120	120	100	100	5	10	312.5	17	13	13	5
125	3	80	220	525	100	103	3	5	625	16	17	11	1
250	5	120	-	-	100	125	5	3	1250	14	23	12	0
500	10	250	-	-	100	145	6	3	2500	16	26	15	0
1000	60	750	-	-	100	190	8	3	5000	17	33	21	2

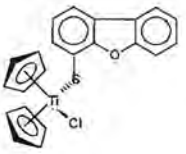
Table 2. Inhibition of CoLo cells by **S-01**, **2-02**, **2-05**, **3-01** and **3-09**.

Conc. µg/ml	 **S-01**	 **2-05**	 **2-02**	 **3-09**	 **3-01**
	Side Scatter (Median Channel Number)				
0	5	5	5	5	5
0.1	5	5	5	5	5
0.2	5	5	5	5	5
0.4	5	5	5	5	5
0.8	5	5	5	5	5
1.5	5	5	5	5	5
3	5	5	5	5	5
6	5	5	5	5	5
12	5	5	5	5	5
25	5	6	6	7	13
50	5	7	8	12	36
100	5	23	27	37	93

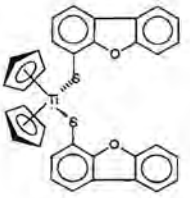
Appendix F

Cp hydrolysis of ***S-01***, ***3-01*** *and* ***3-02***.

S-01

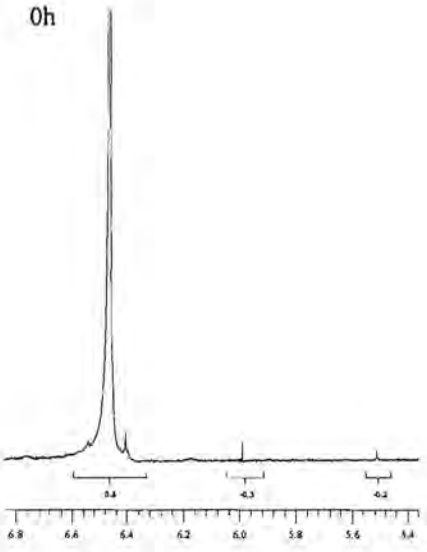


3-01



3-02

0h



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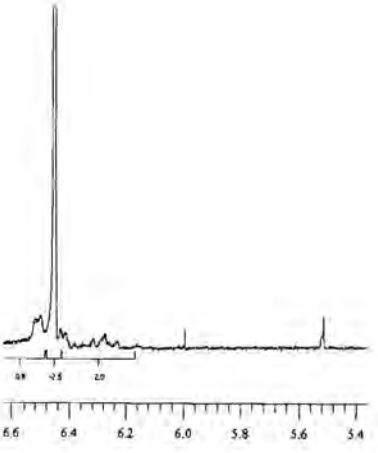

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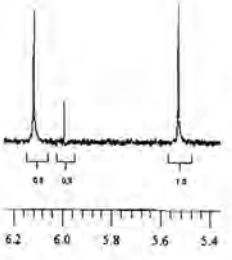

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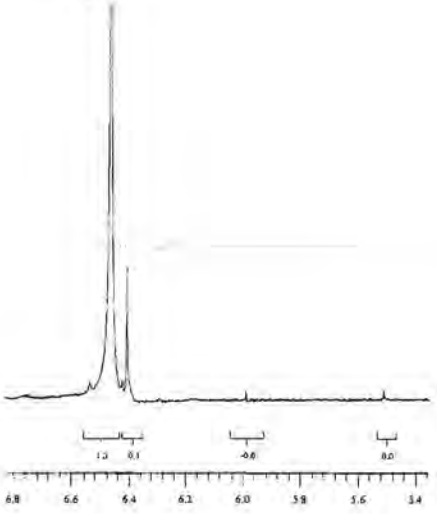

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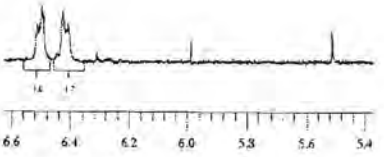

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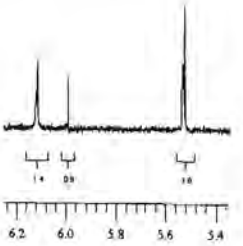

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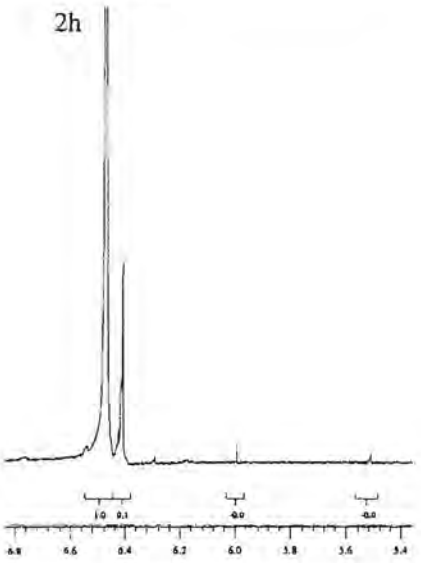

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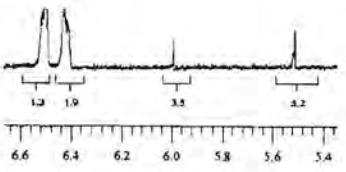

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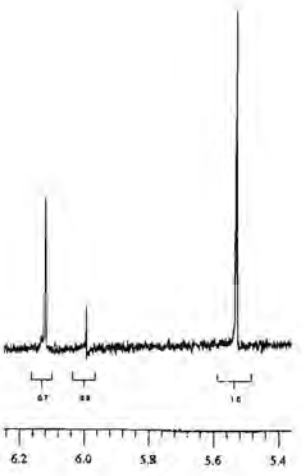

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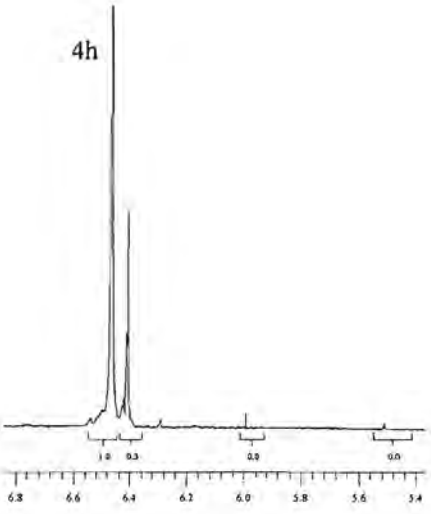

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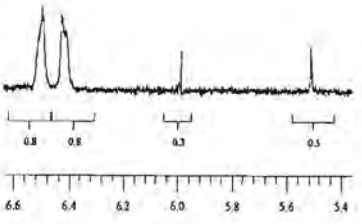

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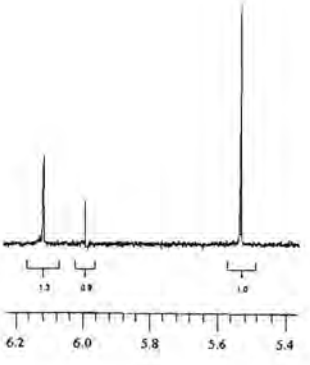

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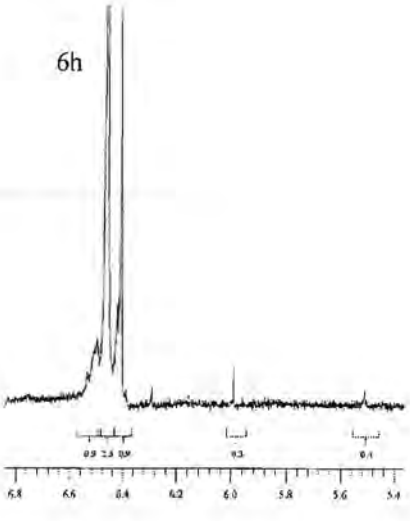

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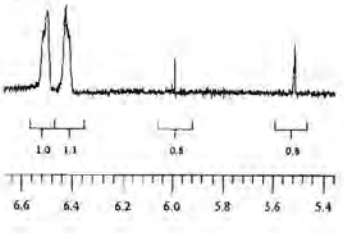
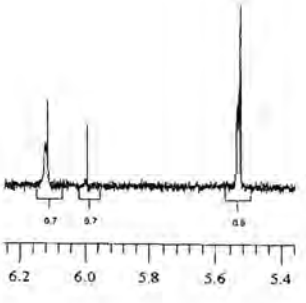


5h



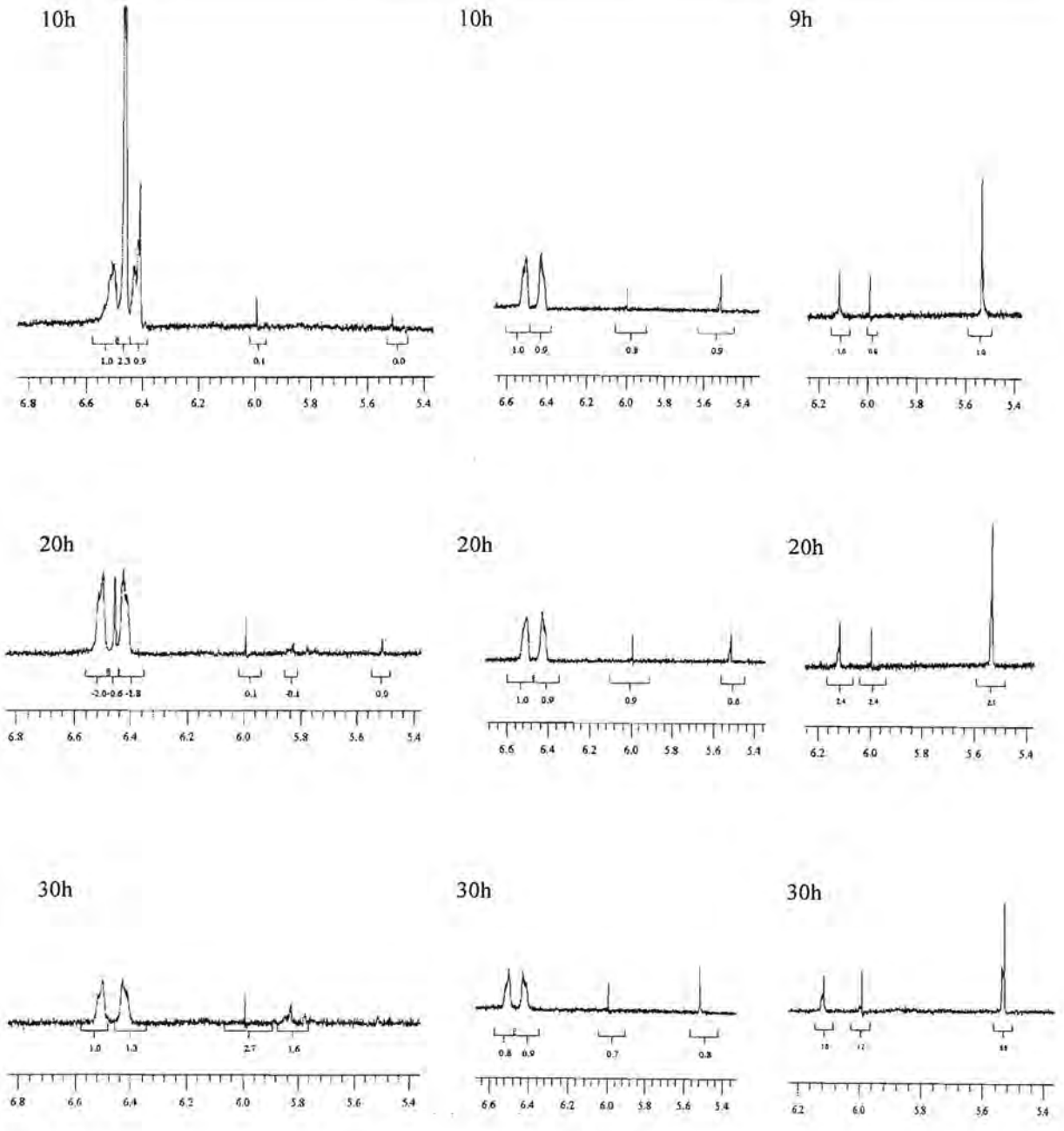
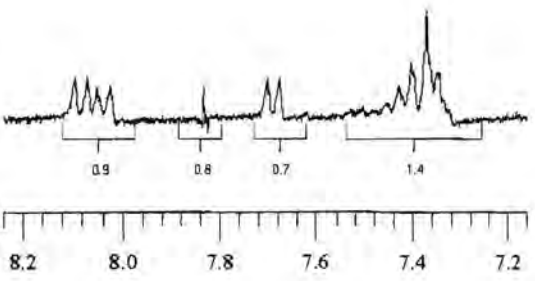


Figure 1. Experiment comparing Cp hydrolysis of **S-01**, **3-01** and **3-02**.

Substitution of the thiolato ligand of complex ***3-01***.

0h



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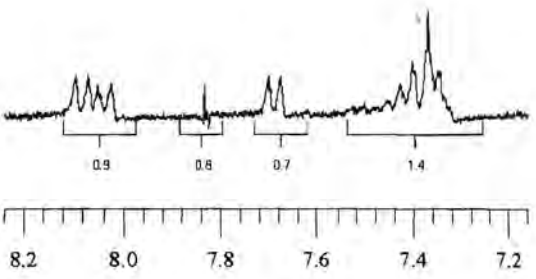

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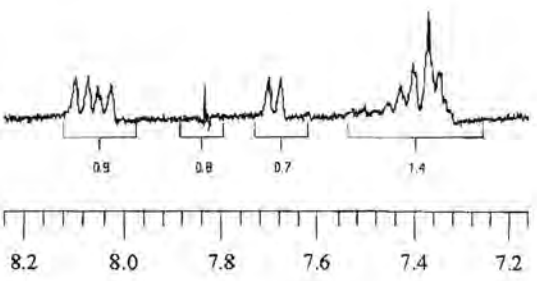

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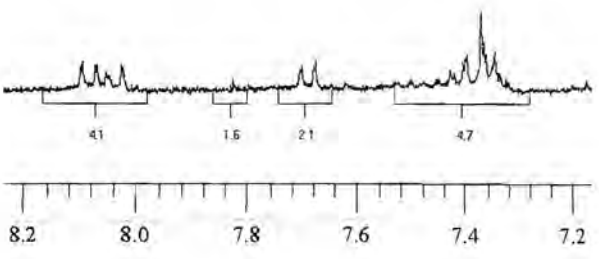

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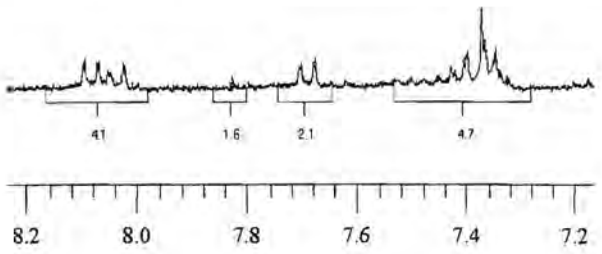

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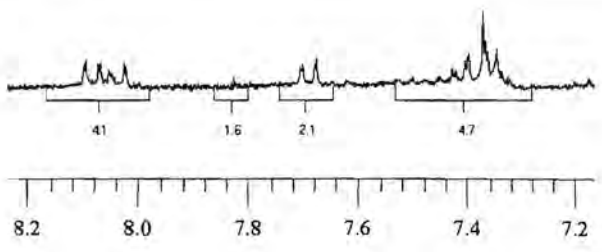

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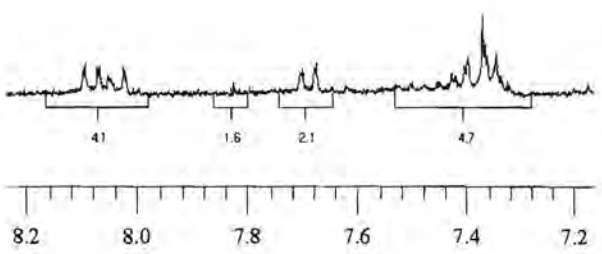
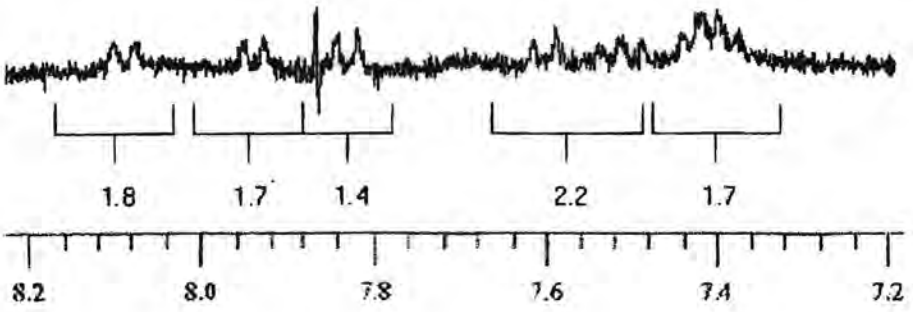


Figure 2. ^{1}H NMR resonances in the aromatic region of **3-01**.

Substitution of the thiolato ligand of complex ***3-02****.*

0h



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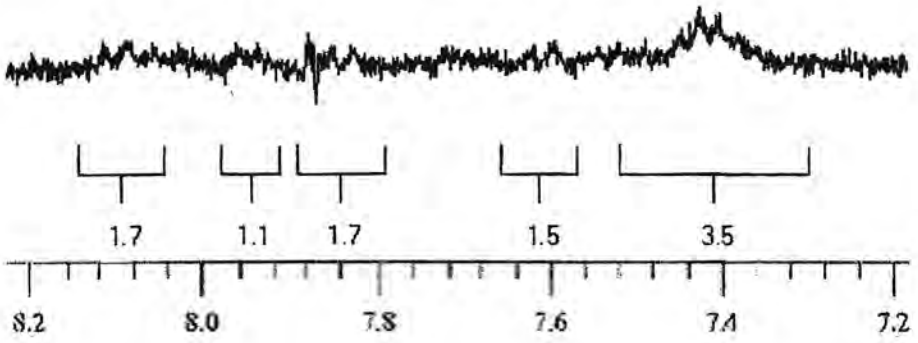

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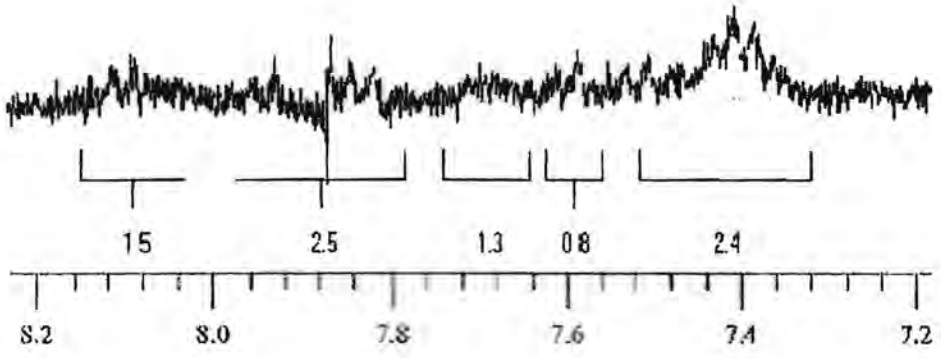

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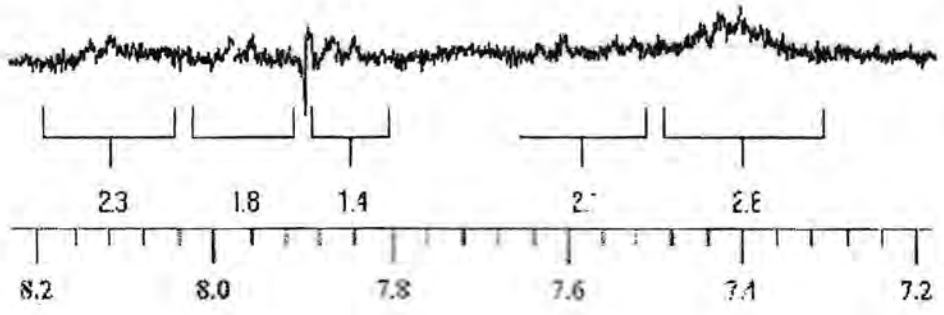

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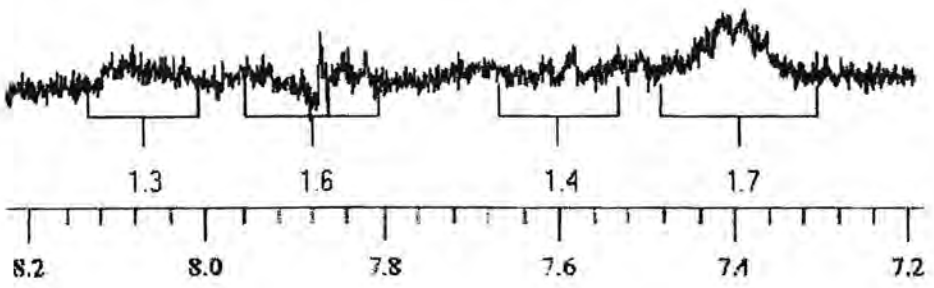

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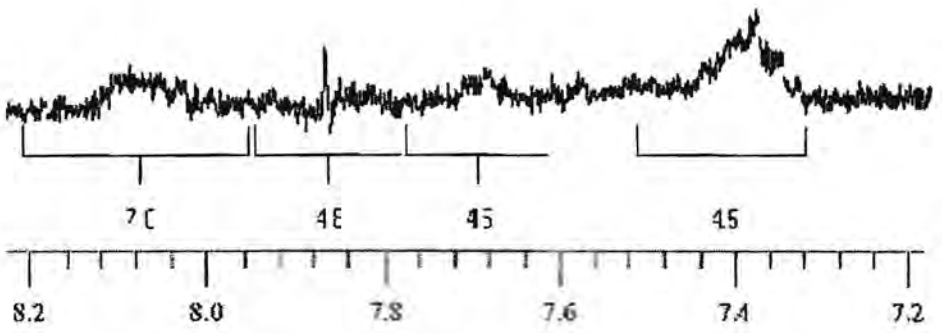

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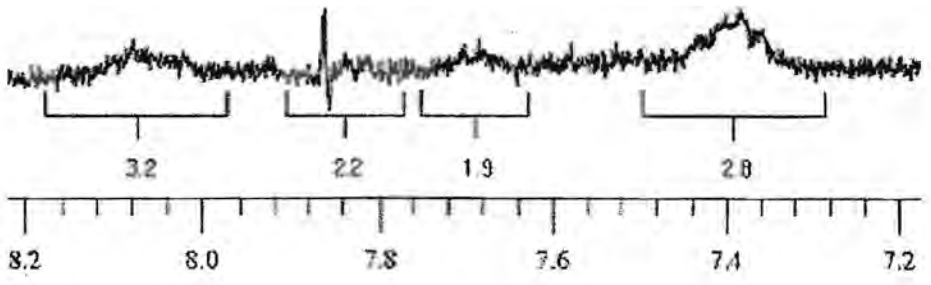

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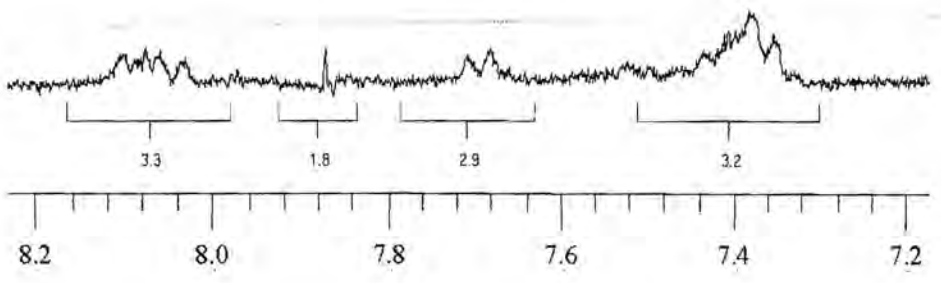

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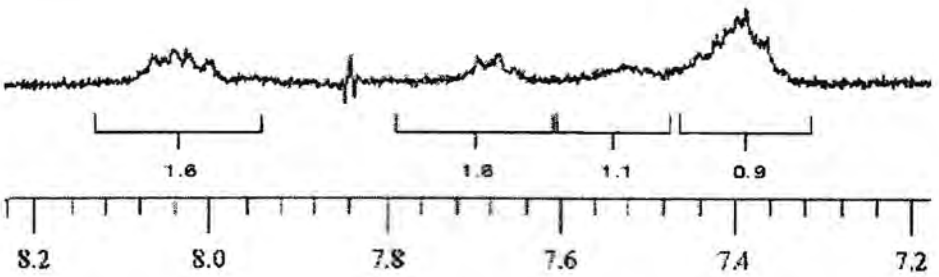

Figure 3. Substitution of the thiolato ligand of complex **3-02**.