**SUPPORTING INFORMATION**

**Title: Synthesis, molecular and electronic structure of a stacked half-sandwich dititanium complex incorporating a cyclic π-faced bridging ligand**

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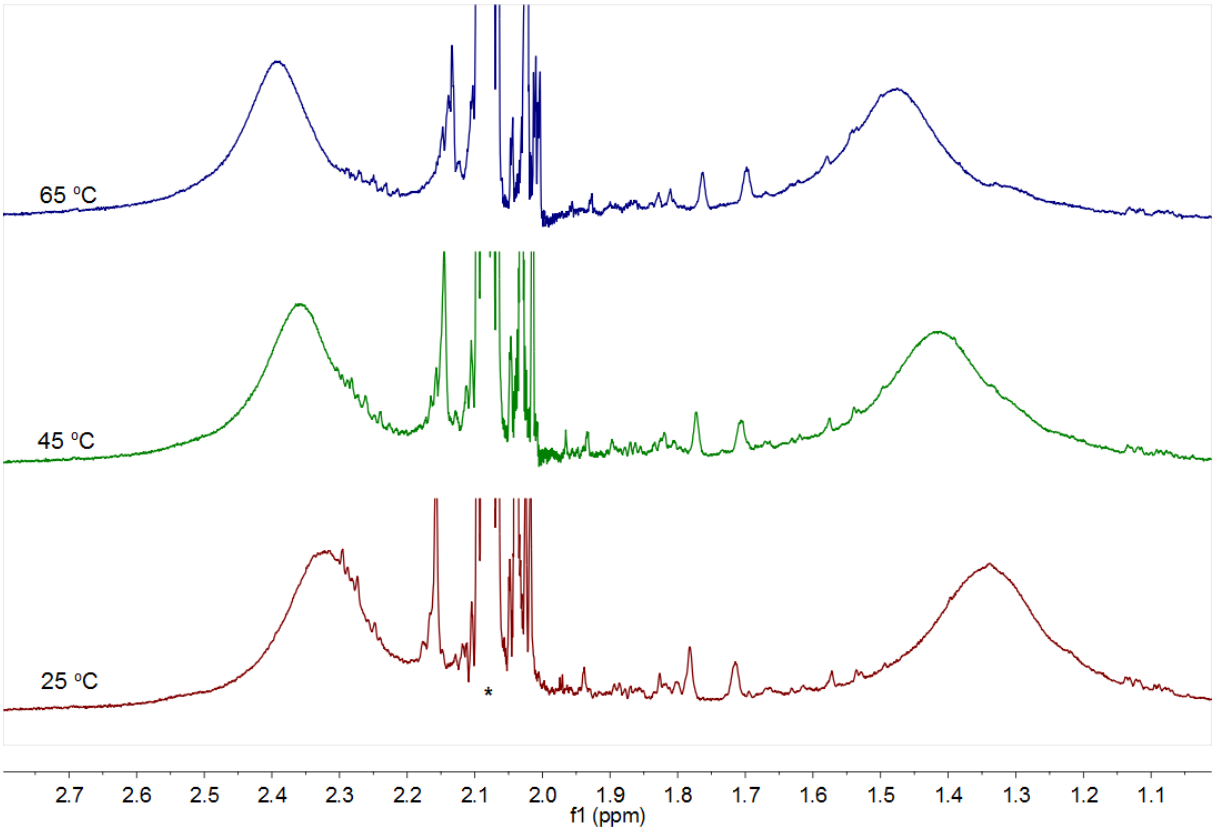
## Contents:

**$^1$H NMR spectra of solution of 3 in toluene-$d_8$ measured at variable temperatures.**

Signals at 1.3 ppm and 2.3 ppm were tentatively assigned to Si$Me_3$ and $C_5Me_5$ groups. The asterisk denotes signal of the solvent.




**Experimental data for 1,2,4,5-tetra(trimethylsilyl)benzene.**

1,2,4,5-tetra(trimethylsilyl)benzene were prepared accordingly to literature. [H. Bock, M. Ansari, N. Nagel and Z. Havlas, *J. Organomet. Chem.* 1995, **499**, 63−71.]

$^1$H NMR (toluene-$d_8$): 0.38 (s, 36 H, Si$Me_3$); 8.11 (s, 2H, $C_6H_2$).

GC-MS (*m/z*, abundance): 366 ($[M]^{+\cdot}$, 30); 351 ($[M - Me]^+$, 100); 335 (93); 263 (66); 152 (18); 73 ($[SiMe_3]^+$, 67).

**Additional analytical data for 2**.

Mp. > 360 °C. EI-MS (380 °C): *m/z* (relative abundance) 789 (15), 788 (24), 787 (37), 786 (38), 785 (40), 784 ($M^{+\cdot}$; 39), 783 (23), 782 (17), 781 (12), 392 ($M^{2+}$; 31), 183 (9), 169 (13), 136 (10), 135 ($[Cp^*]^+$; 16), 121 (22), 119 (36), 105 (23), 91 (31), 85 (16), 83 (12), 81 (10), 77 (12), 71 (16), 69 (20), 67 (13), 57 (31), 55 (34). The isotope peaks distribution pattern for *m/z* 784 corresponded to theory for $C_{44}H_{64}Ti_4$. IR (KBr, $cm^{-1}$): 2972 (m), 2904 (vs), 2855 (s), 2719 (vw), 1490 (w), 1432 (m,b), 1373 (s), 1064 (vw), 1024 (m), 801 (vw), 597 (s), 584 (vs), 506 (m), 476 (w), 450 (w), 416 (m). The reported in ref.[5] strong absorption band at 790 $cm^{-1}$ is to be attributed to an oxygenation impurity since it appeared to grow in intensity after exposition of the KBr pellet to air while intensities of a very strong band at 584 $cm^{-1}$ and a strong band at 597 $cm^{-1}$ were decreasing. UV-near IR (m-xylene, d = 1.0 cm): 310 > 530 >> 950 nm.

Crystal data and structure refinement for **3**.

| | |
|---|---|
| Empirical formula | C38 H68 Si4 Ti2 |
| Formula weight | 733.08 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Monoclinic, P 21/n |
| Unit cell dimensions | a = 11.8817(3) A alpha = 90 deg.<br>b = 13.3685(4) A beta = 99.0810(10) deg.<br>c = 12.8886(3) A gamma = 90 deg. |
| Volume | 2021.57(9) A^3 |
| Z, Calculated density | 2, 1.204 Mg/m^3 |
| Absorption coefficient | 0.538 mm^-1 |
| F(000) | 792 |
| Crystal size | 0.70 x 0.63 x 0.46 mm |
| Theta range for data collection | 2.21 to 27.50 deg. |
| Limiting indices | -15<=h<=14, -17<=k<=17, -12<=l<=16 |
| Reflections collected / unique | 33636 / 4649 [R(int) = 0.0173] |
| Completeness to theta = 27.50 | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7918 and 0.7061 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 4649 / 0 / 210 |
| Goodness-of-fit on F^2 | 0.947 |
| Final R indices [I>2sigma(I)] | R1 = 0.0235, wR2 = 0.0652 |
| R indices (all data) | R1 = 0.0271, wR2 = 0.0693 |
| Largest diff. peak and hole | 0.322 and -0.265 e.A^-3 |

Bond distances (Å) for **3**.

| Atoms | distances |
|---|---|
| Ti(1)-C(13) | 2.2229(11) |
| Ti(1)-C(13)#1 | 2.2621(11) |
| Ti(1)-C(11) | 2.2809(11) |
| Ti(1)-C(12)#1 | 2.2851(10) |
| Ti(1)-C(12) | 2.3155(11) |
| Ti(1)-C(11)#1 | 2.3184(10) |
| Ti(1)-C(5) | 2.3946(11) |
| Ti(1)-C(4) | 2.4234(12) |
| Ti(1)-C(1) | 2.4313(11) |
| Ti(1)-C(3) | 2.4428(11) |
| Ti(1)-C(2) | 2.4500(11) |
| Si(1)-C(15) | 1.8673(13) |
| Si(1)-C(16) | 1.8747(14) |
| Si(1)-C(14) | 1.8800(13) |
| Si(1)-C(11) | 1.8889(11) |
| Si(2)-C(18) | 1.8681(13) |
| Si(2)-C(17) | 1.8727(14) |
| Si(2)-C(19) | 1.8779(14) |
| Si(2)-C(12) | 1.8871(11) |
| C(1)-C(5) | 1.4179(17) |
| C(1)-C(2) | 1.4182(16) |
| C(1)-C(6) | 1.5061(17) |
| C(2)-C(3) | 1.4136(18) |
| C(2)-C(7) | 1.5062(17) |
| C(3)-C(4) | 1.4190(17) |
| C(3)-C(8) | 1.5028(17) |
| C(4)-C(5) | 1.4240(17) |
| C(4)-C(9) | 1.5024(17) |
| C(5)-C(10) | 1.5011(16) |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |
| C(11)-C(13)#1 | 1.4735(15) |
| C(11)-C(12) | 1.4896(15) |
| C(11)-Ti(1)#1 | 2.3184(10) |
| C(12)-C(13) | 1.4720(14) |
| C(12)-Ti(1)#1 | 2.2851(10) |
| C(13)-C(11)#1 | 1.4735(15) |
| C(13)-Ti(1)#1 | 2.2621(11) |
| C(13)-H(13) | 0.9500 |
| C(14)-H(14A) | 0.9800 |
| C(14)-H(14B) | 0.9800 |

Bond distances (Å) for **3**.

| Atoms | distances |
|---|---|
| C(14)-H(14C) | 0.9800 |
| C(15)-H(15A) | 0.9800 |
| C(15)-H(15B) | 0.9800 |
| C(15)-H(15C) | 0.9800 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(18)-H(18C) | 0.9800 |
| C(19)-H(19A) | 0.9800 |
| C(19)-H(19B) | 0.9800 |
| C(19)-H(19C) | 0.9800 |
| Ti(1)-Cg(1) | 2.1076(6) |
| Ti(1)-RING(1) | 2.1068(2) |
| Ti(1)-Cg(2) | 1.7381(5) |
| Ti(2)-RING(2) | 1.7381(2) |

Cg(2) = C(11), C(12), C(13), C(11)a, C(12)a, C(13)a
Cg(1) = C(1), C(2), C(3), C(4), C(5)

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

Valence angles (º) for **3**.

| Atoms | angle |
|---|---|
| C(13)-Ti(1)-C(13)#1 | 78.38(4) |
| C(13)-Ti(1)-C(11) | 68.22(4) |
| C(13)#1-Ti(1)-C(11) | 37.85(4) |
| C(13)-Ti(1)-C(12)#1 | 68.21(4) |
| C(13)#1-Ti(1)-C(12)#1 | 37.77(4) |
| C(11)-Ti(1)-C(12)#1 | 69.99(4) |
| C(13)-Ti(1)-C(12) | 37.78(4) |
| C(13)#1-Ti(1)-C(12) | 67.03(4) |
| C(11)-Ti(1)-C(12) | 37.81(4) |
| C(12)#1-Ti(1)-C(12) | 81.85(4) |
| C(13)-Ti(1)-C(11)#1 | 37.79(4) |
| C(13)#1-Ti(1)-C(11)#1 | 66.93(4) |
| C(11)-Ti(1)-C(11)#1 | 81.81(4) |
| C(12)#1-Ti(1)-C(11)#1 | 37.75(4) |
| C(12)-Ti(1)-C(11)#1 | 68.82(4) |
| C(13)-Ti(1)-C(5) | 106.99(4) |
| C(13)#1-Ti(1)-C(5) | 174.61(4) |
| C(11)-Ti(1)-C(5) | 144.06(4) |
| C(12)#1-Ti(1)-C(5) | 143.52(4) |
| C(12)-Ti(1)-C(5) | 117.37(4) |
| C(11)#1-Ti(1)-C(5) | 117.07(4) |
| C(13)-Ti(1)-C(4) | 122.77(4) |
| C(13)#1-Ti(1)-C(4) | 142.15(4) |
| C(11)-Ti(1)-C(4) | 168.47(4) |
| C(12)#1-Ti(1)-C(4) | 115.94(4) |
| C(12)-Ti(1)-C(4) | 149.25(4) |
| C(11)#1-Ti(1)-C(4) | 108.99(4) |
| C(5)-Ti(1)-C(4) | 34.38(4) |
| C(13)-Ti(1)-C(1) | 121.66(4) |
| C(13)#1-Ti(1)-C(1) | 143.01(4) |
| C(11)-Ti(1)-C(1) | 116.08(4) |
| C(12)#1-Ti(1)-C(1) | 169.40(4) |
| C(12)-Ti(1)-C(1) | 108.32(4) |
| C(11)#1-Ti(1)-C(1) | 148.23(4) |
| C(5)-Ti(1)-C(1) | 34.16(4) |
| C(4)-Ti(1)-C(1) | 56.51(4) |
| C(13)-Ti(1)-C(3) | 156.25(4) |
| C(13)#1-Ti(1)-C(3) | 118.16(4) |
| C(11)-Ti(1)-C(3) | 135.41(4) |
| C(12)#1-Ti(1)-C(3) | 113.35(4) |
| C(12)-Ti(1)-C(3) | 161.54(4) |
| C(11)#1-Ti(1)-C(3) | 129.60(4) |
| C(5)-Ti(1)-C(3) | 56.65(4) |
| C(4)-Ti(1)-C(3) | 33.90(4) |
| C(1)-Ti(1)-C(3) | 56.10(4) |
| C(13)-Ti(1)-C(2) | 154.72(4) |
| C(13)#1-Ti(1)-C(2) | 118.55(4) |
| C(11)-Ti(1)-C(2) | 112.49(4) |
| C(12)#1-Ti(1)-C(2) | 136.83(4) |
| C(12)-Ti(1)-C(2) | 127.96(4) |
| C(11)#1-Ti(1)-C(2) | 163.12(4) |
| C(5)-Ti(1)-C(2) | 56.54(4) |
| C(4)-Ti(1)-C(2) | 56.20(4) |
| C(1)-Ti(1)-C(2) | 33.78(4) |

Valence angles (º) for **3**.

| Atoms | angle |
|---|---|
| C(3)-Ti(1)-C(2) | 33.59(4) |
| C(15)-Si(1)-C(16) | 107.12(7) |
| C(15)-Si(1)-C(14) | 108.39(6) |
| C(16)-Si(1)-C(14) | 104.09(7) |
| C(15)-Si(1)-C(11) | 112.65(5) |
| C(16)-Si(1)-C(11) | 116.55(6) |
| C(14)-Si(1)-C(11) | 107.48(5) |
| C(18)-Si(2)-C(17) | 106.92(7) |
| C(18)-Si(2)-C(19) | 108.86(6) |
| C(17)-Si(2)-C(19) | 103.10(7) |
| C(18)-Si(2)-C(12) | 111.27(6) |
| C(17)-Si(2)-C(12) | 117.96(6) |
| C(19)-Si(2)-C(12) | 108.18(5) |
| C(5)-C(1)-C(2) | 108.03(10) |
| C(5)-C(1)-C(6) | 126.04(11) |
| C(2)-C(1)-C(6) | 124.35(11) |
| C(5)-C(1)-Ti(1) | 71.50(6) |
| C(2)-C(1)-Ti(1) | 73.83(6) |
| C(6)-C(1)-Ti(1) | 131.68(8) |
| C(3)-C(2)-C(1) | 108.06(10) |
| C(3)-C(2)-C(7) | 126.01(12) |
| C(1)-C(2)-C(7) | 124.35(12) |
| C(3)-C(2)-Ti(1) | 72.93(7) |
| C(1)-C(2)-Ti(1) | 72.39(6) |
| C(7)-C(2)-Ti(1) | 131.68(8) |
| C(2)-C(3)-C(4) | 108.27(10) |
| C(2)-C(3)-C(8) | 125.15(12) |
| C(4)-C(3)-C(8) | 125.17(13) |
| C(2)-C(3)-Ti(1) | 73.49(7) |
| C(4)-C(3)-Ti(1) | 72.30(6) |
| C(8)-C(3)-Ti(1) | 130.74(8) |
| C(3)-C(4)-C(5) | 107.68(11) |
| C(3)-C(4)-C(9) | 124.84(12) |
| C(5)-C(4)-C(9) | 125.67(12) |
| C(3)-C(4)-Ti(1) | 73.79(7) |
| C(5)-C(4)-Ti(1) | 71.70(6) |
| C(9)-C(4)-Ti(1) | 132.12(8) |
| C(1)-C(5)-C(4) | 107.93(10) |
| C(1)-C(5)-C(10) | 125.45(11) |
| C(4)-C(5)-C(10) | 126.33(12) |
| C(1)-C(5)-Ti(1) | 74.34(6) |
| C(4)-C(5)-Ti(1) | 73.92(6) |
| C(10)-C(5)-Ti(1) | 122.45(8) |
| C(1)-C(6)-H(6A) | 109.5 |
| C(1)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(1)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(2)-C(7)-H(7A) | 109.5 |
| C(2)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(2)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |

Valence angles (º) for **3**.

| Atoms | angle |
|---|---|
| H(7B)-C(7)-H(7C) | 109.5 |
| C(3)-C(8)-H(8A) | 109.5 |
| C(3)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| C(3)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| C(4)-C(9)-H(9A) | 109.5 |
| C(4)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| C(4)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(5)-C(10)-H(10A) | 109.5 |
| C(5)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(5)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| C(13)#1-C(11)-C(12) | 117.12(9) |
| C(13)#1-C(11)-Si(1) | 112.96(8) |
| C(12)-C(11)-Si(1) | 129.73(8) |
| C(13)#1-C(11)-Ti(1) | 70.38(6) |
| C(12)-C(11)-Ti(1) | 72.36(6) |
| Si(1)-C(11)-Ti(1) | 122.99(5) |
| C(13)#1-C(11)-Ti(1)#1 | 67.59(6) |
| C(12)-C(11)-Ti(1)#1 | 69.91(6) |
| Si(1)-C(11)-Ti(1)#1 | 137.23(6) |
| Ti(1)-C(11)-Ti(1)#1 | 98.19(4) |
| C(13)-C(12)-C(11) | 117.06(9) |
| C(13)-C(12)-Si(2) | 113.49(8) |
| C(11)-C(12)-Si(2) | 129.29(8) |
| C(13)-C(12)-Ti(1)#1 | 70.27(6) |
| C(11)-C(12)-Ti(1)#1 | 72.34(6) |
| Si(2)-C(12)-Ti(1)#1 | 123.48(5) |
| C(13)-C(12)-Ti(1) | 67.70(6) |
| C(11)-C(12)-Ti(1) | 69.83(6) |
| Si(2)-C(12)-Ti(1) | 136.93(5) |
| Ti(1)#1-C(12)-Ti(1) | 98.15(4) |
| C(12)-C(13)-C(11)#1 | 125.52(9) |
| C(12)-C(13)-Ti(1) | 74.52(6) |
| C(11)#1-C(13)-Ti(1) | 74.62(6) |
| C(12)-C(13)-Ti(1)#1 | 71.96(6) |
| C(11)#1-C(13)-Ti(1)#1 | 71.77(6) |
| Ti(1)-C(13)-Ti(1)#1 | 101.62(4) |
| C(12)-C(13)-H(13) | 117.2 |
| C(11)#1-C(13)-H(13) | 117.2 |
| Ti(1)-C(13)-H(13) | 125.5 |
| Ti(1)#1-C(13)-H(13) | 132.8 |
| Si(1)-C(14)-H(14A) | 109.5 |
| Si(1)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 109.5 |
| Si(1)-C(14)-H(14C) | 109.5 |
| H(14A)-C(14)-H(14C) | 109.5 |

Valence angles (º) for **3**.

| Atoms | angle |
|---|---|
| H(14B)-C(14)-H(14C) | 109.5 |
| Si(1)-C(15)-H(15A) | 109.5 |
| Si(1)-C(15)-H(15B) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 |
| Si(1)-C(15)-H(15C) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 |
| Si(1)-C(16)-H(16A) | 109.5 |
| Si(1)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| Si(1)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| Si(2)-C(17)-H(17A) | 109.5 |
| Si(2)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| Si(2)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| Si(2)-C(18)-H(18A) | 109.5 |
| Si(2)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| Si(2)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| Si(2)-C(19)-H(19A) | 109.5 |
| Si(2)-C(19)-H(19B) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 |
| Si(2)-C(19)-H(19C) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 |
| Cg(1)-Ti(1)-Cg(2) | 176.85(2) |

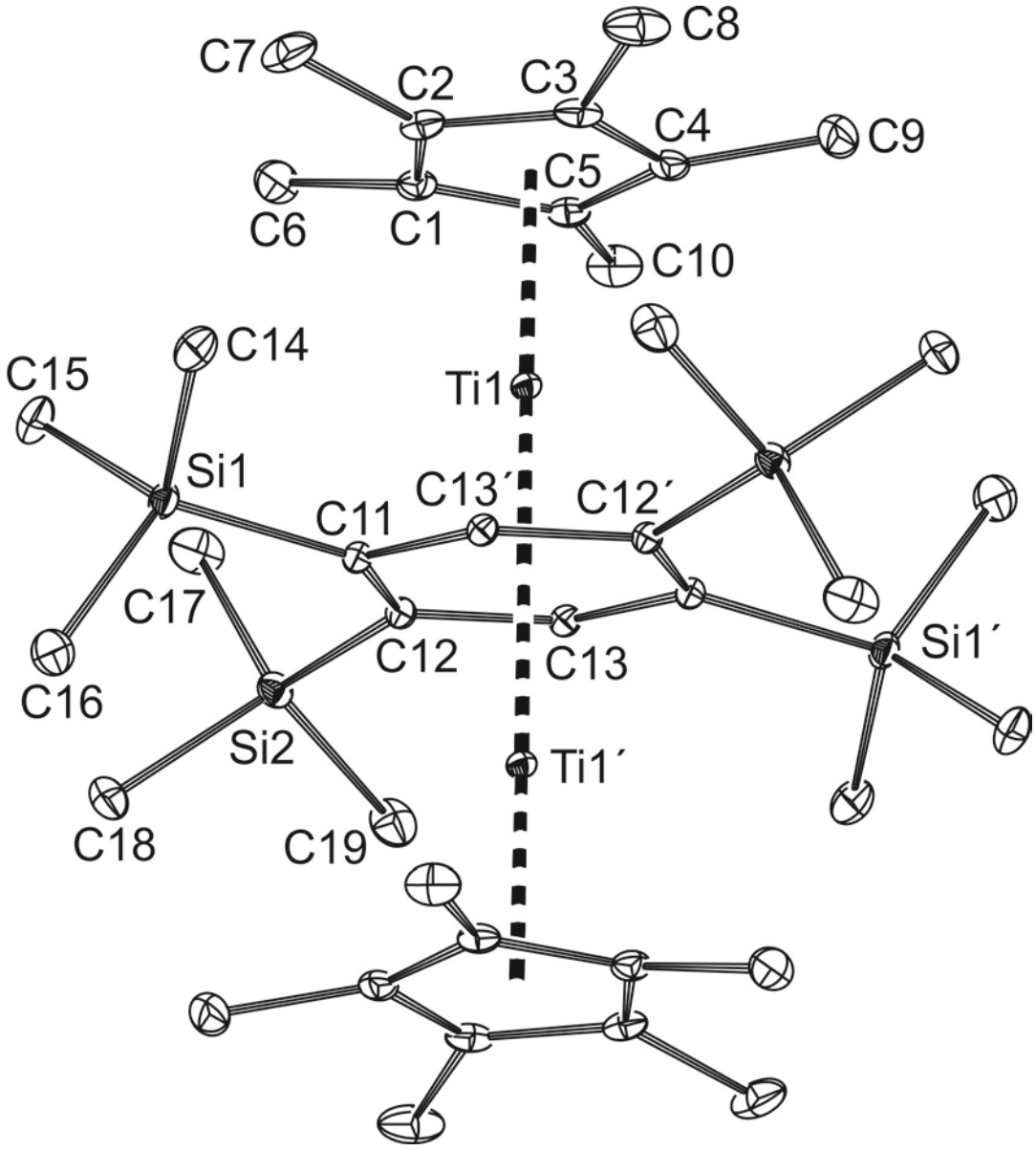
Least-squares planes and atomic deviations therefrom for **3**.

| Plane No. | Formed by * atoms and distances (Å) of some atoms from the plane | | |
|---|---|---|---|
| 1. Ring | * | -0.0072 (0.0007) | C1 |
| | * | 0.0024 (0.0007) | C2 |
| | * | 0.0033 (0.0007) | C3 |
| | * | -0.0076 (0.0007) | C4 |
| | * | 0.0092 (0.0007) | C5 |
| | | 2.1068 (0.0005) | Ti1 |
| | | -0.3228 (0.0021) | C6 |
| | | -0.2823 (0.0021) | C7 |
| | | -0.2629 (0.0022) | C8 |
| | | -0.3427 (0.0021) | C9 |
| | | -0.0855 (0.0021) | C10 |
| 2. Ring | * | -0.0230 (0.0006) | C11 |
| | * | 0.0230 (0.0006) | C12 |
| | * | -0.0242 (0.0006) | C13 |
| | * | 0.0230 (0.0006) | C11_$1 |
| | * | -0.0230 (0.0006) | C12_$1 |
| | * | 0.0242 (0.0006) | C13_$1 |
| | | -1.7381 (0.0002) | Ti1 |
| | | -0.2713 (0.0020) | Si1 |
| | | 0.2606 (0.0020) | Si2 |
| | | 0.2713 (0.0020) | Si1_$1 |
| | | -0.2606 (0.0020) | Si2_$1 |
| 3. Plane | * | -0.0260 (0.0003) | Si1 |
| | * | 0.0686 (0.0007) | C11 |
| | * | -0.0685 (0.0007) | C12 |
| | * | 0.0259 (0.0003) | Si2 |

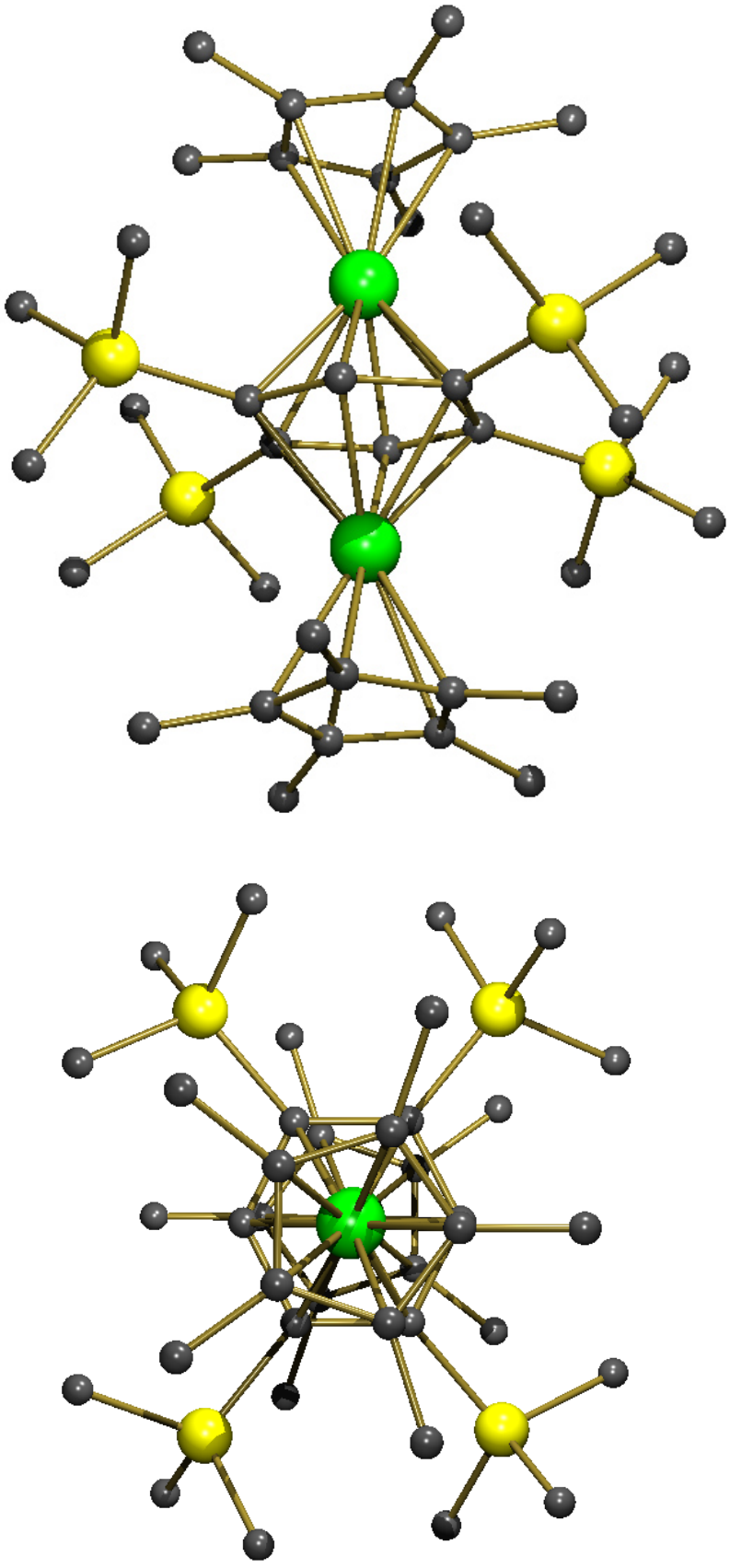
The angles between the planes are:

1 / 2 = 4.62 ( 0.09 )
2 / 3 = 7.05 ( 0.07 )

PLATON drawing with 30% probability for **3**.



PLUTON drawing for **3**.



**CASPT2 energies (in atomic units) for the three lowest roots.**

| CASPT2 Root No. | Singlet Multiplicity | Triplet Multiplicity |
|---|---|---|
| 1 | -4329.09271924 | -4329.05107072 |
| 2 | -4329.03115037 | -4329.05069110 |
| 3 | -4329.02916731 | -4329.01893572 |

CASPT2 energies (in atomic units) for the three lowest roots for 3. Energy values were devised on the solid state geometry and assuming singlet and triplet state for the molecule.