Supporting Information

A geminal dithallated bis(phosphoranomethine) carbon bridged dimer with Tl-Tl idnteractions

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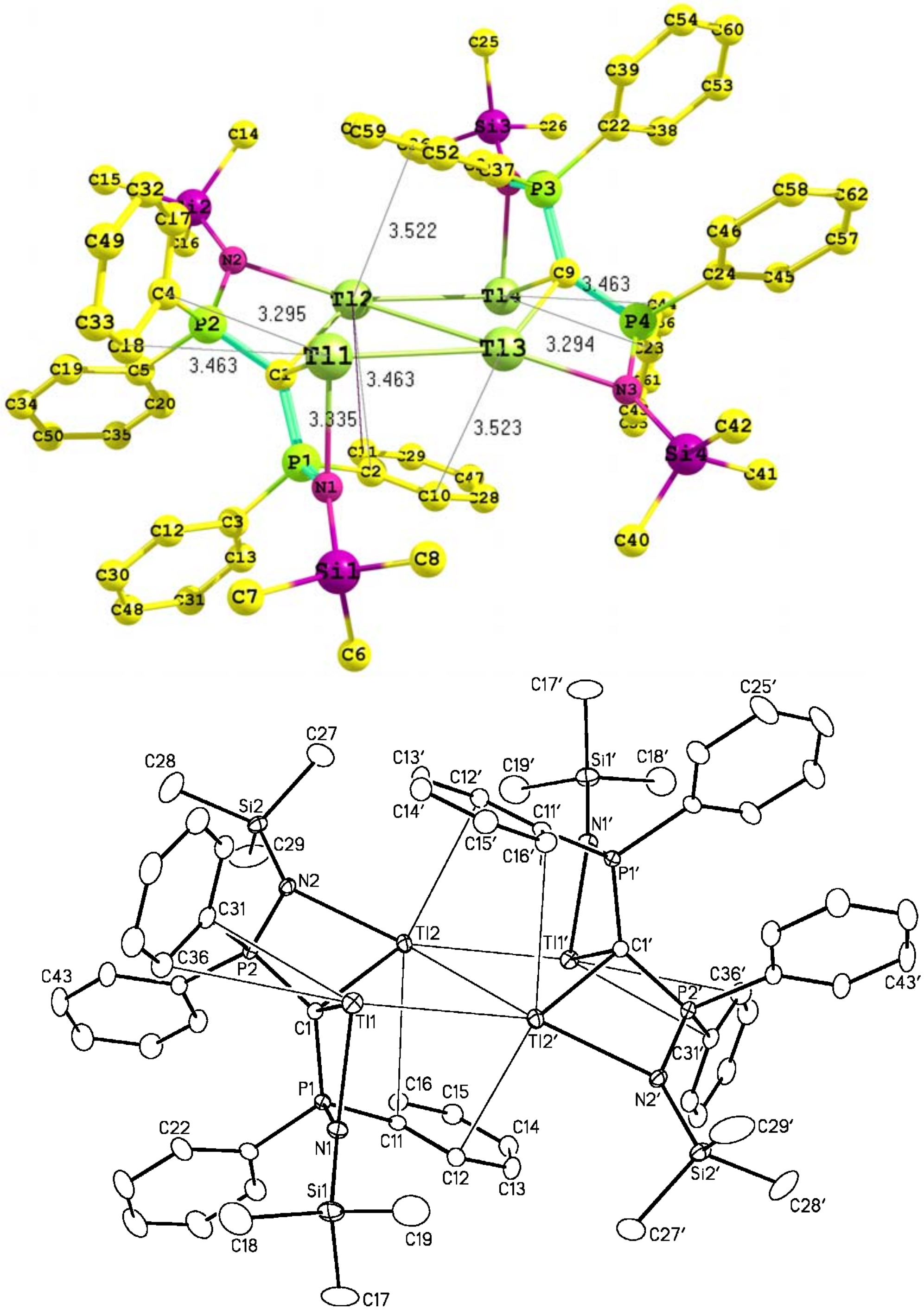

Fig. S-1. View of crystal structure of **2** (Thin line show the weakly covalent contact interactions between Tl(I) and some carbons of surrounding phenyl rings).

Table S2-1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{31}H_{38}N_2P_2Si_2Tl_2$
formula weight	965.49
crystal dimensions (mm)	0.48 × 0.43 × 0.19
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	14.0949 (12)
b (Å)	13.1494 (11)
c (Å)	18.9302 (16)
β (deg)	91.7640 (10)
V (Å^3)	3506.9 (5)
Z	4
ρ_{calcd} (g cm^{-3})	1.829
μ (mm^{-1})	9.360
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.00
total data collected	30102 ($-18 \le h \le 18$, $-17 \le k \le 17$, $-24 \le l \le 24$)
independent reflections	8033 (R_{int} = 0.0345)
number of observed reflections (*NO*)	7469 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.2693–0.0938
data/restraints/parameters	8033 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 353
extinction coefficient (x)[d]	0.00156(5)
goodness-of-fit (S)[e]	1.064 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0195
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0493
largest difference peak and hole	1.288 and –1.077 e Å^{-3}

[a]Obtained from least-squares refinement of 9798 reflections with 4.72° < 2θ < 56.54°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d]$F_c^* = kF_c[1 + x\{0.001F_c^2\lambda^3/\sin(2\theta)\}]^{-1/4}$ where k is the overall scale factor.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0195P)^2 + 2.3396P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2-2. Selected Interatomic Distances (Å)

Tl(1)	Tl(2')	3.4828(3)
Tl(1)	N(1)	2.471(2)
Tl(1)	C(1)	2.635(2)
Tl(1)	C(14')	3.937(3)†
Tl(1)	C(15')	3.983(3)†
Tl(1)	C(31)	3.294(2)†
Tl(1)	C(32)	3.682(3)†
Tl(1)	C(35)	3.988(3)†
Tl(1)	C(36)	3.462(3)†
Tl(2)	Tl(2')	3.7968(3)
Tl(2)	N(2)	2.504(2)
Tl(2)	C(1)	2.415(2)
Tl(2)	C(11)	3.463(2)†
Tl(2)	C(12')	3.522(3)†
Tl(2)	C(13')	3.960(3)†
Tl(2)	C(16)	3.336(3)†
P(1)	N(1)	1.589(2)
P(1)	C(1)	1.711(2)
P(1)	C(11)	1.834(3)
P(1)	C(21)	1.831(3)
P(2)	N(2)	1.595(2)
P(2)	C(1)	1.707(2)
P(2)	C(31)	1.833(3)
P(2)	C(41)	1.819(3)
Si(1)	N(1)	1.700(2)
Si(1)	C(17)	1.864(4)
Si(1)	C(18)	1.854(4)
Si(1)	C(19)	1.861(4)
Si(2)	N(2)	1.708(2)
Si(2)	C(27)	1.849(4)
Si(2)	C(28)	1.872(4)
Si(2)	C(29)	1.851(4)
C(11)	C(12)	1.390(4)
C(11)	C(16)	1.397(4)
C(12)	C(13)	1.389(4)
C(13)	C(14)	1.386(4)
C(14)	C(15)	1.384(4)
C(15)	C(16)	1.387(4)
C(21)	C(22)	1.390(4)
C(21)	C(26)	1.390(4)
C(22)	C(23)	1.386(5)

C(23)	C(24)	1.380(6)
C(24)	C(25)	1.365(6)
C(25)	C(26)	1.395(5)
C(31)	C(32)	1.383(4)
C(31)	C(36)	1.403(4)
C(32)	C(33)	1.395(4)
C(33)	C(34)	1.377(6)
C(34)	C(35)	1.367(5)
C(35)	C(36)	1.392(4)
C(41)	C(42)	1.394(4)
C(41)	C(46)	1.401(4)
C(42)	C(43)	1.396(5)
C(43)	C(44)	1.371(6)
C(44)	C(45)	1.388(5)
C(45)	C(46)	1.379(4)

Table S2-3. Selected Interatomic Angles (deg)

Tl(2')	Tl(1)	N(1)	85.44(5)
Tl(2')	Tl(1)	C(1)	88.18(5)
Tl(2')	Tl(1)	C(14')	79.42(4)
Tl(2')	Tl(1)	C(15')	65.52(4)
Tl(2')	Tl(1)	C(31)	133.75(5)
Tl(2')	Tl(1)	C(32)	126.87(5)
Tl(2')	Tl(1)	C(35)	168.82(6)
Tl(2')	Tl(1)	C(36)	155.25(5)
N(1)	Tl(1)	C(1)	64.03(7)
N(1)	Tl(1)	C(14')	160.41(6)
N(1)	Tl(1)	C(15')	150.83(7)
N(1)	Tl(1)	C(31)	102.02(7)
N(1)	Tl(1)	C(32)	123.95(7)
N(1)	Tl(1)	C(35)	102.66(8)
N(1)	Tl(1)	C(36)	91.60(8)
C(1)	Tl(1)	C(14')	102.84(7)
C(1)	Tl(1)	C(15')	115.10(7)
C(1)	Tl(1)	C(31)	56.95(7)
C(1)	Tl(1)	C(32)	71.97(7)
C(1)	Tl(1)	C(35)	88.50(7)
C(1)	Tl(1)	C(36)	68.60(7)
C(14')	Tl(1)	C(15')	20.12(6)
C(14')	Tl(1)	C(31)	80.18(7)
C(14')	Tl(1)	C(32)	59.19(7)
C(14')	Tl(1)	C(35)	90.92(7)

C(14')	Tl(1)	C(36)	96.95(7)
C(15')	Tl(1)	C(31)	100.27(7)
C(15')	Tl(1)	C(32)	79.07(7)
C(15')	Tl(1)	C(35)	106.48(7)
C(15')	Tl(1)	C(36)	115.81(7)
C(31)	Tl(1)	C(32)	21.98(7)
C(31)	Tl(1)	C(35)	37.47(7)
C(31)	Tl(1)	C(36)	23.80(7)
C(32)	Tl(1)	C(35)	42.05(7)
C(32)	Tl(1)	C(36)	38.94(8)
C(35)	Tl(1)	C(36)	19.98(7)
Tl(1')	Tl(2)	Tl(2')	65.714(4)
Tl(1')	Tl(2)	N(2)	154.55(5)
Tl(1')	Tl(2)	C(1)	139.55(6)
Tl(1')	Tl(2)	C(11)	88.23(4)
Tl(1')	Tl(2)	C(12')	81.59(4)
Tl(1')	Tl(2)	C(13')	101.68(4)
Tl(1')	Tl(2)	C(16)	81.01(5)
Tl(2')	Tl(2)	N(2)	133.88(5)
Tl(2')	Tl(2)	C(1)	84.50(5)
Tl(2')	Tl(2)	C(11)	67.06(4)
Tl(2')	Tl(2)	C(12')	71.09(4)
Tl(2')	Tl(2)	C(13')	77.07(4)
Tl(2')	Tl(2)	C(16)	84.66(5)
N(2)	Tl(2)	C(1)	65.55(7)
N(2)	Tl(2)	C(11)	113.38(7)
N(2)	Tl(2)	C(12')	90.14(7)
N(2)	Tl(2)	C(13')	73.19(7)
N(2)	Tl(2)	C(16)	113.21(7)
C(1)	Tl(2)	C(11)	53.95(7)
C(1)	Tl(2)	C(12')	115.14(7)
C(1)	Tl(2)	C(13')	97.24(7)
C(1)	Tl(2)	C(16)	69.01(8)
C(11)	Tl(2)	C(12')	137.43(6)
C(11)	Tl(2)	C(13')	134.73(6)
C(11)	Tl(2)	C(16)	23.62(6)
C(12')	Tl(2)	C(13')	20.32(6)
C(12')	Tl(2)	C(16)	154.40(6)
C(13')	Tl(2)	C(16)	158.25(6)
N(1)	P(1)	C(1)	110.36(12)
N(1)	P(1)	C(11)	109.82(12)
N(1)	P(1)	C(21)	110.11(12)
C(1)	P(1)	C(11)	105.63(11)

C(1)	P(1)	C(21)	115.78(12)
C(11)	P(1)	C(21)	104.80(12)
N(2)	P(2)	C(1)	107.49(12)
N(2)	P(2)	C(31)	109.52(13)
N(2)	P(2)	C(41)	111.49(12)
C(1)	P(2)	C(31)	109.15(12)
C(1)	P(2)	C(41)	114.08(12)
C(31)	P(2)	C(41)	105.04(12)
N(1)	Si(1)	C(17)	113.99(15)
N(1)	Si(1)	C(18)	110.62(18)
N(1)	Si(1)	C(19)	106.99(16)
C(17)	Si(1)	C(18)	107.8(2)
C(17)	Si(1)	C(19)	109.5(2)
C(18)	Si(1)	C(19)	107.8(3)
N(2)	Si(2)	C(27)	107.48(14)
N(2)	Si(2)	C(28)	112.83(16)
N(2)	Si(2)	C(29)	111.99(16)
C(27)	Si(2)	C(28)	108.4(2)
C(27)	Si(2)	C(29)	108.3(2)
C(28)	Si(2)	C(29)	107.7(3)
Tl(1)	N(1)	P(1)	96.99(10)
Tl(1)	N(1)	Si(1)	122.43(11)
P(1)	N(1)	Si(1)	139.43(15)
Tl(2)	N(2)	P(2)	93.24(9)
Tl(2)	N(2)	Si(2)	129.28(12)
P(2)	N(2)	Si(2)	133.59(14)
Tl(1)	C(1)	Tl(2)	103.15(9)
Tl(1)	C(1)	P(1)	88.19(9)
Tl(1)	C(1)	P(2)	108.64(11)
Tl(2)	C(1)	P(1)	120.69(12)
Tl(2)	C(1)	P(2)	93.64(10)
P(1)	C(1)	P(2)	137.70(16)
Tl(2)	C(11)	P(1)	79.19(8)
Tl(2)	C(11)	C(12)	116.05(17)
Tl(2)	C(11)	C(16)	73.06(15)
P(1)	C(11)	C(12)	119.55(19)
P(1)	C(11)	C(16)	121.92(19)
C(12)	C(11)	C(16)	118.4(2)
C(11)	C(12)	C(13)	120.4(3)
C(12)	C(13)	C(14)	120.7(3)
C(13)	C(14)	C(15)	119.6(3)
C(14)	C(15)	C(16)	119.8(3)
Tl(2)	C(16)	C(11)	83.32(15)

Tl(2)	C(16)	C(15)	111.9(2)
C(11)	C(16)	C(15)	121.2(3)
P(1)	C(21)	C(22)	117.3(2)
P(1)	C(21)	C(26)	124.4(2)
C(22)	C(21)	C(26)	118.3(3)
C(21)	C(22)	C(23)	121.1(3)
C(22)	C(23)	C(24)	119.7(4)
C(23)	C(24)	C(25)	120.1(3)
C(24)	C(25)	C(26)	120.6(4)
C(21)	C(26)	C(25)	120.1(3)
Tl(1)	C(31)	P(2)	82.96(9)
Tl(1)	C(31)	C(32)	94.99(16)
Tl(1)	C(31)	C(36)	84.84(16)
P(2)	C(31)	C(32)	120.1(2)
P(2)	C(31)	C(36)	121.2(2)
C(32)	C(31)	C(36)	118.1(3)
Tl(1)	C(32)	C(31)	63.04(15)
Tl(1)	C(32)	C(33)	100.5(2)
C(31)	C(32)	C(33)	120.6(3)
C(32)	C(33)	C(34)	120.3(3)
C(33)	C(34)	C(35)	120.0(3)
Tl(1)	C(35)	C(34)	94.2(2)
Tl(1)	C(35)	C(36)	58.20(17)
C(34)	C(35)	C(36)	120.2(3)
Tl(1)	C(36)	C(31)	71.36(16)
Tl(1)	C(36)	C(35)	101.8(2)
C(31)	C(36)	C(35)	120.7(3)
P(2)	C(41)	C(42)	124.4(2)
P(2)	C(41)	C(46)	117.2(2)
C(42)	C(41)	C(46)	118.3(3)
C(41)	C(42)	C(43)	119.6(3)
C(42)	C(43)	C(44)	121.2(3)
C(43)	C(44)	C(45)	119.7(3)
C(44)	C(45)	C(46)	119.6(3)
C(41)	C(46)	C(45)	121.5(3)

Gaussian 03 input file for **2**
Tl4L2

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1	11.549100000	5.166400000	8.293200000
1	12.433700000	3.988200000	7.670700000
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6	8.430700000	10.729900000	11.775600000
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6	2.218000000	7.599000000	13.791700000
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6	1.989900000	8.871900000	11.038600000
1	9.675200000	7.192700000	7.400100000
6	9.094400000	9.141500000	7.493800000
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1	6.061800000	7.935700000	5.735000000
1	7.554100000	3.350500000	4.418100000
6	7.522700000	3.893500000	2.463500000
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1	7.685100000	7.346600000	3.827800000
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1	0.298500000	5.074400000	9.118100000
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1	6.396900000	1.929000000	5.655600000
1	4.014400000	2.130200000	4.662200000
6	3.675000000	3.053300000	2.868500000
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1	4.578900000	6.144700000	4.686800000
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6	12.242200000	7.167700000	12.650700000
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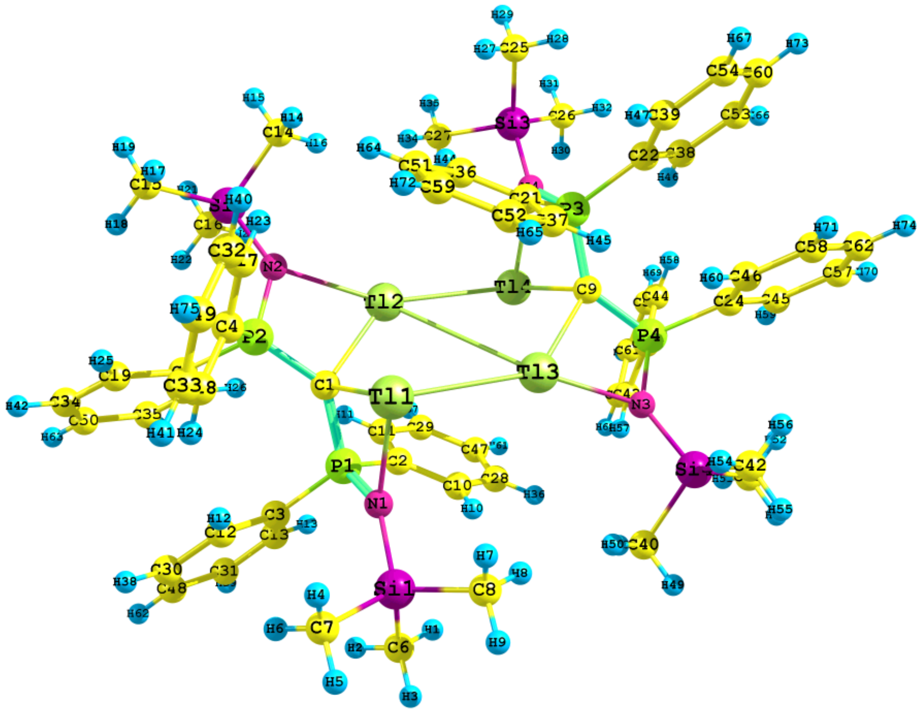
1	3.994000000	6.253900000	2.442700000
1	3.837000000	5.956700000	11.521100000
6	4.417800000	4.007900000	11.427500000
6	6.543300000	3.562200000	12.432400000
1	7.450400000	5.213700000	13.186200000
1	5.958100000	9.798900000	14.503100000
6	5.989500000	9.255900000	16.457700000
6	5.861700000	6.907400000	16.809600000
1	5.827100000	5.802800000	15.093500000
1	11.897900000	8.701000000	9.140800000
1	13.213700000	8.075000000	9.803100000
1	11.945700000	7.144100000	9.509800000
1	11.873100000	10.781200000	11.366000000
1	11.886600000	10.302600000	12.892900000
1	13.183300000	10.096100000	11.979000000
1	11.927300000	6.274900000	12.397200000
1	13.221200000	7.188800000	12.626100000

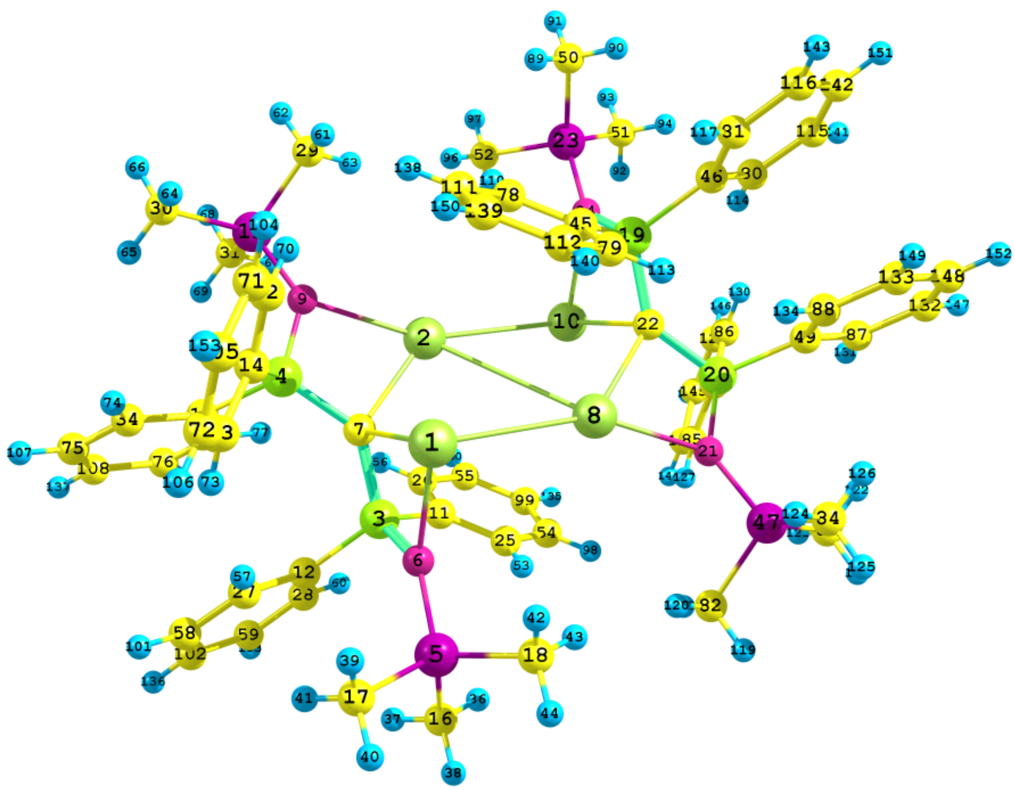
1	11.933800000	7.376800000	13.557100000
1	9.624700000	10.698400000	10.136100000
6	8.663100000	12.498500000	10.149200000
6	7.199500000	12.811500000	11.996100000
1	7.115300000	11.220400000	13.265700000
1	9.497800000	11.019200000	14.259000000
6	9.837200000	10.096100000	16.052800000
6	9.506600000	7.733200000	16.030600000
1	8.933300000	7.004700000	14.234400000
1	8.178800000	10.957400000	7.383100000
1	7.582200000	4.837700000	0.667900000
1	3.443200000	4.292000000	1.286600000
1	3.643900000	3.700200000	10.970500000
6	5.419400000	3.111100000	11.764500000
1	7.229300000	2.950700000	12.677200000
1	6.060500000	10.136900000	16.807700000
6	5.927900000	8.175000000	17.313300000
1	5.819400000	6.167100000	17.403700000
1	9.052800000	12.824600000	9.347100000
6	7.770600000	13.282200000	10.845600000
1	6.582900000	13.353200000	12.474800000
1	10.076400000	10.886400000	16.522000000
6	9.839400000	8.894300000	16.713500000
1	9.518200000	6.895500000	16.478500000
1	5.333400000	2.192000000	11.538200000
1	5.930000000	8.311700000	18.253300000
1	10.069000000	8.857400000	17.634600000
1	5.961500000	-0.999400000	8.395300000
1	7.550700000	14.148800000	10.525900000

Si C H 0
6-31G*
****
N P 0
6-311G**
****
Tl 0
SDD
****

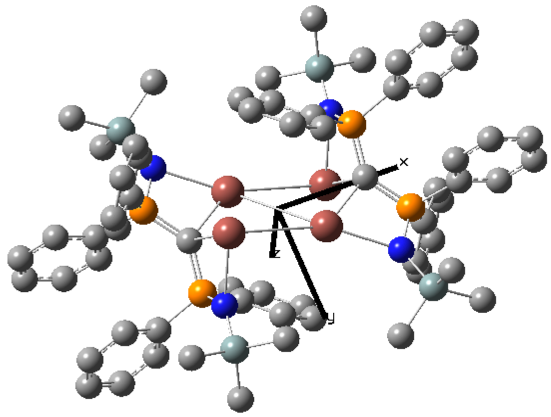
Tl 0
SDD

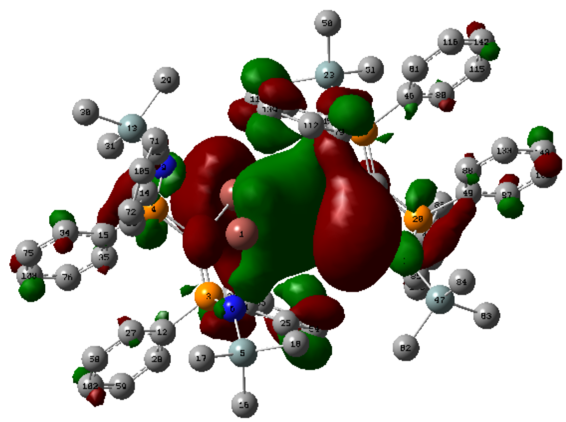
$[Tl2C(Ph_2P{=}NSiMe_3)_2]_2$





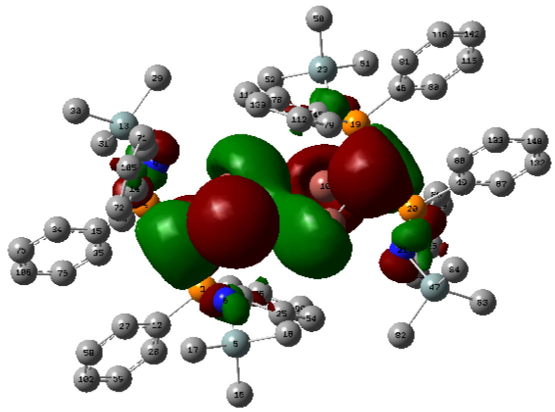
GaussView of the molecular orbitals





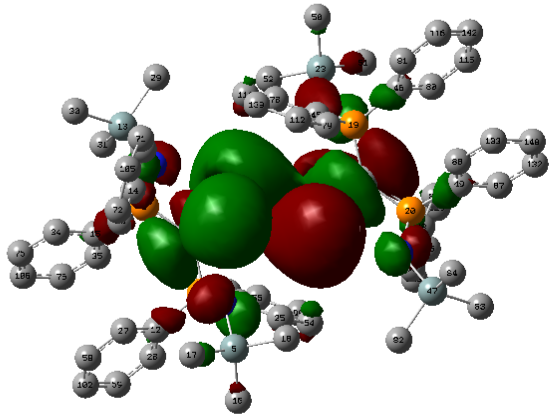
LUMO (MO-303, E=-0.046 a.u.)

Tl(2):	2s (0.165)
	$3p_x$ (-0.116)
	$3p_y$ (-0.138)
	$3p_z$ (0.153)
	$4p_x$ (-0.153)
	$4p_y$ (-0.138)
	$4p_z$ (0.205)
Tl(8)	2s (0.165)
	$3p_x$ (-0.116)
	$3p_y$ (0.138)
	$3p_z$ (-0.153)
	$4p_x$ (0.143)
	$4p_y$ (0.138)
	$4p_z$ (-0.205)
C(7)	3s (0.215)
C(22)	3s (0.215)



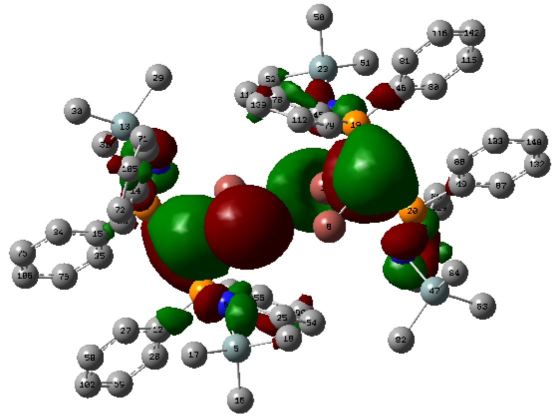
MOMO (MO-302, E=-0.175 a.u.)

Tl(1): 1s (0.163)
2s (0.180)
3p_z (-0.095)
Tl(2) 1s (-0.125)
2s (-0.145)
Tl(8) 1s (-0.124)
2s (-0.144)
3p_x (0.115)
Tl(10) 1s (0.164)
2s (0.181)
3p_z (0.095)
C(7) 2p_x (0.108)
2p_y (-0.103)
2p_z (0.226)
C(22) 2p_x (-0.106)
2p_y (0.102)
2p_z (-0.226)
3p_z (-0.216)



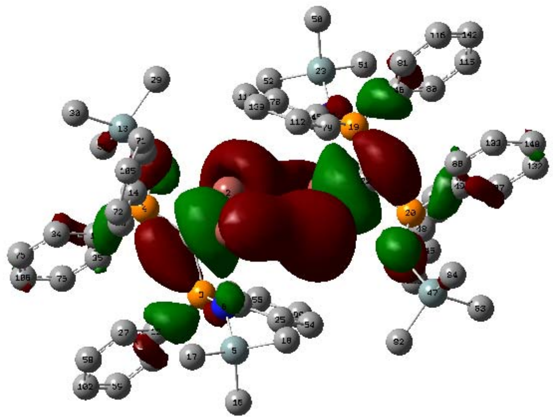
HOMO-1 (MO-301, E=-0.176 a.u.)

Tl(1):	1s (-0.176)
	2s (-0.163)
	$3p_z$ (0.097)
Tl(2)	1s (-0.204)
	2s (-0.215)
	$3p_x$ (-0.116)
Tl(8)	1s (0.205)
	2s (0.216)
	$3p_x$ (-0.117)
Tl(10)	1s (0.175)
	2s (0.162)
	$3p_z$ (0.097)
C(7)	$2p_x$ (0.191)
	$3p_x$ (0.174)
C(22)	$2p_x$ (0.192)
	$2p_y$ (-0.061)
	$3p_x$ (0.175)



HOMO-2 (MO-300, E=-0.182 a.u.)

Tl(1):	1s (0.115)
	2s (0.123)
	$3p_z$ (-0.096)
Tl(10)	1s (-0.115)
	2s (-0.124)
	$3p_z$ (-0.096)
C(7)	$2p_z$ (0.270)
	$3p_z$ (0.253)
C(22)	$2p_z$ (0.271)
	$3p_z$ (0.253)



HOMO-3 (MO-299, E=-0.195 a.u.)

Tl(1): 1s (0.076)
2s (0.058)
$3p_z$ (-0.084)

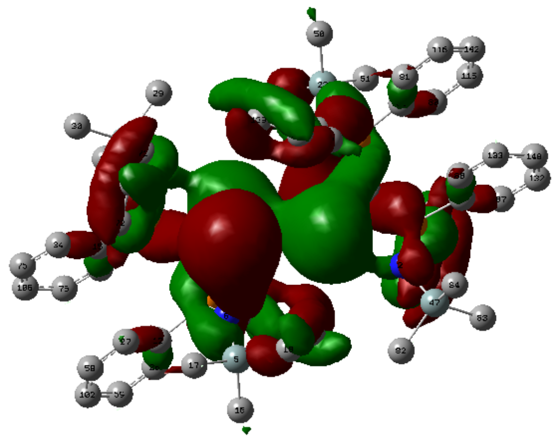
Tl(2) 1s (0.130)
2s (0.129)
$3p_x$ (0.108)

Tl(8) 1s (0.130)
2s (0.128)
$3p_x$ (-0.108)

Tl(10) 1s (0.076)
2s (0.060)
$3p_z$ (0.084)

C(7) $2p_x$ (-0.228)
$2p_z$ (0.116)
$3p_x$ (-0.199)
$3p_z$ (0.109)

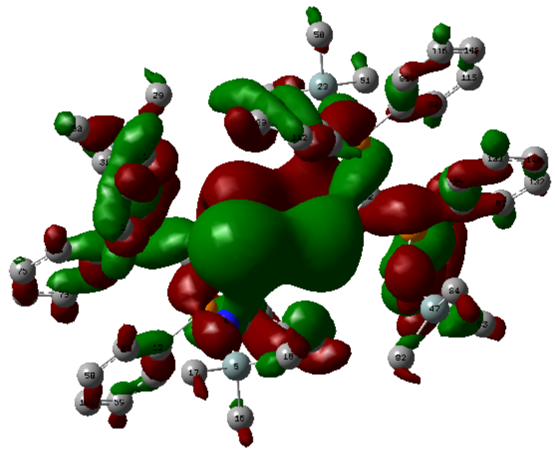
C(22) $2p_x$ (0.228)
$2p_z$ (-0.116)
$3p_x$ (0.199)
$3p_z$ (-0.110)



MO-266 (E=-0.318 a.u.)

6s Tl overlap with C(14) $2p_z$, C(11) $2p_x$, C(25) $2p_x$, C(45) $2p_z$

Tl(1):	1s (0.192)
	2s (0.126)
Tl(2)	1s (-0.153)
	2s (-0.099)
Tl(8)	1s (-0.153)
	2s (-0.099)
Tl(10)	1s (0.192)
	2s (0.126)
C(14)	$2p_z$ (-0.101)
C(32)	$2p_z$ (0.072)
C(33)	$2p_z$ (0.049)
C(11)	$2p_x$ (-0.101)
	$2p_z$ (-0.05)
C(26)	$2p_x$ (0.029)
	$2p_z$ (0.035)
C(25)	$2p_x$ (0.065)
	$2p_y$ (0.023)
	$2p_z$ (0.027)
C(45)	$2p_x$ (0.101)
	$2p_z$ (0.050)
	$2p_z$ (0.027)
C(48)	$2p_z$ (0.101)
	$3p_z$ (0.042)
C(79)	$2p_x$ (-0.030)
	$2p_z$ (-0.035)
C(86)	$2p_z$ (-0.049)



MO-264 (E=-0.328 a.u.)

6s Tl overlap with C(14) $2p_z$, C(11) $2p_x$, C(45) $2p_x$, C(48) $2p_z$

Tl(1): 1s (-0.165)
2s (-0.099)

Tl(2) 1s (0.142)
2s (0.090)

Tl(8) 1s (-0.141)
2s (-0.090)

Tl(10) 1s (0.165)
2s (0.099)

C(7) $2p_y$ (0.104)

C(14) $2p_z$ (0.103)

C(11) $2p_x$ (0.071)

C(26) $2p_x$ (-0.03)
$2p_z$ (-0.033)

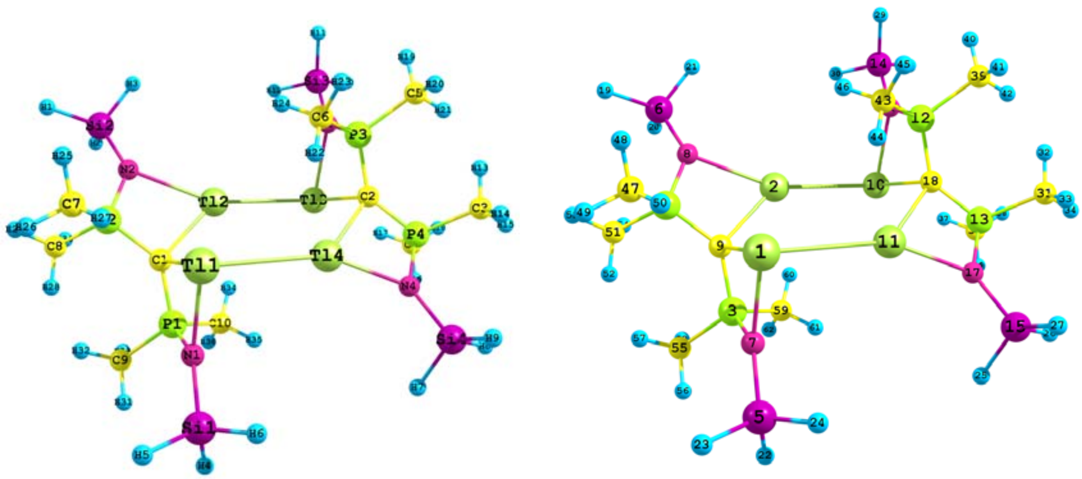
C(25) 3s (0.025)
$3p_x$ (-0.036)

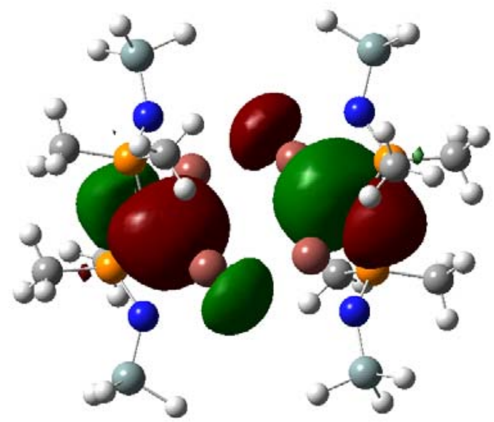
C(45) $2p_x$ (0.071)
$2p_y$ (0.03)
$2p_z$ (0.05)

C(79) $2p_z$ (-0.033)
$2p_x$ (-0.028)

C(48) $2p_z$ (0.103)

C(86) $2p_z$ (-0.06)



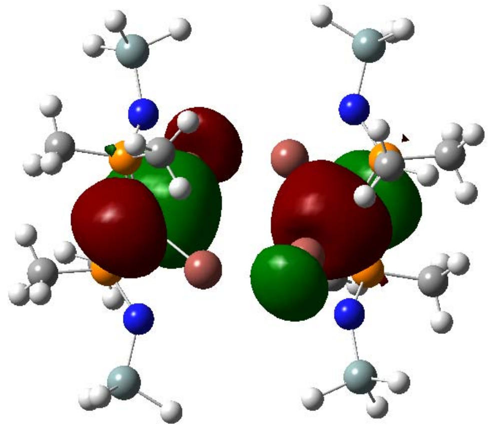


(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.75649) BD (1)Tl 1 - C 9
(7.23%) 0.2690*Tl 1 s(2.17%)p45.07(97.82%)d 0.00(0.01%)
-0.1409 0.0431 -0.0258 0.0149 0.7639
0.0777 -0.6208 -0.0473 -0.0019 -0.0057
-0.0063 0.0051 -0.0007
(92.77%) 0.9631* C 9 s(8.79%)p10.38(91.20%)d 0.00(0.01%)
-0.0003 -0.2962 0.0105 -0.2227 0.0048
-0.4971 0.0102 0.7843 -0.0098 0.0045
-0.0087 -0.0029 0.0024 0.0028

19. (1.75672) BD (1)Tl 10 - C 18
(7.24%) 0.2690*Tl 10 s(2.17%)p45.07(97.82%)d 0.00(0.01%)
0.1409 -0.0431 -0.0260 0.0149 0.7643
0.0780 -0.6203 -0.0476 0.0020 0.0056
0.0063 -0.0048 0.0007
(92.76%) 0.9631* C 18 s(8.76%)p10.42(91.23%)d 0.00(0.01%)
0.0003 0.2957 -0.0105 -0.2219 0.0048
-0.4975 0.0102 0.7844 -0.0097 -0.0045

0.0087 0.0030 -0.0024 -0.0028

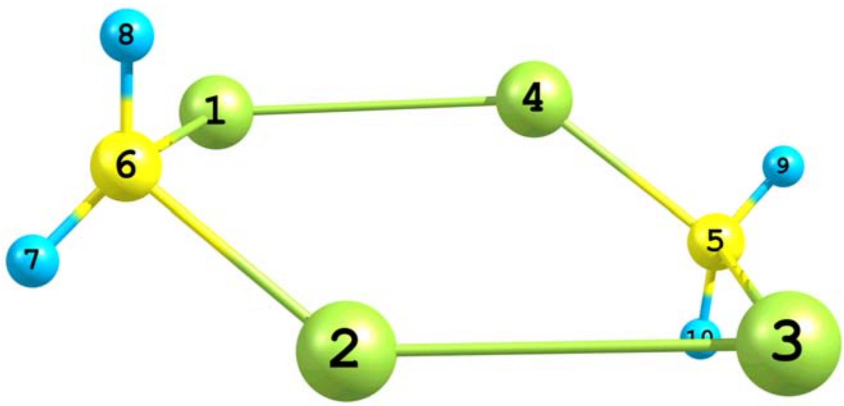


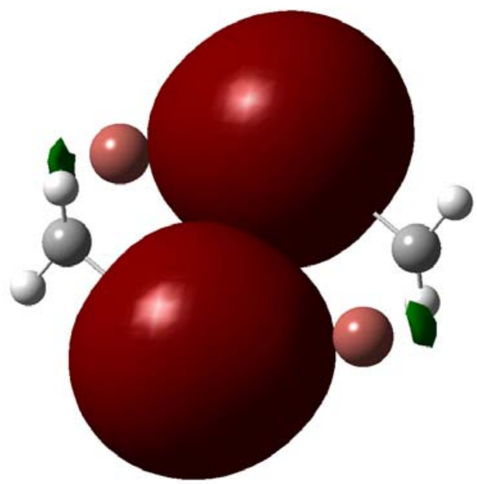
(Occupancy) Bond orbital/ Coefficients/ Hybrids

```
  2. (1.80622) BD ( 1)Tl   2 - C   9
           (  6.72%)   0.2592*Tl   2 s(  5.27%)p17.49( 92.09%)d 0.50(  2.64%)
                                    0.2193 -0.0676 -0.7702 -0.1348  0.5320
                                    0.1120  0.1169  0.0161  0.1283 -0.0044
                                   -0.0098 -0.0602  0.0787
           ( 93.28%)   0.9658* C   9 s( 15.23%)p 5.57( 84.76%)d 0.00(  0.01%)
                                    0.0005  0.3899 -0.0148  0.8228 -0.0175
                                   -0.3896  0.0200  0.1341  0.0081  0.0032
                                    0.0012 -0.0010 -0.0095  0.0047

 20. (1.80624) BD ( 1)Tl  11 - C  18
           (  6.72%)   0.2592*Tl  11 s(  5.26%)p17.49( 92.09%)d 0.50(  2.65%)
                                   -0.2192  0.0677 -0.7698 -0.1352  0.5322
                                    0.1121  0.1178  0.0163 -0.1285  0.0044
                                    0.0096  0.0603 -0.0788
           ( 93.28%)   0.9658* C  18 s( 15.25%)p 5.56( 84.74%)d 0.00(  0.01%)
                                   -0.0005 -0.3902  0.0148  0.8231 -0.0175
                                   -0.3891  0.0199  0.1333  0.0081 -0.0032
                                   -0.0012  0.0010  0.0094 -0.0046
```

NBO analysis for the Tl4C2 ring





NBO of Tl(1)-Tl(4) and Tl(2)-Tl(3) bonds

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.96317) BD (1)Tl 1 -Tl 4

(6.02%) 0.2454*Tl 1 s(0.54%)p99.99(99.32%)d 0.26(0.14%)

0.0518 -0.0524 0.9175 -0.0394 0.1946

0.0244 0.3317 -0.0365 0.0119 0.0145

-0.0104 0.0269 -0.0150

(93.98%) 0.9694*Tl 4 s(92.47%)p 0.08(7.52%)d 0.00(0.01%)

0.9616 0.0021 -0.2392 -0.0048 0.1310

0.0040 0.0273 -0.0016 0.0063 0.0042

-0.0008 0.0032 -0.0040

3. (1.96317) BD (1)Tl 2 -Tl 3

(93.98%) 0.9694*Tl 2 s(92.47%)p 0.08(7.52%)d 0.00(0.01%)

0.9616 0.0021 0.2392 0.0048 -0.1310

-0.0040 -0.0273 0.0016 0.0063 0.0042

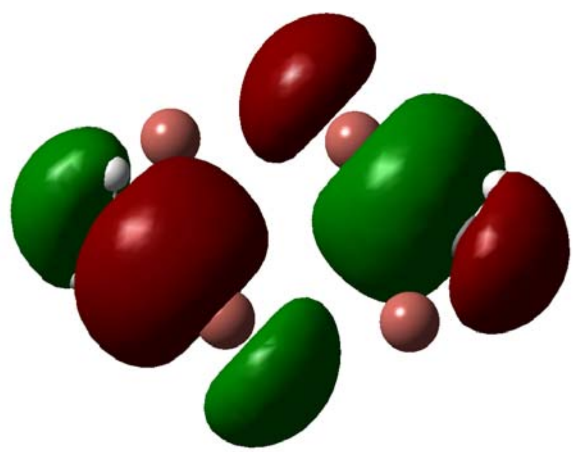
-0.0008 0.0032 -0.0040

(6.02%) 0.2454*Tl 3 s(0.54%)p99.99(99.32%)d 0.26(0.14%)

0.0518 -0.0524 -0.9175 0.0394 -0.1946

-0.0244 -0.3317 0.0365 0.0119 0.0145

-0.0104 0.0269 -0.0150



NBO of Tl(2)-C(6) and Tl(4)-C(5) bonds

(Occupancy) Bond orbital/ Coefficients/ Hybrids

4. (1.86874) BD (1)Tl 2 - C 6

(17.18%) 0.4145*Tl 2 s(7.12%)p13.05(92.85%)d 0.00(0.03%)

0.2626 -0.0469 -0.6977 -0.0816 0.5878

0.0028 0.2991 -0.0112 0.0124 0.0061

-0.0062 -0.0077 0.0003

(82.82%) 0.9101* C 6 s(12.83%)p 6.79(87.16%)d 0.00(0.00%)

0.0009 0.3567 -0.0336 0.8478 -0.0236

-0.3761 0.0240 0.1011 0.0088 -0.0012

-0.0006 -0.0016 -0.0028 0.0016

6. (1.86874) BD (1)Tl 4 - C 5

(17.18%) 0.4145*Tl 4 s(7.12%)p13.05(92.85%)d 0.00(0.03%)

-0.2626 0.0469 -0.6977 -0.0816 0.5878

0.0028 0.2991 -0.0112 -0.0124 -0.0061

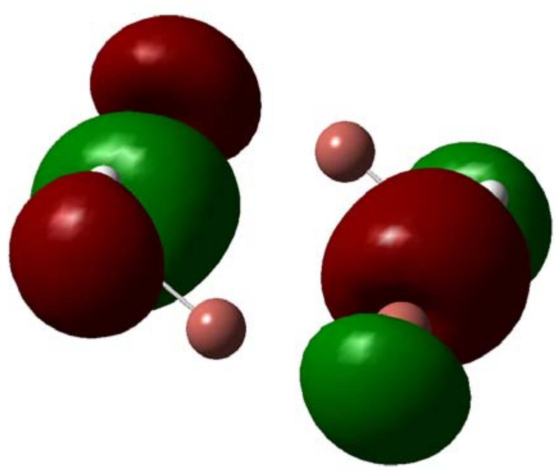
0.0062 0.0077 -0.0003

(82.82%) 0.9101* C 5 s(12.83%)p 6.79(87.16%)d 0.00(0.00%)

-0.0009 -0.3567 0.0336 0.8478 -0.0236

-0.3761 0.0240 0.1011 0.0088 0.0012

0.0006 0.0016 0.0028 -0.0016



NBO of Tl(1)-C(6) and Tl(3)-C(5) bonds

(Occupancy) Bond orbital/ Coefficients/ Hybrids

2. (1.78177) BD (1)Tl 1 - C 6

(18.02%) 0.4245*Tl 1 s(2.82%)p34.34(96.95%)d 0.08(0.23%)

-0.1658 0.0272 -0.0086 0.0270 0.8695
0.0295 -0.4591 -0.0314 0.0307 -0.0270
0.0134 0.0174 0.0101
(81.98%) 0.9054* C 6 s(5.83%)p16.16(94.17%)d 0.00(0.00%)
-0.0006 -0.2384 0.0375 -0.2139 0.0067
-0.4945 0.0260 0.8061 -0.0297 0.0017
-0.0017 0.0025 -0.0001 -0.0004

5. (1.78177) BD (1)Tl 3 - C 5
(18.02%) 0.4245*Tl 3 s(2.82%)p34.34(96.95%)d 0.08(0.23%)
0.1658 -0.0272 -0.0086 0.0270 0.8695
0.0295 -0.4591 -0.0314 -0.0307 0.0270
-0.0134 -0.0174 -0.0101
(81.98%) 0.9054* C 5 s(5.83%)p16.16(94.17%)d 0.00(0.00%)
0.0006 0.2384 -0.0375 -0.2139 0.0067
-0.4945 0.0260 0.8061 -0.0297 -0.0017
0.0017 -0.0025 0.0001 0.0004

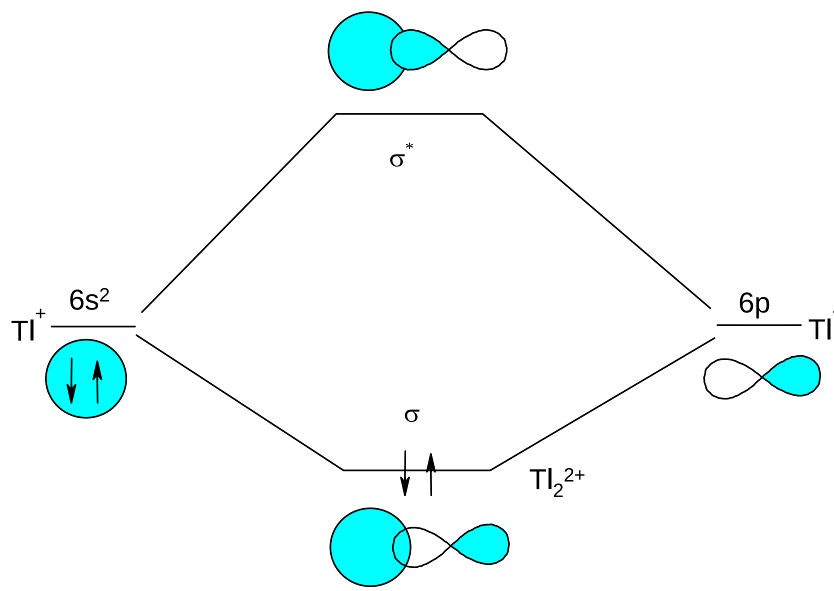
ADF Program calculated energies of fragments, dimer and energy difference between dimer and fragments:

	Non-relativistic (kJ mol^{-1})	**Relativistic (kJ mol^{-1})**	**Columbic potential energy (CPE) (kJ mol^{-1})**	**ΔE (kJ mol^{-1})**	
Tl^+	528.66	-115881.32			
Tl_2^{2+}	1416.86	-231388.27	398.92	-39.98[a]	-24.55[b]
Tl_2CH_2	-1622.71	-234434.34			
$[Tl_2CH_2]_2$	-3309.34	-468905.86	0.00	-63.92[a]	-37.18[b]

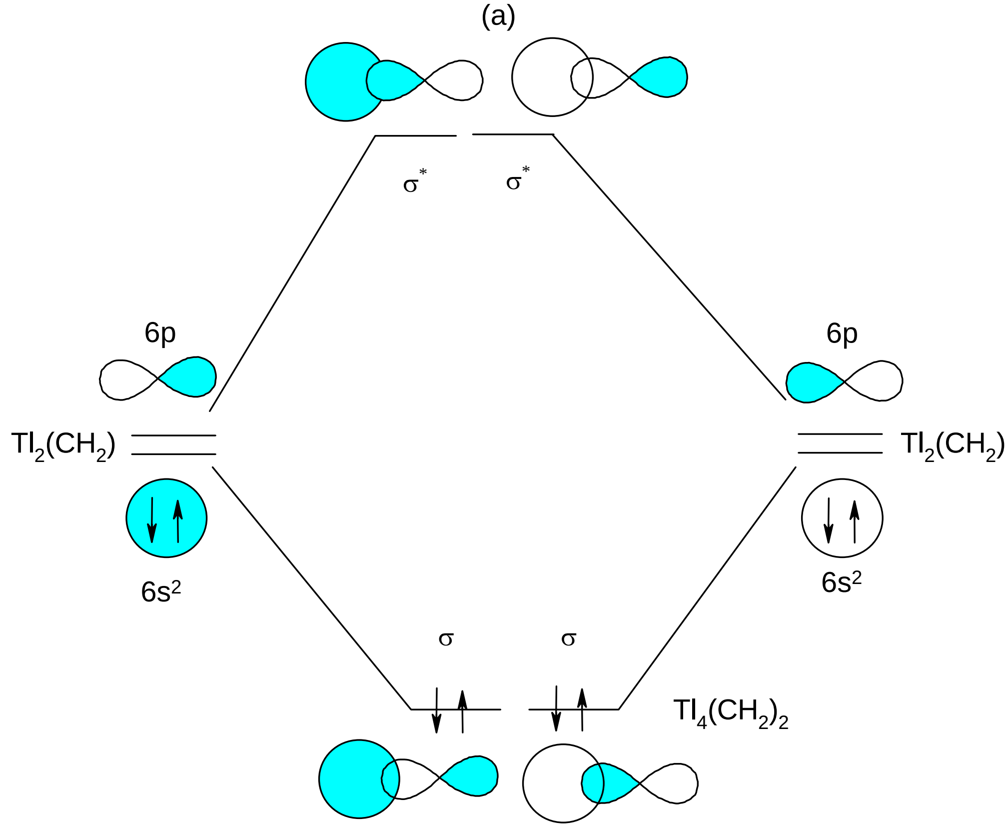
$\Delta E = E(Tl_2^{2+}) - 2E(Tl^+) - E(CPE)$ or $\Delta E = E([Tl_2(CH_2)]_2) - 2E(Tl_2(CH_2)) - E(CPE)$ and [a] Non-relativistic [b] Relativistic.

E(CPE) calculation use the Tl(I)-Tl(I) distance as shown in the molecular structure (3.4828(3) Å) and Bohr (a_0) = 0.52917 Angstroms (Å).

Energy Level Diagram for Formation of the Tl-Tl bond in the bimetal dimer (a) Tl_2^{2+} and in the Model Molecular dimer (b) $[Tl_2(CH_2)]_2$, based on the results obtained from NBO analysis and ADF energy calculations of both fragments and molecules.



(a)



(b)

Full Gaussian Reference citation:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 03*, *Revision C02 Gaussian, Inc.*, *Pittsburgh PA,* 2004.

NBO Citation: E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, Gaussian NBO Version 3.1 (c) C. N. Carlson, T. P. Hanusa, W. W. Brennessel, *J. Am. Chem. Soc.* **2004**, *126*, 10550-10551.

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References for other Multi Thallated Tl(I) systems

Crystal structures of 31 compounds which present Tl-Tl interaction supported by different bound ligands (other than C) are reported in the CCDC database .

(CCDC reference codes given in brackets)

A. With N-donor ligands on Tl (11 compounds):

(A1) W. M. Boesveld, P. B. Hitchcock, M. F. Lappert, H. Noth, (**2000**) *Angew. Chem., Int. Ed. Engl. ,39***,** 222. (CUQBIZ)

(A2) J. Beck, J. Strahle (**1986**) *Z. Naturforsch., Teil B, 41***,** 1381. (Two structures were reported in this paper). (FAMPOY, FAMPIS)

(A3) M. Veith, A. Spaniol, J. Pohlmann, F. Gross, V. Huch (**1993**) *Chem. Ber., 126***,** 2625. (LECHAC)

(A4) K. W. Hellmann, L. H. Gade, R. Fischer, T. Kottke (**1997**) *Chemistry-A European Journal, 3***,** 1801. (NEXLIL)

(A5) A. L. Rheingold, L. M. Liable-Sands, S. Trofimenko (**1997**) *Chem. Commun.,* 1691. (NISWER)

(A6) K. W. Hellmann, L. H. Gade, I. J. Scowen, M. McPartlin (**1996**) *Chem. Commun.,* 2515. (Two structures reported in this paper). (RACJEK, RACJIO)

(A7) M. S. Hill, R. Pongtavornpinyo, P. B. Hitchcock (**2006**) *Chem. Commun.,* 3720. (KENGEQ)

(A8) D. R. Manke, D. G. Nocera (**2006**) *Polyhedron, 25***,** 493. (Two structures were reported in this paper) (DEDZOC, DEFBAS).

B. With Gold Au(I) alone or Au(I) and O mixed binding to Tl (8 compounds):

(B1) E. J. Fernandez, J. M. Lopez-de-Luzuriaga, M. Monge, M. E. Olmos, J. Perez, A. Laguna (**2002**) *J. Am. Chem. Soc., 124*, 5942. (EFOWOL)

(B2) E. J.Fernandez, J. M.Lopez-de-Luzuriaga, M. E. Olmos, Perez, A. Laguna, M. C. Lagunas (**2005**) *Inorg. Chem.,44*, 6012. (Three structures reported in this paper) (WATHIJ, WATHOP, WATHUV).

(B3) E. J. Fernandez, A. Laguna, J. M. Lopez-de-Luzuriaga, M. Montiel, M. E. Olmos, J. Perez (**2005**) *Inorg. Chim. Acta, 358*, 4293. (TAXZIC)

(B4) M. V. Childress, D. Millar, T. M. Alam, K. A. Kreisel, G. P. A. Yap, L. N. Zakharov, J. A. Golen, A. L. Rheingold, L. H. Doerrer (**2006**) *Inorg. Chem., 45*, 3864. (Three structures were reported in this paper). (FAJNUA01, FAJPAI01, IDIHUZ)

C. With Silicon bound to Tl (3 compounds):

(C1) S. Henkel, K. W. Klinkhammer, W. Schwarz (**1994**) *Angew. Chem., Int. Ed. Engl., 33*, 681. (LEMHOA)

(C2) N. Wiberg, T. Blank, K. Amelunxen, H. Noth, H. Schnokel, E. Baum, A. Purath, D. Fenske (**2002**) *Eur. J. Inorg. Chem.,* 341. (XIJCEY)

(C3) three citations for one compound:

(a) N. Wiberg, K. Amelunxen, H. Noth, M. Schmidt, H. Schwenk (1996) *Angew. Chem., Int. Ed. Engl., 35*, 65. (coded ZOGBEC)

(b) N. Wiberg, K. Amelunxen, T. Blank, H.-W. Lerner, K. Polborn, H. Noth, R. Littger, M. Rackl, M. Schmidt-Amelunxen, H. Schwenk-Kircher, M. Warchold (**2001**) *Z. Naturforsch., Teil B, 56*, 634. (coded ZOGBEC01)

and in ref C2 (above) (coded ZOGBEC02)

D. With mixed N and O atoms bound to Tl (1 compound):

(D1) G. B. Deacon, E. E. Delbridge, C. M. Forsyth, B. W. Skelton, A. H. White (**2000**) *J. Chem. Soc., Dalton Trans.,* 745. (MAPREA)

E. With Cl and Si bonds to Tl (2 compounds):

(E1) N. Wiberg, T. Blank, H.-W. Lerner, D. Fenske, G. Linti (**2001**) *Angew. Chem., Int. Ed. Engl., 40,* 1232. (Two structures were reported in this paper). (QOFZOA, QOFZUG)

F. With Mn-Tl bonds (1 compound):

(F1) M. Schollenberger, B. Nuber, M. L. Ziegler, E. Hey-Hawkins (**1993**) *J. Organomet. Chem., 460*, 55. (YAXREU)

G. With carbon-Tl bonds (5 compounds):

(1). Compounds quoted as Ref. 17 in the present communication (two structures were reported in this paper). (MAKCEH, MAKCIL)

(2) A compound quoted as Ref. 15(a) in the present communication. (TIWNOC)

(3) Compounds quoted as Ref. 15(b) in present communication (two structures were reported in this paper). (TOCCAP, TOCCET)

Reference 16 in the present communication refers to a Tl(I)-C compound (coded NOSTAQ) but there are no Tl-Tl interactions in this compound being prevented by the bulk of the ligand and so this compound is not listed here.

END