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BIS[BIS(T-BUTYL)CYCLOPENTADIENYL]URANIUM CHLORIDE

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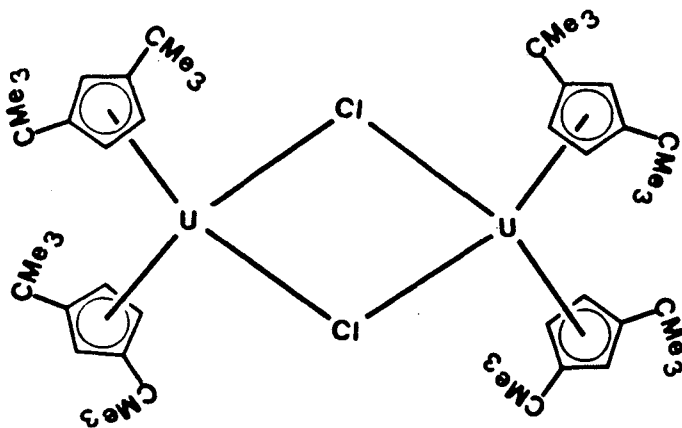
Bis[bis(t-butyl)cyclopentadienyl]uranium chloride

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Abstract. $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{UCl}_2$, $M_r = 1256.22$, orthorhombic, $Pccn$, $a = 13.040(3)$, $b = 17.086(3)$, $c = 24.587(3)$ Å, $V = 5478$ Å³, $Z = 4$, $D_x = 1.523$ g/cm³, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu = 57.24$ cm⁻¹, $F(000) = 2456$, $T = 296$ K, $R = 0.027$ [1293 data, $F^2 > 2\sigma(F^2)$]. Two $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{UCl}_2$ groups form a double chlorine-bridged dimer in which the uranium atom is bonded to two cyclopentadienyl rings and to two chlorine atoms with U-Cp and U-Cl distances of 2.516 and 2.856(4) Å, respectively.

Introduction. The title compound was prepared as part of a systematic synthetic and X-ray crystallographic study aimed at elucidating the solid state stereochemistry and geometrical alterations in trivalent uranium metallocenes as a function of coordination environment. It has been shown that the tris-cyclopentadienyl compounds of the type $(RC_5H_4)_3(L)$, where R is H or CH_3 and L is a Lewis base such as an ether, amine, thioether, or phosphine, can be isolated (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983), (Zalkin & Brennan, 1985,1987), (Brennan & Zalkin, 1985). When R is a sterically large group, such as Me_3Si , the base-free compound $(Me_3SiC_5H_4)_3U$ is isolated (Brennan, Andersen & Zalkin, 1986). Increasing the number of bulky substituents on the cyclopentadienyl ring by one gives the dimeric molecule $[1,3-(Me_3Si)_2C_5H_3]_4U_2(\mu-Cl)_2$ (Blake, Lappert, Taylor, Atwood, Hunter & Zhang, 1986). The title compound, $[1,3-(Me_3C)_2C_5H_3]_4U_2(\mu-Cl)_2$ is a related member of this series. The latter two compounds are an excellent pair of compounds in which the issue of intra-molecular steric effects in two molecules of identical empirical formulae that differ only in the replacement of the silicon atoms by carbon atoms may be addressed. A structural representation of the complex is shown below.



Experimental. The title compound was prepared from $K[1,3-(Me_3C)_2C_5H_3]$ and UCl_3 in tetrahydrofuran followed by crystallization from hexane as bright green crystals. An air-sensitive crystal, $0.1 \times 0.1 \times 0.25$ mm, was sealed inside a quartz capillary in an argon filled dry box. X-ray diffraction intensities (θ - 2θ scans) were obtained using a modified Picker FACS-I automatic diffractometer equipped with a graphite monochromator. Cell dimensions from 20 reflections, $22^\circ < 2\theta < 34^\circ$; analytical absorption correction, range 1.72-1.90; $\max \sin\theta/\lambda = 0.60$, h 0 to 15, k -20 to 19, l 0 to 14; three standard reflections, 1.4%, 1.0%, 4.3% variation in standards intensities from average, intensities adjusted isotropically; 5477 data, 2629 unique (with 1293, $F^2 > 2\sigma$), $R_{int} = 0.072$; structure solved by Patterson and Fourier methods; refined on F , 254 parameters; 42 hydrogen atoms in calculated positions and fixed isotropic thermal parameters; anisotropic thermal parameters for non-hydrogen atoms; $R = 0.12$ for all the data, $R = 0.027$ for $F^2 > 2\sigma$ data, $wR = 0.021$, $S = 1.01$; $w = 4F^2[\sigma^2(F^2) + (pf^2)^2]^{-1}$; $\max(\text{shift}/\sigma) = 0.14$; no extinction correction indicated; $\max.$ and $\min.$ of ΔF synthesis 3.3 and $-3.7 e \text{ \AA}^3$; atomic f for neutral U, Cl and C, and spherical bonded H from International Tables (1974); local unpublished programs and ORTEP (Johnson, 1965). Atomic parameters are listed in Table I*. A list of selected distances and angles is given in Table II. Figure 1 shows the molecule and its numbering scheme.

*Lists of anisotropic thermal parameters, calculated hydrogen positions, least-squares planes, distances and angles and additional ORTEP drawings have been deposited with the British Library Lending Division as Supplementary Publication No. XXXXX (pp.). Copies may be obtained through

The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results. The compound is a dimer in which the uranium atom is bonded to two cyclopentadienyl rings in a pentahapto fashion and to two chlorides which bridge the two uranium atoms. The cyclopentadienyl rings are rigorously planar but the tertiary carbon atoms of the t-butyl groups are out of the cyclopentadienyl ring plane and directed away from the uranium atom by an average of 0.27(4) Å. The rings of the bent sandwich molecule are in a staggered configuration with respect to each other about both the U1 and U2 atoms. The averaged U-C distance of 2.79(4) Å and the U-Cp(centroid) distance of 2.51 Å are not significantly different from these values in other trivalent uranium metallocenes. The averaged U-Cl distance of 2.856(1) Å is in the range found in other trivalent uranium compounds with bridging chloride ligands which range from 2.78(1) Å in $[(\text{Me}_6\text{C}_6)_3\text{U}_3(\mu\text{-Cl})_3(\mu_3\text{-Cl})_2(\mu\text{-Cl}_2\text{AlCl}_2)_3(\text{AlCl}_4)]$ (Cotton, Schwotzer & Simpson, 1986), 2.810±0.001 Å in $[1,3\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_4\text{U}_2(\mu\text{-Cl})_2$ (Blake, Lappert, Taylor, Atwood, Hunter & Zhang, 1986), and 2.90±0.01 Å in $[\text{Me}_5\text{C}_5]_6\text{U}(\mu\text{-Cl})_3$ (Fagan, Manriquez, Marks, Day, Vollmer & Day, 1982).

A comparison between the geometrical parameters in $[1,3\text{-}(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_4\text{U}_2(\mu\text{-Cl})_2$ and $[1,3\text{-}(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{U}_2(\mu\text{-Cl})_2$ is shown in Table III. The U-Cl distance in the $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$ compound is 0.046 Å longer and the U...U distance is 0.183 Å longer than the equivalent distances in the $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ compound. As a consequence the Cl-U-Cl angle in the $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$ compound is closed by 4°, the Cp-U-Cp angle is closed by 11° and the U-Cl-U angle is opened by 4° relative to the equivalent angles in the $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ compound. The geometry changes are small though they may be

rationalized by the fact that Me_3C groups are sterically larger than Me_3Si groups since carbon is 0.4 Å smaller than silicon, and accordingly the $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$ ligand is sterically larger than the $(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ ligand. The bulkier $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$ groups on a uranium center minimize their intramolecular ligand-ligand repulsions between the $(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3$ groups on the neighboring uranium atom in the dimer. This postulate accounts for the geometry changes listed in Table III.

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References

- Blake, P. C., Lappert, M. F., Taylor, R. G., Atwood, J. L., Hunter, W. E. & Zhang, H. (1986) J. Chem. Soc. Chem. Comm., 1394-1395.
- Brennan, J. G., Andersen, R. A. & Zalkin, A. (1986). Inorg. Chem. 25, 1756-1760.
- Brennan, J. G., Zalkin, A. (1985). Acta Cryst. C41, 1038-1040.
- Cotton, F. A., Schwotzer, W., & Simpson, C. Q. (1986) Angew. Chem. Int. Ed., 25, 637-639.
- Fagan, P. J., Manriquez, J. M., Marks, T. J., Day, C. S., Vollmer, S. H. & Day, V. W. (1982). Organometallics 1, 170-180.
- International Tables for X-ray Crystallography (1974). Vol. IV; Table 2.2, pp 71-102. Birmingham: Kynoch Press.
- Johnson, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- Wasserman, H. J., Zozulin, A. J., Moody, D. C., Ryan, R. R. & Salazar, K. V. (1983). J. Organomet. Chem. 254, 305-311.
- Zalkin, A. & Brennan, J. G. (1985). Acta Cryst. C41, 1295-1297.
- Zalkin, A. & Brennan, J. G. (1987). Acta Cryst. C43, 1919-1922.

Table I. Atomic Parameters

$$B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

Atom	x	y	z	Beq
U1	1/4	1/4	0.29597(3)	3.38(2)
U2	1/4	1/4	0.11133(2)	3.53(2)
C2	0.34838(28)	0.18173(22)	0.20369(18)	4.2(1)
C1	0.4315(12)	0.3388(10)	0.3085(6)	4.3(6)
C2	0.3501(14)	0.3894(9)	0.3226(7)	4.4(6)
C3	0.3094(10)	0.3609(10)	0.3723(6)	3.1(5)
C4	0.3638(12)	0.2915(9)	0.3847(8)	4.1(5)
C5	0.4378(12)	0.2780(8)	0.3467(6)	3.9(5)
C6	0.3645(16)	0.3900(11)	0.1003(7)	5.2(7)
C7	0.2806(11)	0.3994(11)	0.0632(6)	3.9(6)
C8	0.2990(14)	0.3402(10)	0.0242(8)	5.9(6)
C9	0.3883(14)	0.2977(9)	0.0336(7)	4.8(6)
C10	0.4306(15)	0.3298(12)	0.0829(8)	5.2(7)
C11	0.3325(14)	0.4719(10)	0.2998(11)	3.7(5)
C12	0.3705(15)	0.4785(9)	0.2431(8)	8.2(7)
C13	0.3826(16)	0.5314(10)	0.3345(8)	8.8(8)
C14	0.2148(12)	0.4904(12)	0.2980(12)	5.9(8)
C15	0.5267(12)	0.2195(9)	0.3504(7)	4.8(6)
C16	0.5965(11)	0.2431(19)	0.3961(7)	8.9(7)
C17	0.5917(13)	0.2171(11)	0.2988(8)	9.4(9)
C18	0.4880(13)	0.1375(11)	0.3635(10)	10.2(9)
C19	0.2033(15)	0.4635(11)	0.0624(8)	6.4(8)
C20	0.231(3)	0.5217(10)	0.0216(8)	12.5(10)
C21	0.1933(15)	0.5066(11)	0.1174(10)	9.5(9)
C22	0.0988(15)	0.4313(11)	0.0488(10)	10.7(9)
C23	0.5381(15)	0.3129(15)	0.1019(10)	5.3(8)
C24	0.5530(11)	0.3334(11)	0.1613(7)	7.0(6)
C25	0.6111(14)	0.3700(12)	0.0693(7)	8.7(7)
C26	0.5748(15)	0.2329(22)	0.0929(11)	11.4(19)

Table II. Selected Distances(Å) and Angles(°)^a

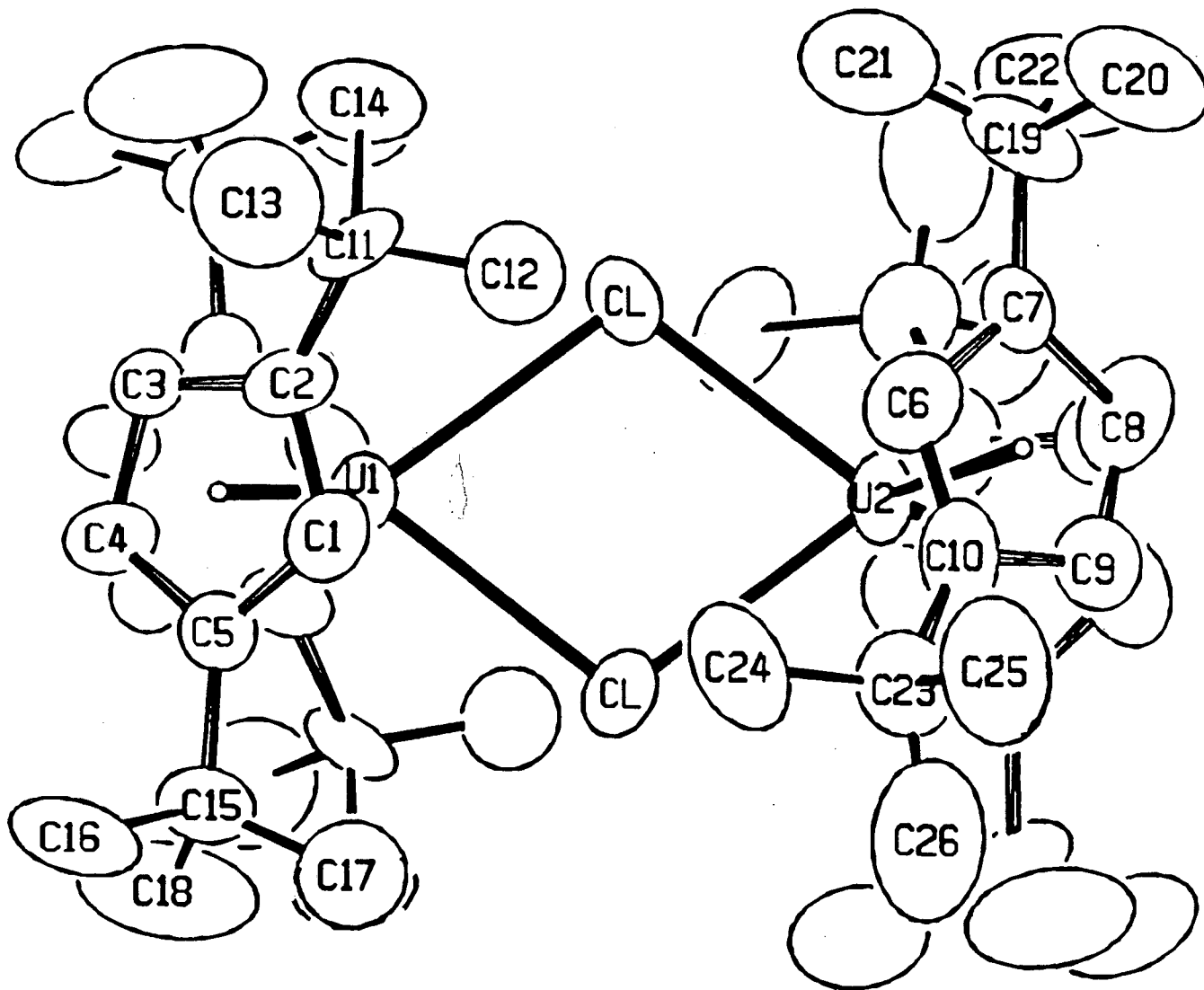
<U1 - C>	2.78(4)
<U2 - C>	2.79(5)
U1 - Cp1	2.516
U2 - Cp2	2.516
U1 - Cl	2.856(4)
U2 - Cl'	2.857(4)
U1 - U2	4.540(1)
Cl - Cl	3.468(7)
Cp1 - U1 - Cp1'	120.2
Cp2 - U2 - Cp2'	120.9
Cp1 - U1 - Cl	108.9
Cp1 - U1 - Cl'	117.9
Cp2 - U2 - Cl	115.8
Cp2 - U2 - Cl'	110.5
Cl - U1 - Cl'	74.77(17)
Cl - U2 - Cl'	74.73(15)
U1 - Cl - U2	105.25(11)

^a Cp1 and Cp2 are the centroids of cyclopentadienyl ring atoms C1 - C5 and C6 - C10 respectively. Cp1', Cp2' and Cl' represent the equivalent groups or atoms at 1/2-x, 1/2-y, z.

Table III. Bond Lengths and Angles Comparison

Parameter	$[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_4\text{U}_2(\mu\text{-Cl})_2$	$[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_4\text{U}_2(\mu\text{-Cl})_2$
U-C(ave), Å	2.78(2)	2.78(4)
U-Cp(ave), Å	2.50	2.52
U-Cl(ave), Å	2.710(4)	2.856(1)
U...U, Å	4.357(1)	4.540(1)
Cl-U-Cl, °	78.5(1)	74.7(2)
Cl-U-Cp(ave), °	107	113
Cp-U-Cp(ave), °	131	120
Cl-Cl-U, °	101.5()	105.3

Fig 1. ORTEP drawing with thermal ellipsoids at 50% probability level.



Supplemental Materials

Bis[bis(t-butyl)cyclopentadienyl]uranium chloride

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Department of Chemistry, University of California, Berkeley, CA 94720

Abstract. $(((\text{CH}_3)_3\text{C})_2\text{C}_5\text{H}_3)_2\text{UCl}_2$, $M_r = 1256.22$, orthorhombic, $Pccn$, $a = 13.040(3)$, $b = 17.086(3)$, $c = 24.587(1)$ Å, $V = 5478$ Å³, $Z = 4$, $D_x = 1.523$ g/cm³, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu = 57.24$ cm⁻¹, $F(000) = 2456$, $T = 296$ K, $R = 0.027$ [1293 data, $F^2 > 2\sigma(F^2)$]. Two $(\text{Me}_3\text{C})_2\text{CpUCl}$ groups form a double chlorine-bridged dimer in which the uranium atom is bonded to two cyclopentadienyl rings and to two chlorine atoms with U-Cp and U-Cl distances of 2.516 and 2.856(4) Å, respectively.

Supplemental Table 1. Anisotropic Thermal Parameters (\AA^2) with Estimated Standard Deviations for $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{UCl}_2\}_2$

Atom	B11	B22	B33	B12	B13	B23
U1	3.64(4)	3.84(4)	2.67(3)	-0.11(16)	0	0
U2	3.76(4)	4.25(5)	2.58(4)	-1.19(15)	0	0
C1	4.45(20)	4.55(20)	3.53(15)	-0.13(17)	1.16(28)	-0.30(27)
C2	3.5(8)	5.2(9)	4.2(11)	-0.6(8)	-0.1(8)	-1.1(8)
C3	4.4(10)	3.7(10)	5.2(9)	1.1(8)	-0.4(8)	-1.3(8)
C4	2.7(8)	3.6(9)	3.1(7)	0.3(6)	-0.4(6)	-0.6(7)
C5	3.0(7)	4.0(10)	5.3(9)	0.4(7)	1.1(8)	0.4(8)
C6	4.0(8)	3.9(11)	3.6(7)	0.2(7)	0.4(7)	0.5(6)
C7	4.6(11)	5.0(12)	6.0(11)	-1.5(10)	1.6(10)	0.1(9)
C8	2.6(12)	5.7(10)	3.3(8)	-0.3(7)	0.1(6)	1.2(7)
C9	7.4(14)	4.6(9)	5.6(9)	-2.8(9)	-0.6(9)	-2.7(8)
C10	4.4(10)	5.3(10)	4.8(13)	-0.4(8)	-0.2(9)	0.2(8)
C11	5.7(13)	6.2(12)	3.8(10)	-1.9(10)	-0.2(9)	0.0(9)
C12	3.5(11)	2.6(8)	5.1(10)	-0.1(7)	0.9(13)	-2.0(10)
C13	12.1(16)	6.4(11)	6.2(11)	2.4(11)	0.0(13)	0.2(10)
C14	11.2(16)	4.8(10)	10.4(14)	-2.7(10)	-1.4(13)	-0.4(10)
C15	3.9(16)	4.3(9)	9.4(13)	0.0(7)	0.0(13)	0.9(13)
C16	3.1(8)	5.5(12)	5.8(10)	1.0(7)	-1.4(8)	-0.6(8)
C17	6.2(9)	10.3(14)	10.2(11)	4.9(17)	-2.2(9)	0.8(24)
C18	6.1(10)	14.6(24)	7.4(10)	4.3(10)	2.2(12)	1.8(14)
C19	2.8(9)	7.9(13)	19.9(23)	0.0(9)	-1.6(13)	1.6(15)
C20	7.2(14)	3.4(9)	8.6(16)	0.5(9)	-1.2(10)	2.9(10)
C21	15.5(25)	9.5(11)	12.5(15)	5.4(21)	3.6(22)	7.4(11)
C22	10.2(18)	6.2(12)	12.1(18)	1.3(10)	-2.2(14)	-0.9(12)
C23	7.0(12)	7.1(11)	18.0(23)	0.9(10)	-2.5(18)	0.4(16)
C24	1.4(9)	8.3(17)	6.2(13)	-1.5(9)	0.0(9)	0.7(12)
C25	3.2(9)	11.5(14)	6.3(10)	-1.7(9)	-3.6(8)	0.4(10)
C26	6.2(11)	12.2(15)	7.7(11)	-3.9(11)	0.3(9)	1.6(11)
C27	2.4(11)	23.6(53)	8.0(13)	-1.2(22)	-0.7(9)	-1.0(27)

* The anisotropic temperature factor has the form $T = -0.25 \exp(\sum_i h_i B_{ij} a_i^* a_j^*)$

Supplemental Table 2. Positional and Thermal Parameters of Fixed Atoms
for $[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{UCl}_2$

Atom	x	y	z	B(Å ²)
H1	0.4765	0.3458	0.2770	10.000
H2	0.2549	0.3857	0.3940	10.000
H3	0.3490	0.2577	0.4158	10.000
H4	0.3749	0.4205	0.1335	10.000
H5	0.2532	0.3304	-0.0063	10.000
H6	0.4167	0.2553	0.0114	10.000
H7	0.3346	0.4406	0.2200	10.000
H8	0.4443	0.4673	0.2426	10.000
H9	0.3583	0.5314	0.2296	10.000
H10	0.4563	0.5212	0.3358	10.000
H11	0.3537	0.5289	0.3711	10.000
H12	0.3704	0.5836	0.3190	10.000
H13	0.1876	0.4876	0.3356	10.000
H14	0.1798	0.4518	0.2756	10.000
H15	0.2040	0.5429	0.2837	10.000
H16	0.5578	0.2432	0.4307	10.000
H17	0.6236	0.2956	0.3896	10.000
H18	0.6533	0.2058	0.3992	10.000
H19	0.6204	0.2690	0.2918	10.000
H20	0.5479	0.2017	0.2680	10.000
H21	0.6469	0.1790	0.3031	10.000
H22	0.4417	0.1200	0.3345	10.000
H23	0.4517	0.1378	0.3982	10.000
H24	0.5467	0.1014	0.3657	10.000
H25	0.2324	0.4965	-0.0146	10.000
H26	0.2975	0.5439	0.0296	10.000
H27	0.1785	0.5631	0.0210	10.000
H28	0.2600	0.5294	0.1280	10.000
H29	0.1729	0.4688	0.1462	10.000
H30	0.1421	0.5479	0.1154	10.000
H31	0.0791	0.3926	0.0772	10.000
H32	0.1003	0.4050	0.0137	10.000
H33	0.0485	0.4735	0.0486	10.000
H34	0.5058	0.3018	0.1833	10.000
H35	0.5395	0.3887	0.1667	10.000
H36	0.6240	0.3212	0.1722	10.000
H37	0.5924	0.4236	0.0773	10.000
H38	0.6035	0.3596	0.0301	10.000
H39	0.6826	0.3602	0.0799	10.000
H40	0.5726	0.2206	0.0540	10.000
H41	0.5304	0.1963	0.1127	10.000
H42	0.6454	0.2277	0.1061	10.000

* The isotropic temperature factor has the form: $T = \exp[-B(\sin\theta/\lambda)^2]$.

Supplemental Table 3. Additional Distances in $\{[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_3]_2\text{UCl}_2\}_2$

Atoms	d(Å)	Atoms	d(Å)	Atoms	d(Å)
U1 - C1	2.829(16)	C15 - C16	1.501(22)	H19 - C17	0.980
U1 - C2	2.794(16)	C15 - C17	1.525(20)	H20 - C17	0.984
U1 - C3	2.777(14)	C15 - C18	1.525(21)	H21 - C17	0.975
U1 - C4	2.732(17)	C19 - C20	1.456(23)	H22 - C18	0.980
U1 - C5	2.790(15)	C19 - C21	1.546(25)	H23 - C18	0.975
U2 - C6	2.832(17)	C19 - C22	1.507(23)	H24 - C18	0.985
U2 - C7	2.841(17)	C23 - C24	1.515(26)	H25 - C20	0.989
U2 - C8	2.715(18)	C23 - C25	1.581(30)	H26 - C20	0.972
U2 - C9	2.752(15)	C23 - C26	1.465(42)	H27 - C20	0.982
U2 - C10	2.810(18)	H1 - C1	0.980	H28 - C21	0.989
C1 - C2	1.412(18)	H2 - C3	0.984	H29 - C21	0.995
C1 - C5	1.404(17)	H3 - C4	0.978	H30 - C21	0.973
C2 - C3	1.418(19)	H4 - C6	0.978	H31 - C22	0.995
C2 - C11	1.535(23)	H5 - C8	0.973	H32 - C22	0.972
C3 - C4	1.415(16)	H6 - C9	0.979	H33 - C22	0.975
C4 - C5	1.362(18)	H7 - C12	0.979	H34 - C24	0.981
C5 - C15	1.533(16)	H8 - C12	0.982	H35 - C24	0.970
C6 - C7	1.434(20)	H9 - C12	0.977	H36 - C24	0.986
C6 - C10	1.408(21)	H10 - C13	0.976	H37 - C25	0.968
C7 - C8	1.413(19)	H11 - C13	0.977	H38 - C25	0.986
C7 - C19	1.489(19)	H12 - C13	0.983	H39 - C25	0.982
C8 - C9	1.391(19)	H13 - C14	0.990	H40 - C26	0.981
C9 - C10	1.442(21)	H14 - C14	0.974	H41 - C26	0.981
C10 - C23	1.504(24)	H15 - C14	0.974	H42 - C26	0.980
C11 - C12	1.483(30)	H16 - C16	0.991		
C11 - C13	1.480(24)	H17 - C16	0.977		
C11 - C14	1.568(21)	H18 - C16	0.980		

Supplemental Table 4. Additional Angles in $\{[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{UCl}\}_2$

Atoms	Angle(°)	Atoms	Angle(°)
Cl - U1 - Cl	74.77(17)	C6 - C7 - C19	127.5(18)
Cl - U2 - Cl	74.73(15)	C8 - C7 - C19	129.2(17)
U1 - Cl - U2	105.25(11)	C7 - C8 - C9	113.8(16)
C2 - C1 - C5	109.4(15)	C8 - C9 - C10	105.1(16)
C1 - C2 - C3	106.5(15)	C6 - C10 - C9	107.4(17)
C1 - C2 - C11	125.8(18)	C6 - C10 - C23	128.1(21)
C3 - C2 - C11	125.1(17)	C9 - C10 - C23	123.0(20)
C2 - C3 - C4	106.6(14)	C2 - C11 - C12	111.3(14)
C3 - C4 - C5	110.5(15)	C2 - C11 - C13	110.7(18)
C1 - C5 - C4	107.0(15)	C2 - C11 - C14	110.0(20)
C1 - C5 - C15	124.4(17)	C12 - C11 - C13	110.0(19)
C4 - C5 - C15	127.3(17)	C12 - C11 - C14	106.6(24)
C7 - C6 - C10	110.9(18)	C13 - C11 - C14	108.0(19)
C6 - C7 - C8	102.8(15)		

Supplemental Table 5. Least Squares Planes and Deviations Therefrom
 $((\text{Me}_3\text{C})_2\text{C}_5\text{H}_3)_2\text{UCl}_2$

Plane #1

$$8.47624 a + 9.32984 b + 12.99402 c - 10.81250$$

Distance(Å) to the plane

atoms in the plane		atoms not in plane	
C1	0.015(23)	U1	-2.515(8)
C2	-0.020(22)	C11	0.30(4)
C3	0.015(21)	C15	0.25(3)
C4	-0.010(23)		
C5	-0.003(21)		

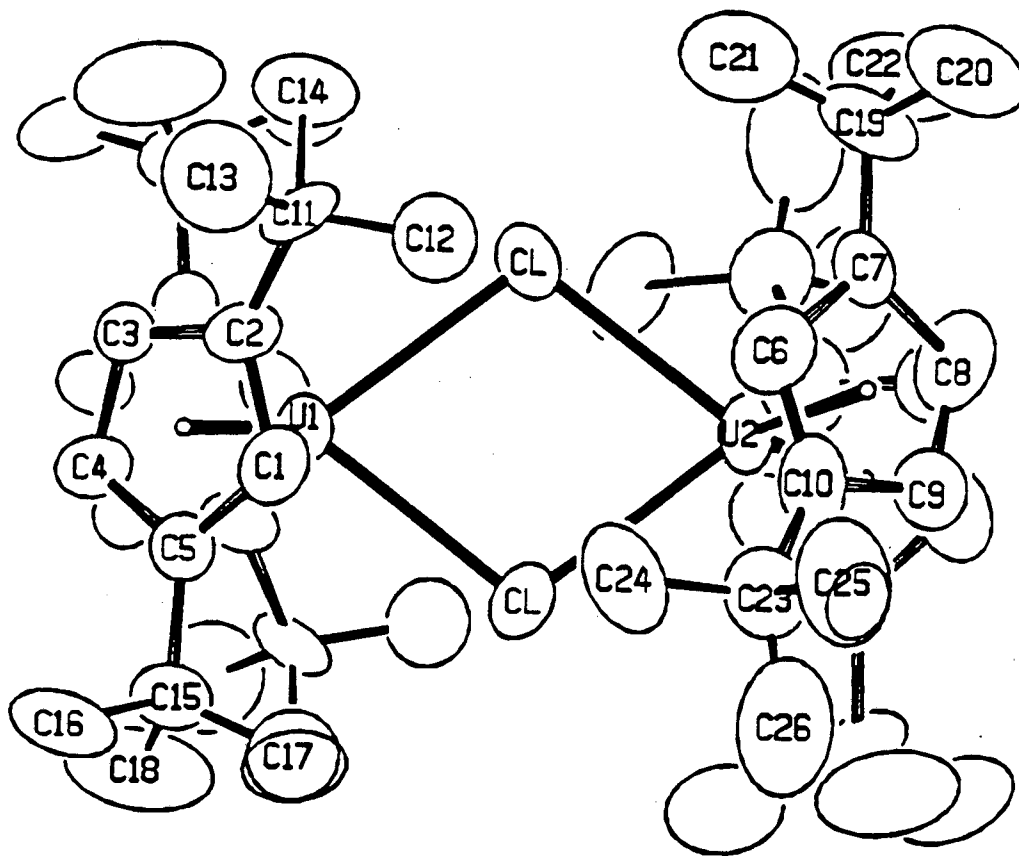
Plane #2

$$6.88778 a + 11.21458 b - 13.24486 c - 5.56382$$

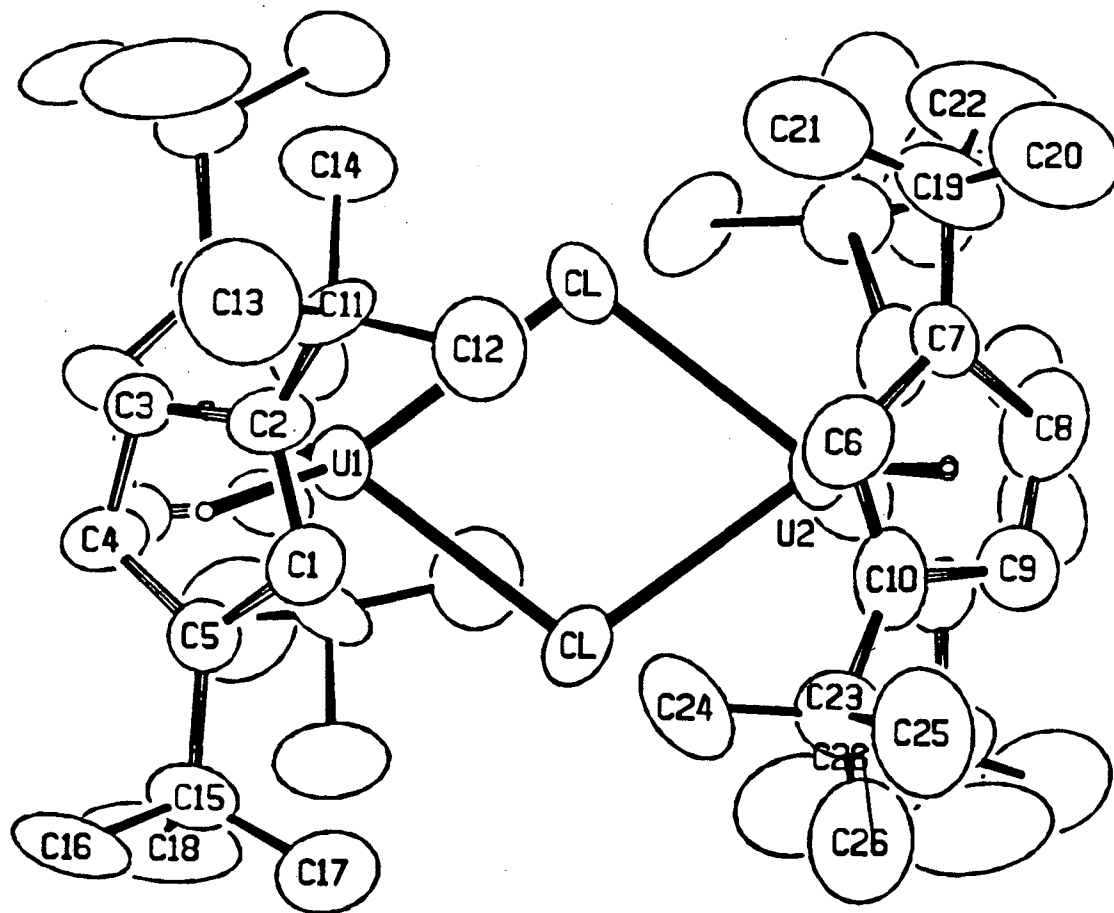
Distance(Å) to the plane

atoms in the plane		atoms not in plane	
C6	-0.008(25)	U2	-2.513(9)
C7	0.011(25)	C19	0.21(4)
C8	-0.010(24)	C23	0.30(4)
C9	0.004(23)		
C10	0.002(25)		

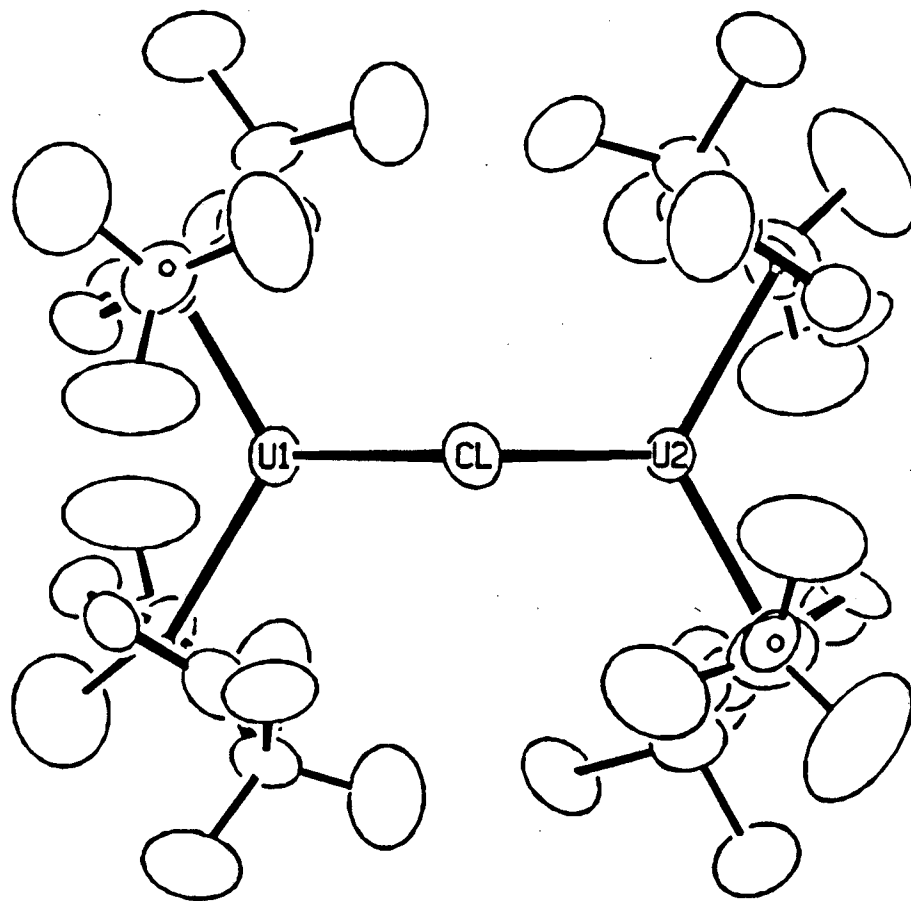
Supplemental Figure 1. ORTEP drawing looking down the line through the centroids of Cp1; 50% probability ellipsoids.



Supplemental Figure 2. ORTEP drawing looking down the line through the centroids of Cp2; 50% probability ellipsoids.



Supplemental Figure 3. ORTEP drawing looking down the line through the Cl atoms; 50% probability ellipsoids.



OBSERVED STRUCTURE AMPLITUDES, STANDARD DEVIATIONS, AND DIFFERENCES (ALL X 2.0)
 {(CH3)3C}2C5H3}2UCL-Pccn F(0,0,0) = 4747

SG = Estimated standard deviation of Fob. DEL = /Fob/- /Fca/, where
 Fob and Fca are the observed and calculated structure amplitudes.
 F000 = 2.0 x (no. of electrons in the unit cell adjusted for dispersion and omitted atoms).
 * indicates zero weighted data.

K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL								
	H,L= 0, 0			14	98 56		17*	0	120 11		8	13	65100		-10*	H,L= 1, 2	3	50 55	6*	11	414 8		-5	7	21 87		-2*												
21	458 19	-29		15	282 10		-6	1	219 6	11		14	154 25	14		0	328 4	-3		41040	11	6		12	100 30		-4*	8	560 8		-4								
41	359 14	27		16	73101		13*	2	86 26		-20*	H,L= 0, 22	1	437 5	1	5	256 4	2		13	392 8	2		9	56 90		1*	10	448 28		9								
6	564 7	1		17	235 13		9	3	114 15	-5		0	575 10	7		2	226 3	1		6	881 10	-4		14	104 49	15*		11	65 97		59*	11	58 9		0				
8	609 9	-4		18	89 94		43*	4	131 14	2		1	46 87	5*		3	390 4	4		7	57 59	-33*		15	295 10	10		11	65 97		59*	12	319 10		0				
10	563 7	-3		19	177 18	11		5	70 76	-34*		2	479 8	4		4	312 4	6		8	877 10	-12		16	0108	-55*		12	319 10		0								
12	514 7	3		H,L= 0, 8				6	108 37	-24*		3	0101	-14*		5	353 4	5		9	91 25	-34		17	210 15	-2		13	66104		51*	14	253 12		9				
14	499 8	13		0	179 6	2		7	137 16	23		4	454 7	14		6	227 4	3		10	581 7	11		18	59107	42*		15	0111	-10*		15	0111	-10*					
16	272 11	-16		1	77 20	-7		8	110 23	15		5	67 82	30*		7	183 5	6		11	42 91	-10*		19	124 52	-16*		16	212 15	13		16	212 15	13					
18	245 13	15		2	37 57	2*		9	188 13	-12		6	325 8	2		8	71 26	-5*		12	470 8	-16		H,L= 1, 11				16	212 15	13		16	212 15	13					
20	154 21	11		3	54 57	12*		10	56 97	-8*		7	26 94	-43*		9	282 5	-1		13	86 89	-6*		1	0139	-14*		H,L= 1, 11				16	212 15	13		16	212 15	13	
	H,L= 0, 2			4	164 6	6		11	88 89	-15*		8	310 8	11		10	80 24	-17*		14	347 9	16		2	0 75	-57*		0	203 16	-12		0	203 16	-12		0	203 16	-12	
1	312 4	0		5	130 7	-5		12	0 99	-33*		9	0 97	-46*		11	142 14	-13		15	28 99	-13*		3	0 85	-24*		1	101 46	-15*		1	101 46	-15*		1	101 46	-15*	
2	419 5	11		6	41 61	-24*		13	38 90	-31*		10	268 10	3		12	170 13	6		16	271 11	9		4	47 69	-45*		2	183 13	-1		2	183 13	-1		2	183 13	-1	
3	42 48	9*		7	26 64	5*		14	65104	25*		11	56 98	40*		13	224 11	1		17	38106	4*		5	60 78	55*		3	30 97	-108*		3	30 97	-108*		3	30 97	-108*	
4	526 6	8		8	153 8	3		15	86104	71*		12	264 10	16		14	60103	-75*		18	186 17	-5		6	26 81	23*		4	317 7	2		4	317 7	2		4	317 7	2	
5	89 18	-15		9	101 36	-10*		16	96107	71*		13	64100	44*		15	84103	-59*		19	0112	-33*		H,L= 1, 12				5	163 19	-15		5	163 19	-15		5	163 19	-15	
6	119 10	6		10	0 90	-35*		17	53108	12*		H,L= 0, 24				16	92 66	14*		H,L= 1, 7				0	252 5	-2		6	251 9	-2		6	251 9	-2					
7	45 55	12*		11	44 94	-20*		H,L= 0, 16			0	0121	-87*		7	130 23	-5		1	54 62	52*		1	764 8	-1		7	184 12	-12		7	184 12	-12		7	184 12	-12		
8	239 5	4		12	59 96	47*		0	0104	-18*		1	63101	-13*		18	34 96	4*		2	0109	-22*		2	320 5	0		8	242 9	-5		8	242 9	-5		8	242 9	-5	
9	51 62	28*		13	91 69	80*		1	600 8	-3		2	87 89	9*		19	47109	-2*		3	90 24	-16		3	620 7	-1		9	59 91	-49*		9	59 91	-49*		9	59 91	-49*	
10	178 7	-1		14	78100	-27*		2	101 21	23		3	44 85	2*		20	102109	75*		4	96 21	20		4	190 6	-11		10	174 13	-4		10	174 13	-4		10	174 13	-4	
11	119 29	-33		15	0101	-28*		3	618 8	-4		4	75 92	16*		H,L= 1, 3				5	64 68	38*		5	487 6	6		11	55 87	-17*		11	55 87	-17*		11	55 87	-17*	
12	203 12	0		16	8 94	4*		4	29 82	5*		5	45 86	32*		1	59 11	-4		6	64 64	-14*		6	118 15	-20		12	132 27	-17		12	132 27	-17		12	132 27	-17	
13	182 14	-7		17	0105	-24*		5	689 9	-2		6	13 93	2*		2	202 5	6		7	42 67	39*		7	374 7	4		13	36 90	-9*		13	36 90	-9*		13	36 90	-9*	
14	190 14	-4		18	41106	35*		6	52 84	24*		7	47 98	24*		3	60 46	22*		8	46 56	27*		8	148 15	-7		14	89 58	-7*		14	89 58	-7*		14	89 58	-7*	
15	149 29	-6		19	56111	17*		7	554 8	-11		8	0 91	-25*		4	276 5	0		9	30 84	-47*		9	388 8	11		15	80 98	28*		15	80 98	28*		15	80 98	28*	
16	76 92	-53*		H,L= 0, 10				8	86 98	17*		9	61100	47*		5	127 10	1		H,L= 1, 8				10	128 34	-14		H,L= 1, 20				10	128 34	-14		10	128 34	-14	
17	73 88	20*		01067	11	-17		9	539 8	10		10	63 99	21*		6	0 68	-2*		0	32 58	23*		11	347 9	12		0	165 23	1		0	165 23	1		0	165 23	1	
18	47107	-41*		1	116 8	9		10	99 57	70*		11	48100	17*		7	0 62	-12*		1	37 58	27*		12	95 64	-32*		1	292 9	10		1	292 9	10		1	292 9	10	
19	87 97	46*		2	983 10	-16		11	359 9	11		H,L= 0, 26			8	83 43	52*		2	24 58	-18*		13	282 10	-3		2	54101	-76*		2	54101	-76*		2	54101	-76*		
20	0101	-32*		3	271 5	-6		12	0102	-11*		0	0127	-75*		9	0 79	-20*		3	122 7	6		14	29 92	-37*		3	258 10	5		3	258 10	5		3	258 10	5	
	H,L= 0, 4			4	764 8	-2		13	275 11	-5		1	261 12	24		10	77 34	0*		4	96 15	-18		15	230 13	8		4	86 48	-10*		4	86 48	-10*		4	86 48	-10*	
0	742 8	-6		5	134 8	-1		14	72104	59*		2	128 39	31*		H,L= 1, 4				5	35 59	17*		16	21 96	-62*		5	265 8	16		5	265 8	16		5	265 8	16	
11	193 12	3		6	503 6	-5		15	205 15	10		3	234 11	4		0	1154	12	4	6	66 29	1*		17	183 17	1		6	80 85	-35*		6	80 85	-35*		6	80 85	-35*	
2	654 7	0		7	171 7	7		16	47111	40*		4	71 92	-28*		1	223 4	2		7	127 8	-2		18	67111	25*		7	142 24	-20		7	142 24	-20		7	142 24	-20	
3	526 6	16		8	514 7	-2		17	196 17	18		5	256 10	7		2	298 4	3		8	63 45	4*		H,L= 1, 13				8	78 91	-22*		8	78 91	-22*		8	78 91	-22*	
4	215 5	0		9	71 87	24*		H,L= 0, 18			6	51 97	-19*		3	233 4	5		9	66 84	-5*		1	0 98	-91*		9	177 13	6		9	177 13	6		9	177 13	6		
5	859 7	-1		10	424 7	7		0	93109	5*		7	268 10	19		4	708 15	-6		10	99 54	32*		2	108 16	-20		10	73 87	-9*		10	73 87	-9*		10	73 87	-9*	
6	374 5	3		11	79 98	-54*		1	202 12	4		8	0100	-46*		5	207 5	-1		11	90 91	37*		3	38117	-45*		11	154 16	19		11	154 16	19		11	154 16	19	
7	689 7	-5		12	469 8	6		2	88 62	-30*		9	209 14	-6		6	608 7	-9		12	77 96	60*		4	78 53	-24*		12	81 97	4*		12	81 97	4*		12	81 97	4*	
8	343 5	5		13	73 89	-14*		3	266 9	8		H,L= 0, 28			7	368 5	-8		13	91 99	13*		5	0 85	-32*		13	149 17	-7		13	149 17	-7		13	149 17	-7		
9	532 6	0		14	363 9	0		4	159 12	13		0	57130	3*		8	594 7	-10		14	77 96	54*		H,L= 1, 14				14	64 94	-4*		14	64 94	-4*		14	64 94	-4*	

K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	K	FOB	SG	DEL	
10	31100	9*		H,L= 2, 4	13	86	97	71*	7	158	15	-14	12	251	11	7	1	297	5	18	4	45	59	-5*	0	174	16	-25				
11	0101	-39*		0	69	27	10*	14	72	96	34*	8	0	99	-91*	13	96102	79*	2	290	19	18	5	66	31	-8*	1	120	15	12		
	H,L= 1, 26			1	532	6	8	15	72	98	68*	9	123	36	-25*	H,L= 2, 24	3	365	5	7	6	43	64	5*	2	180	10	4				
0	266	16	13	2	151	6	1	16	91	83	83*	10	64100	-16*	0	111115	40*	4	208	6	12	7	38	68	32*	3	162	12	-10			
1	83106	12*		3	497	6	7	17	0107	-6*	11	73	90	-17*	1	81102	-5*	5	142	9	4	8	73	73	11*	4	175	12	-5			
2	234	13	1	4	225	4	-8	18	77104	76*	12	0101	-37*	2	98100	20*	6	60	64	-38*	9	50	85	40*	5	101	37	19*				
3	84	66	-13*	5	627	7	-14	19	58100	52*	13	47102	5*	3	35	92	-34*	7	0	72	-14*	10	45	91	-19*	6	120	19	3			
4	252	10	8	6	303	4	-2	H,L= 2, 9	14	79102	55*	4	85	52	18*	4	85	52	18*	8	41	76	12*	11	121	19	24	7	56	84	-7*	
5	71	92	-14*	7	571	6	-5	1	28	69	-18*	15	0108	-28*	5	85	92	44*	9	53	81	41*	12	0100	-52*	8	91	68	-23*			
6	254	10	10	8	243	5	5	2	0	70	-26*	16	30108	9*	6	41	94	1*	H,L= 3, 4	13	28	98	22*	9	0	99	-62*					
7	76	99	22*	9	506	6	-8	3	59	65	-46*	17	84113	37*	7	0	96	-40*	0	741	8	13	14	79	84	16*	10	87	88	-7*		
8	236	12	8	10	101	36	-52*	4	104	25	-34*	H,L= 2, 16	8	28	97	-16*	1	416	5	4	15	36100	12*	11	71	88	-33*					
9	76100	29*		11	306	8	-16	5	148	10	-5	0	96106	-44*	9	81	96	54*	2	622	7	5	16	63104	52*	12	75100	-4*				
	H,L= 1, 28			12	45	94	-75*	6	113	14	9	1	583	8	-1	10	0101	-42*	3	308	4	6	17	47	94	43*	13	54101	4*			
0	119136	-75*		13	307	9	-2	7	44	80	22*	2	44	79	-25*	11	49	99	15*	4	693	8	-6	18	99107	94*	14	42103	-9*			
1	68	75	5*	14	82101	-3*		H,L= 2, 10	3	599	8	-5	3	599	8	-5	H,L= 2, 26	5	325	4	-6	19	83109	82*	15	49	95	3*				
2	156	39	-54	15	193	14	-14	0	901	10	8	4	0	93	-47*	0	18126	-31*	6	527	6	-6	H,L= 3, 9	16	13110	-45*						
3	70	95	-3*	16	101	53	15*	1	210	5	-5	5	605	8	-7	1	257	12	-6	7	162	6	-2	1	31	70	20*	17	45114	22*		
4	232	12	6	17	155	19	-2	2	746	8	-5	6	18	87	-25*	2	102106	35*	8	489	6	-4	2	175	8	9	H,L= 3, 16					
5	81	98	2*	18	20109	-42*		3	212	5	-4	7	523	8	-11	3	242	11	6	9	188	7	-1	3	114	12	0	0	671	10	-13	
	H,L= 2, 0			19	115	60	-18*	4	780	8	-13	8	79	99	42*	4	100	72	18*	10	334	7	-3	4	245	7	-1	1	60	91	16*	
01248	33	32		H,L= 2, 5	5	48	62	-39*	9	476	8	2	5	229	11	0	11	103	58	-33*	5	148	11	4	2	647	8	-8				
2	559	6	24	1	123	10	14	6	589	7	-9	10	23100	19*	6	88	98	21*	12	288	9	-2	6	24	80	-68*	3	39	93	32*		
4	174	12	29	2	252	6	12	7	117	15	-15	11	363	9	1	7	221	12	7	13	109	26	-19	7	10	83	-10*	4	587	8	-5	
5	826	9	10	3	91	14	75	8	575	19	-10	12	23102	18*	8	82	84	34*	14	251	11	1	H,L= 3, 10	5	38	96	3*					
8	862	10	4	4	143	9	8	9	74	81	-15*	13	298	11	-4	H,L= 2, 28	15	0100	-89*	0	0	60	-30*	6	486	8	-3					
10	608	7	-12	5	107	12	1	10	429	7	6	14	79108	71*	0	33130	-31*	16	194	14	1	1	754	8	-4	7	81	99	34*			
12	535	7	7	6	53	69	51*	11	116	40	-16*	15	233	13	3	1	231	14	6	17	0	94	-82*	2	166	6	6	8	425	8	1	
14	446	8	0	7	44	74	-5*	12	382	8	1	16	77112	72*	2	73107	3*	18	160	19	13	3	820	9	-10	9	33101	18*				
16	312	10	3	8	47	69	-2*	13	60	89	-10*	H,L= 2, 18	0	145	23	-5	3	234	12	4	19	0112	-51*	4	178	6	-8	10	367	9	-7	
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	H,L= 2, 1			0	188	6	-3	16	239	13	9	2	103	46	-52*	H,L= 3, 0	2	51	69	8*	7	609	21	-8	13	84104	80*					
1	188	4	5	1	886	9	11	17	14	94	-17*	3	220	11	-4	11280	25	27	3	58	70	-13*	8	102	37	-9*	14	270	12	-2		
2	155	6	-4	2	184	5	0	18	150	38	-16	4	133	30	-6	31214	29	49	4	19	69	16*	9	481	24	-14	15	0110	-16*			
3	108	11	25	3	944	16	3	H,L= 2, 11	5	252	9	9	51009	23	-5	51009	23	-5	5	85	16	-2	10	71	48	-51*	16	154	41	-54		
4	60	60	19*	4	133	7	-7	1	51	73	25*	6	173	12	13	7	916	10	2	6	10	72	-27*	11	387	8	-9	H,L= 3, 18				
5	35	59	-1*	5	991	11	-13	2	0	82	-2*	7	164	20	-40	9	778	9	3	7	42	68	23*	12	115	40	18*	0	309	12	4	
6	69	55	23*	6	217	5	3	3	0	70	-19*	8	132	23	8	11	562	7	2	8	47	78	32*	13	308	9	16	1	185	13	-4	
7	56	70	26*	7	795	9	-9	4	0106	-21*	9	189	11	1	13	435	8	-9	9	59	43	7*	14	0101	-46*	2	246	10	2			
8	49	66	30*	8	131	12	-7	5	60	71	-40*	10	39	87	-50*	15	334	9	0	H,L= 3, 6	15	223	13	-7	3	123	37	-8*				
9	137	12	4	9	660	8	-6	6	61	82	43*	11	155	22	0	17	235	13	-23	01070	11	4	16	78	95	28*	4	213	10	-7		
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	H,L= 2, 2			11	460	7	-4	0	777	9	-13	13	159	15	15	H,L= 3, 1	21012	11	4	18	66108	41*	6	213	10	4						
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2	397	5	5	14	0101	-50*		3	219	6	-3	H,L= 2, 20	3	0	70	-3*	3	0	70	-3*	5	219	5	-1	2	79	55	29*	9	96	36	-6*
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4	429	5	12	16	39103	23*		5	88	25	-12	1	146	30	-2	5	162	8	-6	7	223	5	-3	4	120	14	1	11	61	87	-21*	
5	241	4	-3	17	236	13	-2	6	426	7	-2	2	236	11	6	6	167	8	8	8	568	7	-3	5	64	84	30*	12	100	44	-42*	
6	319	4	-7	18	80107	52*		7	165	12	4	3	66	91	-50*	7	51	71	32*	9	77	85	-13*	H,L= 3, 12	13	69	98	-15*				
7	270	4	-1	19	122	55	-35*	8	413	7	-4	4	234	10	-9	8	63	76	8*	10	451	22	-3	0	185	7	-9	14	112	48	-12*	
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12	165	15	-22	4	41	6																										

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