Highly Stereoregular Syndiotactic Polypropylene Formation with Metallocene Catalysts via Influence of Distal Ligand Substituents

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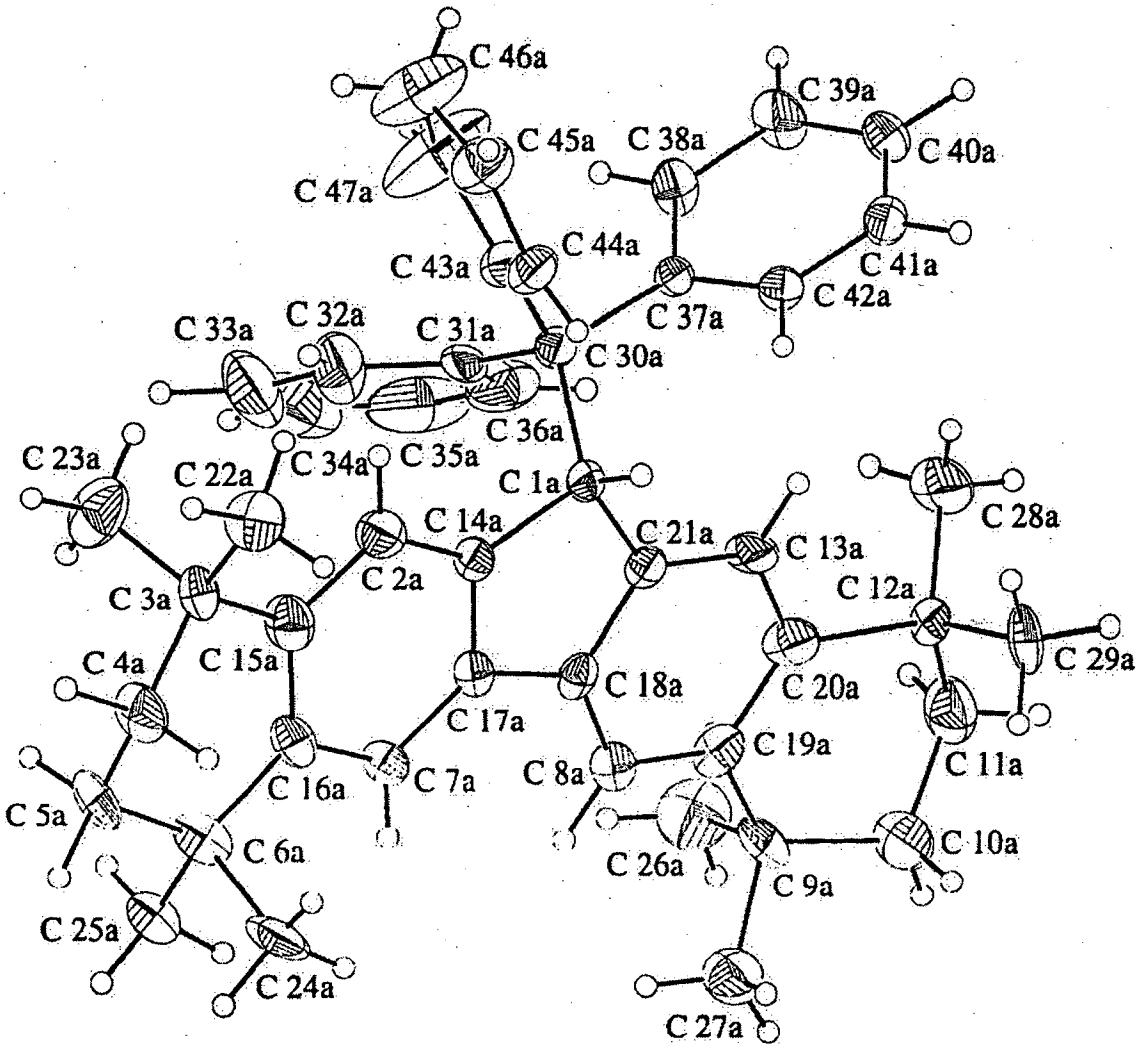
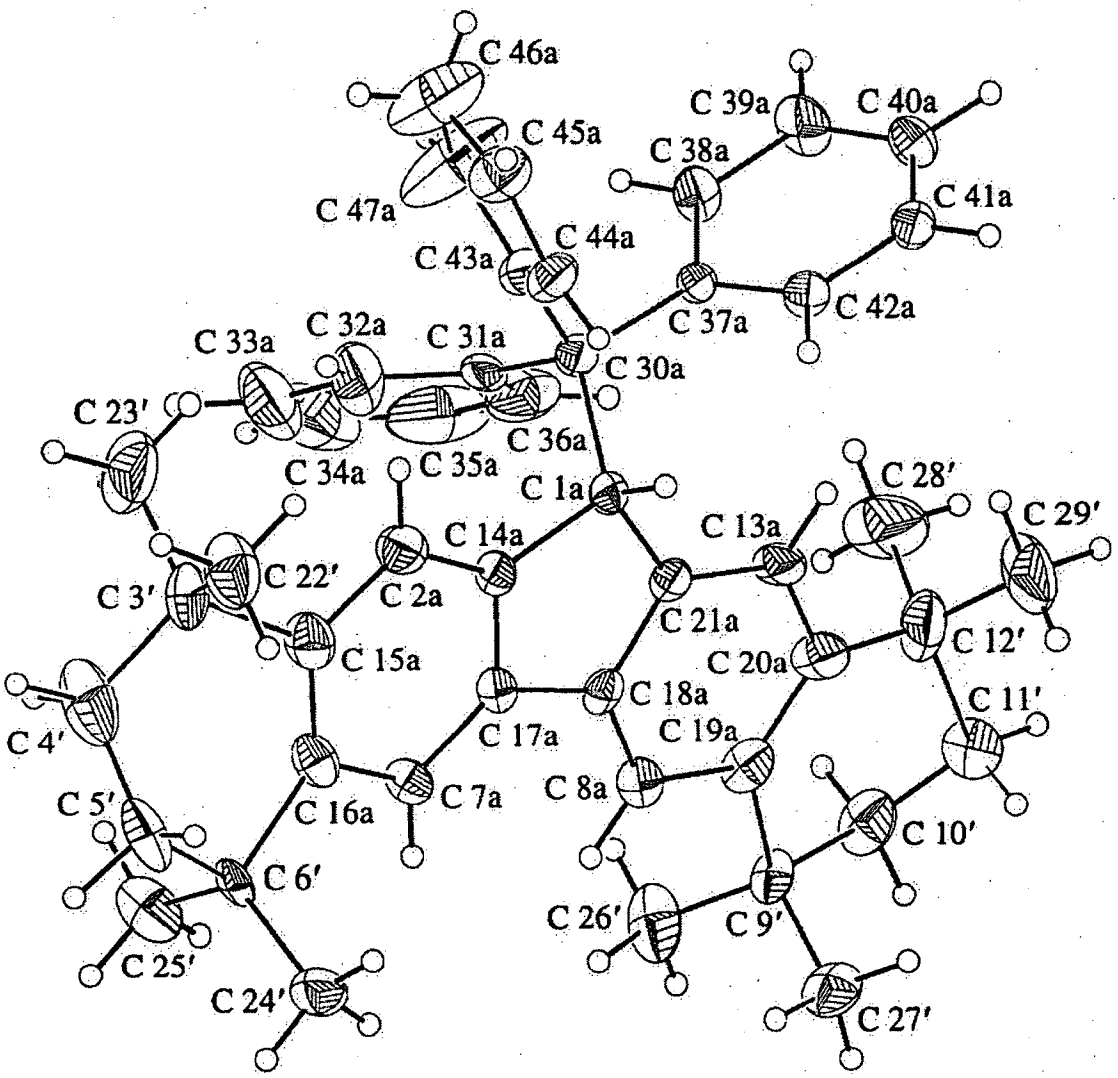
Supporting Information: X-ray crystal structure data for $Ph_2C(OctH)(C_5H_5)$, $Ph_2C(C_{29}H_{36})(C_5H_4)ZrCl_2$ (**8**), and $Ph_2C(C_{21}H_{22})(C_5H_4)ZrCl_2$ (**10**) (25 pages).

X-ray Crystal Structure Data for $Ph_2C(OctH)(C_5H_5)$

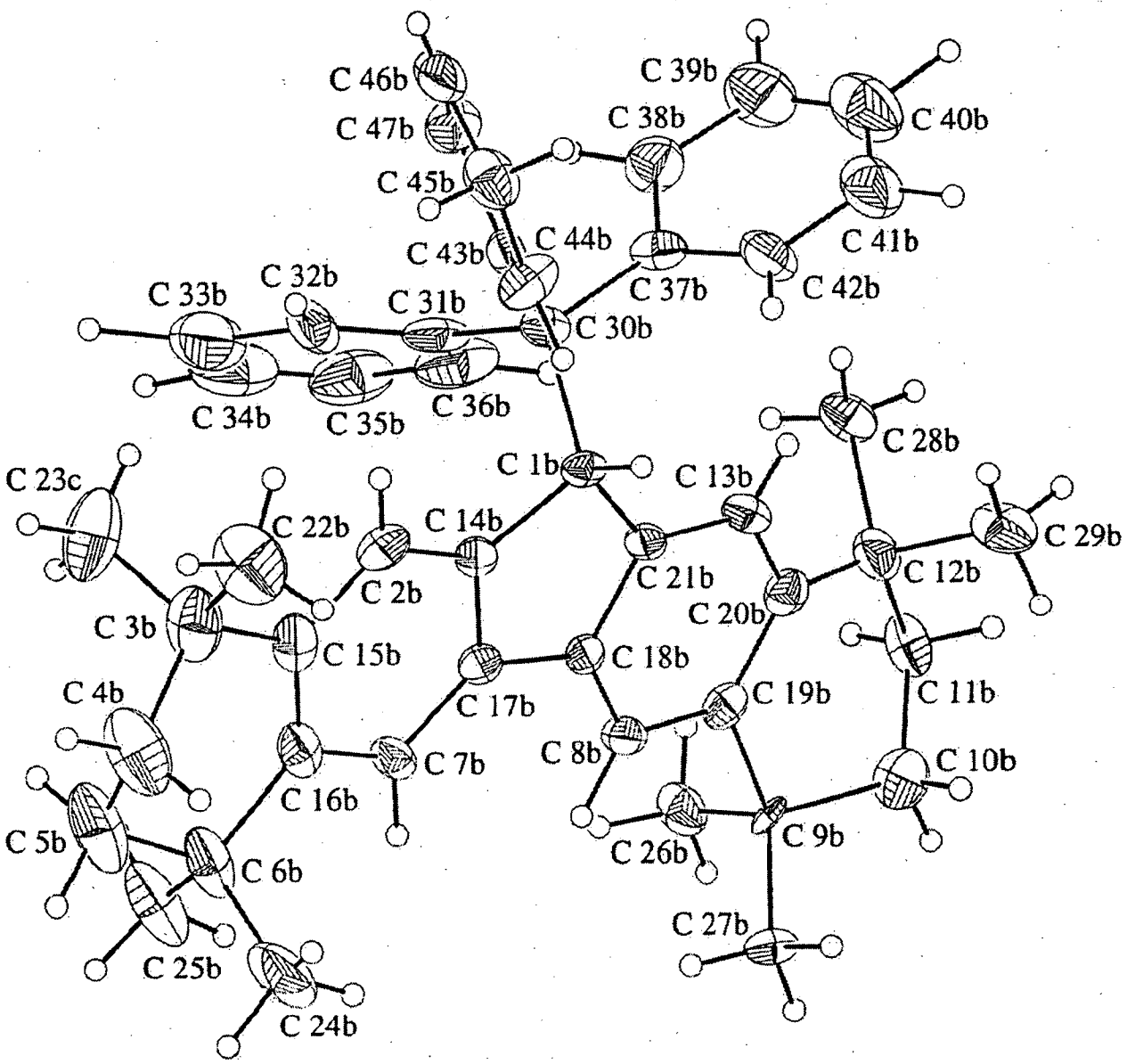
Cambridge Database (CCDC) 105607



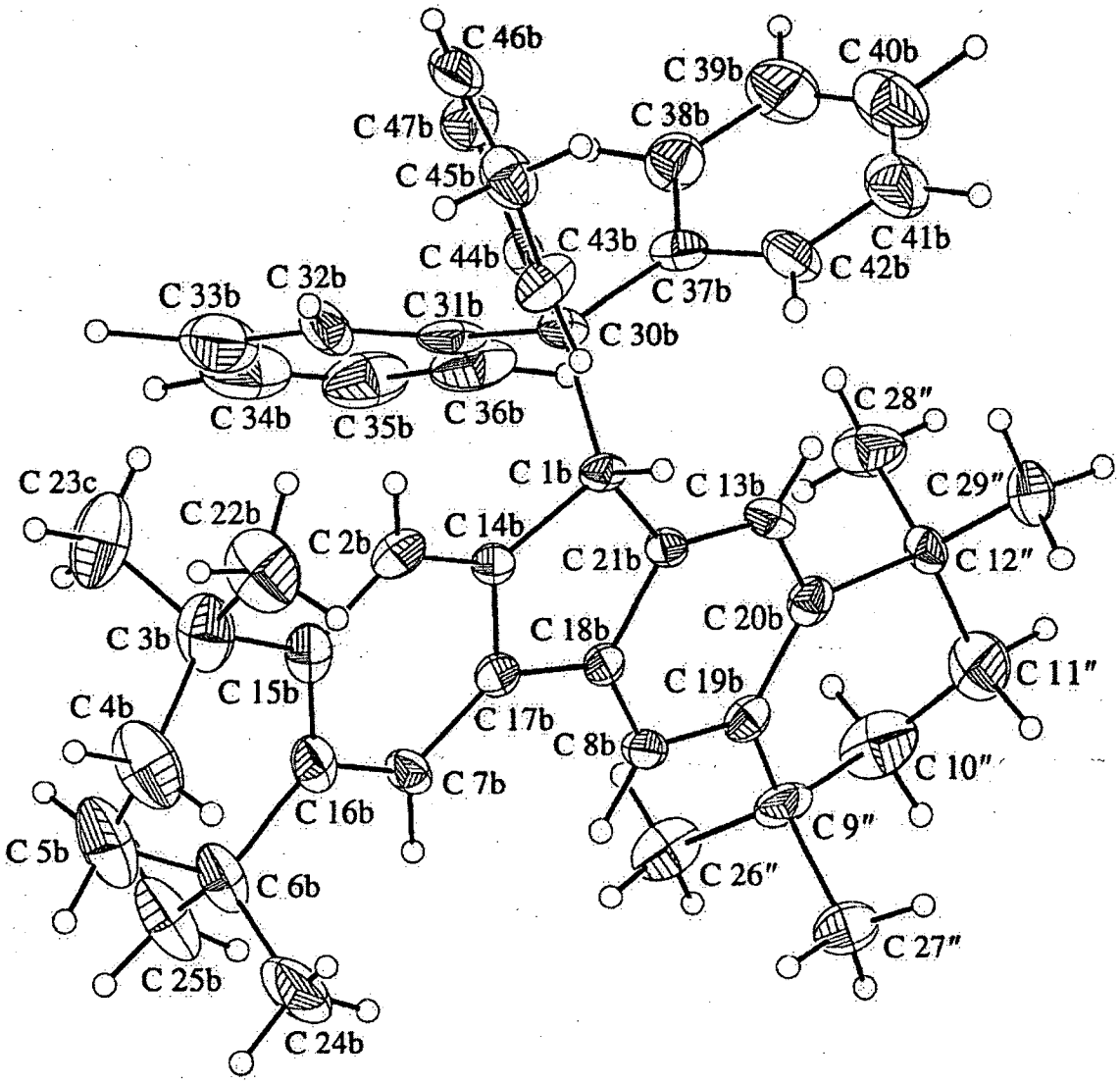
Labeled view of molecule A with 50% probability ellipsoids



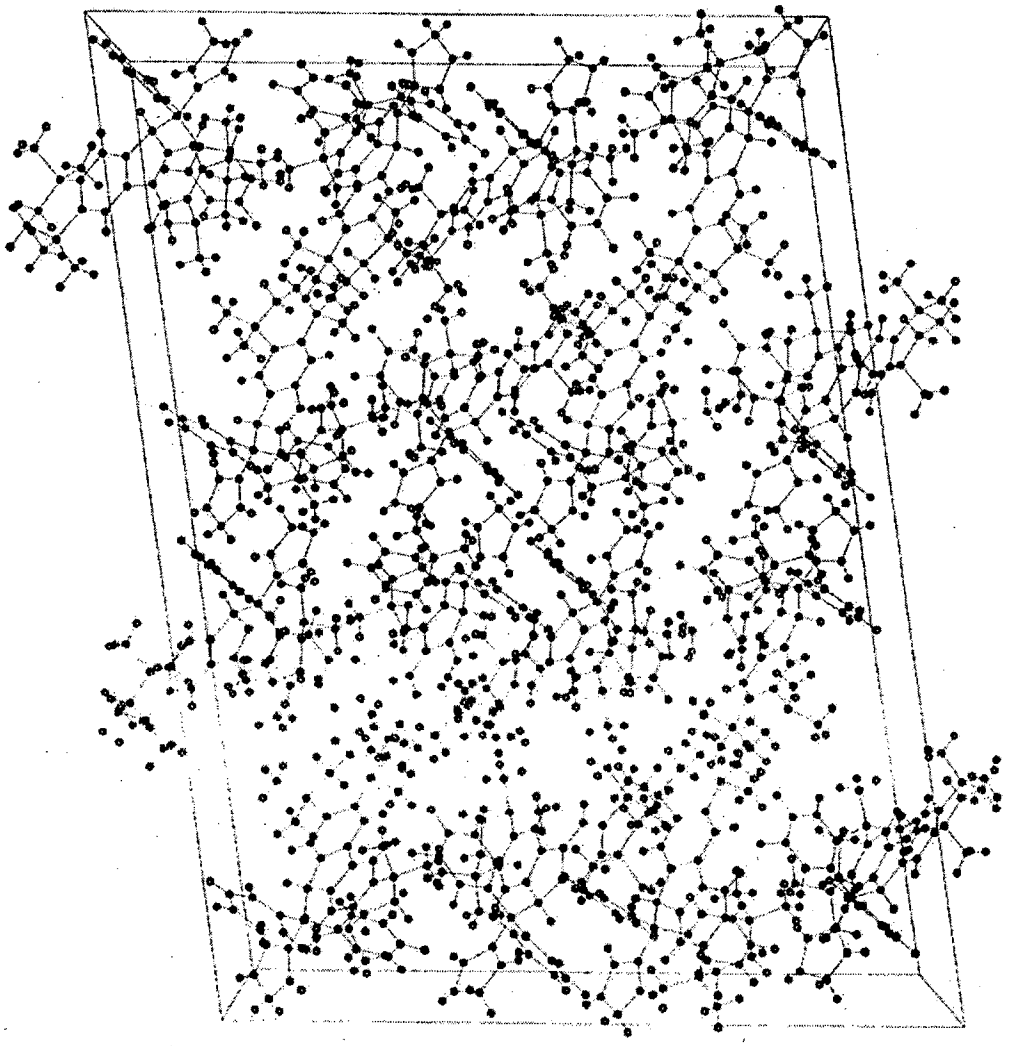
Labeled view of molecule A (with alternate conformation) with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Labeled view of molecule B (with alternate conformation) with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(OctH)(C_5H_5)$.

Empirical formula	$C_{47}H_{52}$	
Formula weight	616.93	
Crystallization solvent	ethanol	
Crystal habit	prismatic	
Crystal size	0.45 x 0.25 x 0.23 mm^3	
Crystal color	very slightly yellow	
Data Collection		
Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKa	
Data collection temperature	85 K	
Theta range for reflections used in lattice determination	10.7 to 12.9°	
Unit cell dimensions	a = 39.813(15) Å	alpha = 90°
	b = 12.631(6) Å	beta = 98.34(4)°
	c = 29.671(15) Å	gamma = 90°
Volume	14763(12) $Å^3$	
Z	16	
Crystal system	Monoclinic	
Space group	C2/c	
Density (calculated)	1.110 Mg/m^3	
F(000)	5344	
Theta range for data collection	1.6 to 23.0°	
Completeness to theta = 23.01°	99.8%	
Index ranges	-43<=h<=0, -13<=k<=13, -32<=l<=32	
Data collection scan type	Omega scans	
Reflections collected	22592	
Independent reflections	10265 [R_{int}= 0.057; GOF_{merge}= 1.02]	
Absorption coefficient	0.062 mm^{-1}	
Absorption correction	None	
Number of standards	3 reflections measured every 75 min.	
Variation of standards	-0.66%.	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Geometrically calculated positions	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	10265 / 795 / 1146	
Treatment of hydrogen atoms	Restrained angles, free distances	
Goodness-of-fit on F^2	1.696	
Final R indices [I>2s(I)]	R1 = 0.0739, wR2 = 0.1104	
R indices (all data)	R1 = 0.1286, wR2 = 0.1219	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	
Max shift/error	0.000	
Average shift/error	0.000	
Largest diff. peak and hole	0.751 and -0.454 $e.Å^{-3}$	

Special Refinement Details

This crystal diffracts weakly, therefore data was collected to a maximum 2θ value of only 23°. To further complicate matters the crystal is disordered and there are two molecules in the asymmetric unit. Some of the atoms in the disordered sites are very close to their equivalent atoms resulting in a tendency for the anisotropic displacement parameters (ADP) of these atom to become non-positive definite. Therefore, all of the atoms had a restraint placed on their ADP to approximate isotropic behavior. The treatment of the disordered sites is discussed below.

The disorder occurs in two places; the tetramethylcylcohexal groups on the ends of the flourinyl moiety, where in three of the four cases the pucker of the ring adopts both possible conformations and in the cylopentene rings. The first disorder was modeled and each disordered site was restrained to the geometry of the site where no disorder is observed. The second disorder was not modeled.

The hydrogen atoms of the Cp-ring in the B-molecule were located in the difference Fourier map and there is reasonable certainty where the CH_2 group is located within this Cp-ring. The hydrogen atoms of the Cp-ring in the A-molecule were not as apparent in the difference Fourier map and the position of the CH_2 group was inferred from the map and from the position in the other molecule. The bond distances within either Cp-ring offer no supporting evidence for the position of the CH_2 group. As noted in Table 1., the angular geometry of all hydrogens were restrained during the refinement.

The variances $[\sigma^2(Fo^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$, and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014\langle I\rangle)^2$.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ph_2C(OctH)(C_5H_5)$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1A)	3955(1)	1315(3)	-1134(1)	23(1)
C(2A)	4272(1)	3024(3)	-1366(1)	33(1)
C(3A)	4540(4)	4774(10)	-1528(4)	28(3)
C(4A)	4427(2)	5828(6)	-1748(3)	38(3)
C(5A)	4278(4)	5721(14)	-2242(5)	34(4)
C(6A)	3973(5)	4999(19)	-2297(8)	33(6)
C(7A)	3742(1)	3253(3)	-2071(1)	24(1)
C(8A)	3233(1)	1210(3)	-2084(1)	25(1)
C(9A)	2732(5)	-1(15)	-2296(7)	33(5)
C(10A)	2472(2)	-653(8)	-2069(3)	45(3)
C(11A)	2641(5)	-1520(14)	-1774(6)	46(6)
C(12A)	2909(3)	-1141(9)	-1391(4)	21(3)
C(13A)	3433(1)	21(3)	-1311(1)	34(1)
C(14A)	4015(1)	2279(3)	-1422(1)	21(1)

C(15A)	4267(1)	3895(3)	-1661(1)	34(1)
C(16A)	3992(1)	4031(3)	-2011(1)	28(1)
C(17A)	3753(1)	2377(3)	-1789(1)	21(1)
C(18A)	3521(1)	1486(3)	-1783(1)	22(1)
C(19A)	3041(1)	326(3)	-2004(1)	29(1)
C(20A)	3139(1)	-267(3)	-1604(1)	35(1)
C(21A)	3628(1)	876(3)	-1400(1)	22(1)
C(22A)	4644(4)	4969(11)	-1017(4)	40(3)
C(23A)	4852(3)	4346(9)	-1727(5)	52(3)
C(24A)	3674(4)	5656(18)	-2167(7)	46(5)
C(25A)	3841(4)	4786(18)	-2820(6)	34(4)
C(26A)	2850(2)	-673(9)	-2681(3)	61(3)
C(27A)	2531(3)	935(9)	-2534(4)	45(3)
C(28A)	3137(2)	-2106(7)	-1230(4)	50(3)
C(29A)	2754(2)	-715(7)	-984(3)	39(3)
C(30A)	4259(1)	504(3)	-1053(1)	25(1)
C(31A)	4333(1)	185(3)	-1530(1)	36(1)
C(32A)	4558(1)	771(4)	-1741(2)	74(2)
C(33A)	4617(2)	527(6)	-2188(3)	111(3)
C(34A)	4451(2)	-287(7)	-2407(2)	116(3)
C(35A)	4223(2)	-873(5)	-2218(2)	87(2)
C(36A)	4160(1)	-617(4)	-1779(1)	54(1)
C(37A)	4170(1)	-450(3)	-764(1)	20(1)
C(38A)	4298(1)	-1452(3)	-822(1)	31(1)
C(39A)	4233(1)	-2284(3)	-546(1)	40(1)
C(40A)	4040(1)	-2144(3)	-202(1)	31(1)
C(41A)	3924(1)	-1150(3)	-127(1)	27(1)
C(42A)	3989(1)	-316(3)	-403(1)	25(1)
C(43A)	4567(1)	969(3)	-759(1)	33(1)
C(44A)	4569(1)	1710(3)	-414(1)	34(1)
C(45A)	4900(1)	1855(3)	-165(1)	41(1)
C(46A)	5115(1)	1150(4)	-373(2)	83(2)
C(47A)	4898(1)	609(4)	-734(2)	89(2)
C(1B)	3944(1)	2004(3)	539(1)	21(1)
C(2B)	3878(1)	226(3)	998(1)	29(1)
C(3B)	3816(1)	-1466(3)	1423(2)	47(1)
C(4B)	3631(1)	-2521(3)	1320(2)	68(2)
C(5B)	3251(1)	-2408(4)	1230(2)	65(2)
C(6B)	3137(1)	-1754(3)	803(2)	43(1)
C(7B)	3258(1)	-5(3)	454(1)	25(1)
C(8B)	3123(1)	1980(3)	-245(1)	25(1)
C(9B)	2811(7)	2975(16)	-902(8)	13(5)
C(10B)	2913(3)	3819(10)	-1224(4)	40(5)
C(11B)	3032(4)	4823(12)	-974(6)	30(5)
C(12B)	3353(7)	4610(30)	-643(11)	34(9)
C(13B)	3671(1)	3330(3)	-104(1)	26(1)
C(14B)	3772(1)	989(3)	674(1)	22(1)
C(15B)	3677(1)	-664(3)	1053(1)	31(1)
C(16B)	3363(1)	-784(3)	777(1)	31(1)
C(17B)	3456(1)	864(3)	400(1)	22(1)
C(18B)	3396(1)	1757(3)	84(1)	19(1)
C(19B)	3114(1)	2901(3)	-504(1)	25(1)
C(20B)	3390(1)	3589(3)	-429(1)	25(1)
C(21B)	3677(1)	2434(3)	159(1)	20(1)

C(22B)	4199(1)	-1642(3)	1440(2)	61(1)
C(23C)	3757(1)	-1030(4)	1891(1)	73(2)
C(24B)	3147(1)	-2430(3)	377(2)	66(2)
C(25B)	2768(1)	-1412(3)	818(2)	63(2)
C(26B)	2512(7)	3358(17)	-679(9)	32(5)
C(27B)	2738(4)	1939(11)	-1162(6)	24(4)
C(28B)	3433(6)	5540(30)	-284(9)	31(6)
C(29B)	3654(5)	4770(30)	-927(9)	39(6)
C(30B)	4062(1)	2798(3)	943(1)	24(1)
C(31B)	3757(1)	2936(3)	1203(1)	36(1)
C(32B)	3739(1)	2334(4)	1596(2)	50(1)
C(33B)	3467(1)	2352(4)	1838(2)	65(2)
C(34B)	3206(1)	2991(4)	1659(2)	66(2)
C(35B)	3199(1)	3617(4)	1279(2)	56(2)
C(36B)	3485(1)	3575(4)	1037(2)	54(1)
C(37B)	4199(1)	3824(3)	756(1)	28(1)
C(38B)	4130(1)	4812(3)	912(1)	41(1)
C(39B)	4278(1)	5691(4)	741(2)	56(1)
C(40B)	4491(1)	5594(4)	432(2)	62(2)
C(41B)	4569(1)	4641(4)	284(2)	52(1)
C(42B)	4431(1)	3766(3)	449(1)	39(1)
C(43B)	4372(1)	2390(3)	1258(1)	27(1)
C(44B)	4589(1)	1617(3)	1179(1)	38(1)
C(45B)	4882(1)	1546(3)	1537(1)	38(1)
C(46B)	4832(1)	2372(4)	1875(1)	71(2)
C(47B)	4505(1)	2905(3)	1681(1)	49(1)
C(3')	4602(4)	4535(10)	-1659(4)	32(4)
C(4')	4564(3)	5305(8)	-2057(3)	59(4)
C(5')	4210(4)	5807(16)	-2157(7)	46(6)
C(6')	3909(5)	5067(18)	-2315(8)	21(5)
C(22')	4640(5)	5137(13)	-1207(4)	51(4)
C(23')	4920(4)	3847(11)	-1662(6)	63(4)
C(24')	3575(4)	5574(19)	-2239(7)	38(4)
C(25')	3952(4)	4740(20)	-2797(7)	44(5)
C(9')	2727(4)	82(13)	-2405(6)	24(4)
C(10')	2620(2)	-1069(6)	-2333(3)	42(3)
C(11')	2612(4)	-1353(15)	-1842(5)	45(5)
C(12')	2973(3)	-1323(11)	-1558(4)	46(4)
C(26')	2814(2)	236(7)	-2883(2)	46(3)
C(27')	2439(2)	843(9)	-2319(3)	38(3)
C(28')	3183(2)	-2266(7)	-1677(4)	72(4)
C(29')	2925(3)	-1383(10)	-1059(4)	67(4)
C(9")	2795(4)	3207(10)	-829(5)	34(4)
C(10")	2796(2)	4333(6)	-1009(3)	52(3)
C(11")	3141(2)	4685(8)	-1109(3)	45(3)
C(12")	3416(3)	4678(13)	-682(5)	24(4)
C(26")	2466(3)	3029(10)	-619(5)	42(3)
C(27")	2777(2)	2447(7)	-1247(3)	37(2)
C(28")	3329(3)	5532(14)	-348(5)	45(4)
C(29")	3758(3)	4848(12)	-835(4)	41(3)
H(1A)	3907(2)	1563(8)	-835(10)	27
H(2A)	4453(6)	2946(4)	-1125(9)	39
H(4B)	4244(9)	6171(17)	-1568(9)	45
H(4C)	4637(10)	6340(20)	-1720(3)	45

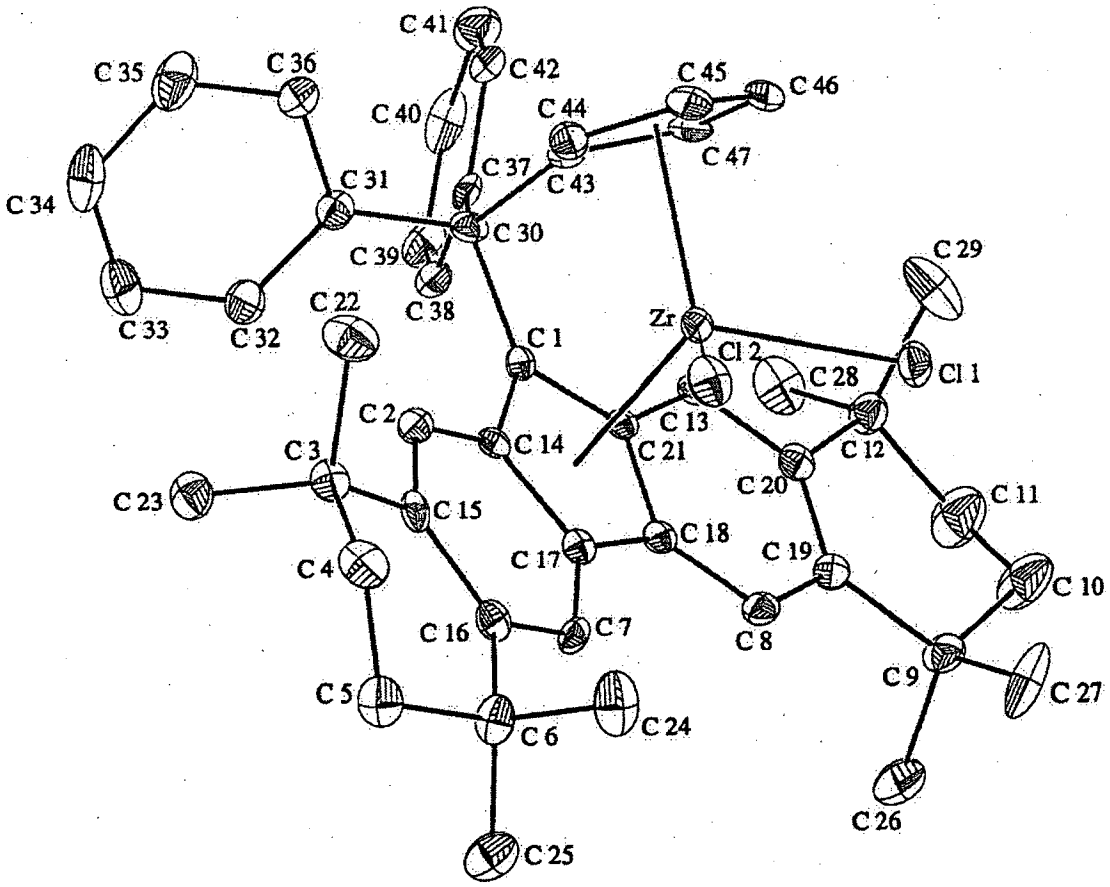
H(5A)	4457(11)	5420(20)	-2420(11)	41
H(5B)	4208(5)	6450(40)	-2372(9)	41
H(7A)	3568(6)	3320(4)	-2302(8)	28
H(8A)	3166(2)	1637(14)	-2352(9)	30
H(10A)	2342(8)	-140(30)	-1866(11)	54
H(10B)	2288(10)	-990(17)	-2327(13)	54
H(11A)	2748(8)	-2020(30)	-1968(12)	55
H(11B)	2465(11)	-1920(30)	-1640(10)	55
H(13A)	3497(3)	-369(15)	-1054(10)	41
H(22A)	4448	5169	-883	48
H(22B)	4809	5527	-974	48
H(22C)	4740	4333	-875	48
H(23A)	4937	3725	-1562	62
H(23B)	5026	4878	-1700	62
H(23C)	4786	4169	-2042	62
H(24A)	3724	5866	-1853	56
H(24B)	3471	5236	-2210	56
H(24C)	3642	6275	-2356	56
H(25B)	3626	4429	-2850	40
H(25A)	4002	4353	-2947	40
H(25C)	3815	5448	-2980	40
H(26A)	3004	-266	-2832	73
H(26B)	2657	-873	-2896	73
H(26C)	2963	-1298	-2552	73
H(27A)	2476	1426	-2308	54
H(27B)	2325	678	-2709	54
H(27C)	2666	1285	-2732	54
H(28A)	3272	-1946	-943	59
H(28B)	3284	-2257	-1452	59
H(28C)	2997	-2711	-1197	59
H(29A)	2614	-113	-1079	47
H(29B)	2932	-506	-748	47
H(29C)	2619	-1257	-872	47
H(32A)	4674(6)	1340(30)	-1586(8)	88
H(33A)	4783(8)	970(20)	-2342(8)	133
H(34A)	4501(3)	-484(13)	-2747(18)	140
H(35A)	4105(6)	-1460(30)	-2385(8)	104
H(36A)	3997(7)	-997(17)	-1652(6)	64
H(38A)	4438(5)	-1572(5)	-1063(8)	37
H(39A)	4325(4)	-2990(30)	-597(2)	48
H(40A)	3986(2)	-2760(20)	-10(7)	37
H(41A)	3793(4)	-1028(5)	125(8)	32
H(42A)	3906(3)	380(20)	-343(2)	30
H(44A)	4386(7)	2052(14)	-354(3)	41
H(45A)	4957(3)	2269(19)	57(10)	49
H(46A)	5268(6)	1495(13)	-480(4)	100
H(46B)	5209(4)	710(17)	-179(7)	100
H(47A)	4963(4)	140(30)	-904(10)	107
H(1B)	4147(6)	1798(7)	402(4)	25
H(2B)	4079(7)	302(4)	1176(7)	35
H(4C)	3708(3)	-2839(10)	1059(8)	81
H(4D)	3690(2)	-2990(14)	1575(7)	81
H(5C)	3172(3)	-2068(10)	1493(8)	78
H(5D)	3148(3)	-3110(20)	1193(2)	78

H(7B)	3032(7)	-82(4)	256(6)	30
H(8B)	2934(6)	1487(17)	-296(2)	30
H(4C)	3107(15)	3530(20)	-1388(14)	49
H(4D)	2707(16)	3989(16)	-1470(20)	49
H(5C)	2856(16)	5090(30)	-810(16)	36
H(5D)	3076(5)	5360(50)	-1192(19)	36
H(13B)	3844(7)	3746(16)	-68(2)	31
H(22D)	4247	-1803	1140	74
H(22E)	4270	-2222	1641	74
H(22F)	4319	-1013	1550	74
H(23D)	3877	-374	1949	88
H(23E)	3838	-1533	2124	88
H(23F)	3519	-912	1890	88
H(24D)	3374	-2683	373	79
H(24E)	3078	-2009	110	79
H(24F)	2996	-3021	380	79
H(25D)	2681	-1064	537	76
H(25E)	2761	-933	1068	76
H(25F)	2633	-2024	857	76
H(26D)	2460	2839	-463	38
H(26E)	2318	3459	-907	38
H(26F)	2570	4016	-525	38
H(27D)	2930	1753	-1308	29
H(27E)	2542	2025	-1388	29
H(27F)	2697	1389	-954	29
H(28D)	3654	5435	-111	38
H(28E)	3265	5547	-82	38
H(28F)	3429	6206	-442	38
H(29D)	3623	4303	-1187	47
H(29E)	3865	4599	-739	47
H(29F)	3659	5487	-1027	47
H(32B)	3982(7)	1752(18)	1735(5)	60
H(33B)	3461(1)	1783(18)	2221(12)	78
H(34B)	2960(9)	3008(4)	1849(7)	79
H(35B)	3016(8)	4050(20)	1184(5)	67
H(36B)	3488(1)	4024(17)	737(11)	65
H(38B)	3963(6)	4904(4)	1165(8)	49
H(39B)	4223(3)	6450(30)	856(5)	67
H(40B)	4603(5)	6310(30)	298(6)	74
H(41B)	4735(6)	4568(5)	44(9)	63
H(42B)	4493(3)	3110(30)	354(4)	47
H(44B)	4557(2)	1182(17)	927(10)	46
H(45C)	5089(5)	1669(4)	1414(3)	46
H(45D)	4893(1)	856(17)	1676(3)	46
H(46B)	4926(7)	2477(9)	2059(13)	85
H(47B)	4419(4)	3400(20)	1793(6)	59
H(4A')	4765(11)	5980(30)	-1979(5)	71
H(4B')	4621(4)	4860(20)	-2381(16)	71
H(5A')	4217(4)	6370(40)	-2398(16)	56
H(5B')	4163(5)	6180(30)	-1870(20)	56
H(22G)	4661	4642	-959	61
H(22H)	4445	5575	-1198	61
H(22I)	4840	5573	-1181	61
H(23G)	4891	3402	-1927	75

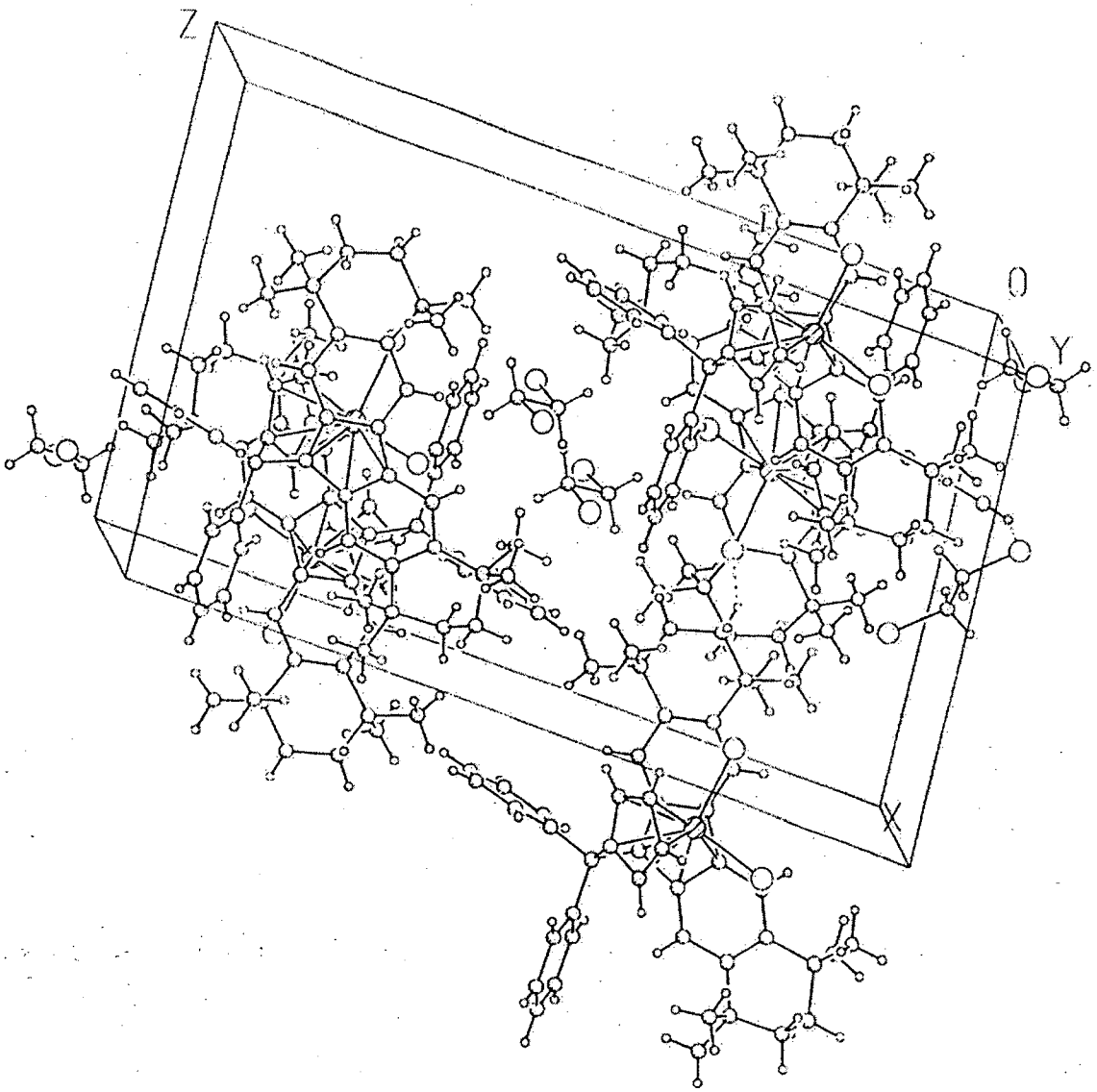
H(23H)	4954	3415	-1393	75
H(23I)	5114	4295	-1668	75
H(24G)	3390	5118	-2357	46
H(24H)	3549	6244	-2392	46
H(24I)	3574	5678	-1918	46
H(25G)	4170	4421	-2795	52
H(25H)	3935	5359	-2989	52
H(25I)	3777	4248	-2911	52
H(10E)	2391(12)	-1186(10)	-2507(10)	50
H(10F)	2780(9)	-1550(30)	-2458(8)	50
H(11E)	2512(7)	-2100(40)	-1824(5)	54
H(11F)	2456(9)	-830(30)	-1703(9)	54
H(26G)	3007	-192	-2922	55
H(26H)	2866	968	-2927	55
H(26I)	2623	30	-3102	55
H(27G)	2513	1562	-2341	46
H(27H)	2381	720	-2020	46
H(27I)	2243	720	-2543	46
H(28G)	3200	-2251	-1996	86
H(28H)	3074	-2911	-1605	86
H(28I)	3405	-2229	-1503	86
H(29G)	3141	-1312	-871	81
H(29H)	2827	-2054	-1001	81
H(29I)	2777	-823	-992	81
H(10G)	2628(8)	4387(7)	-1296(13)	63
H(10H)	2720(4)	4830(20)	-778(11)	63
H(11G)	3120(2)	5470(30)	-1247(7)	55
H(11H)	3219(4)	4170(20)	-1360(12)	55
H(26J)	2472	3456	-350	50
H(26K)	2449	2296	-539	50
H(26L)	2273	3224	-836	50
H(27J)	2780	1726	-1144	44
H(27K)	2969	2571	-1401	44
H(27L)	2572	2577	-1452	44
H(28J)	3110	5387	-263	55
H(28K)	3325	6214	-493	55
H(28L)	3497	5531	-82	55
H(29J)	3931	4870	-574	49
H(29K)	3756	5506	-998	49
H(29L)	3804	4277	-1031	49

X-ray Crystal Structure Data for $Ph_2C(C_{29}H_{36})(C_5H_4)ZrCl_2$ (8)

Cambridge Database (CCDC) 112475



Labeled view with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(Oct)(C_5H_4)ZrCl_2$.

Empirical formula	$C_{47}\,H_{50}\,Cl_2\,Zr\,(C_2\,H_4\,Cl_2)_{1.5}$	
Formula weight	925.48	
Crystallization solvent	1,2-dichloroethane	
Crystal habit	block	
Crystal size	0.44 x 0.33 x 0.32 mm^3	
Crystal color	ruby red	
Data Collection		
Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKa	
Data collection temperature	85 K	
Theta range for reflections used in lattice determination	15.4 to 16.2°	
Unit cell dimensions	a = 13.898(8) Å	alpha = 90°
	b = 13.698(10) Å	beta = 96.91(6)°
	c = 23.275(16) Å	gamma = 90°
Volume	4399(5) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Density (calculated)	1.397 Mg/m^3	
F(000)	1924	
Theta range for data collection	1.63 to 25.05°	
Completeness to theta = 25.05°	99.6%	
Index ranges	-16<=h<=16, -16<=k<=16, 0<=l<=27	
Data collection scan type	Omega scans	
Reflections collected	19403	
Independent reflections	7766 [R_{int}= 0.0242; GOF_{merge}= 1.21]	
Absorption coefficient	0.588 mm^{-1}	
Number of standards	3 reflections measured every 75 min.	
Variation of standards	-0.67%.	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Calculated sites	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	7766 / 7 / 527	
Treatment of hydrogen atoms	Geometrically restrained	
Goodness-of-fit on F^2	4.122	
Final R indices [I>2σ(I)]	R1 = 0.0652, wR2 = 0.1422	
R indices (all data)	R1 = 0.0743, wR2 = 0.1433	
Type of weighting scheme used	Sigma	
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	
Max shift/error	0.004	
Average shift/error	0.000	
Extinction coefficient	0.0011(2)	
Largest diff. peak and hole	1.221 and -1.282 e.$Å^{-3}$	

Special Refinement Details

The unit cell contains 1,2-dichloroethane as a solvent of crystallization. One molecule sits on a center of inversion and therefore one half the molecule is in the list of atomic coordinates. Another molecule sits in a general position.

The variances $[\sigma^2(Fo^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$, and the variances of the merged data were obtained by propagation of error plus the addition of another term, $(0.014\langle I\rangle)^2$.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Ph_2C(Oct)(C_5H_4)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr	4117(1)	3727(1)	2430(1)	14(1)
Cl(1)	5858(1)	3773(1)	2662(1)	20(1)
Cl(2)	3726(1)	4493(1)	3318(1)	23(1)
C(1)	3183(3)	2464(3)	1900(2)	12(1)
C(2)	1958(3)	2889(3)	2638(2)	15(1)
C(3)	880(3)	3391(4)	3373(2)	18(1)
C(4)	932(4)	3516(4)	4027(2)	25(1)
C(5)	1267(4)	2596(4)	4351(2)	23(1)
C(6)	2323(4)	2355(4)	4278(2)	21(1)
C(7)	3315(3)	2038(3)	3469(2)	15(1)
C(8)	5253(3)	1435(3)	2828(2)	16(1)
C(9)	6970(4)	932(4)	2749(2)	21(1)
C(10)	7727(4)	1075(5)	2326(2)	38(2)
C(11)	7421(4)	819(5)	1725(2)	40(2)
C(12)	6547(3)	1438(4)	1450(2)	19(1)
C(13)	4895(3)	1914(3)	1657(2)	13(1)
C(14)	2800(3)	2482(3)	2456(2)	13(1)
C(15)	1796(3)	2875(3)	3217(2)	16(1)
C(16)	2474(3)	2410(3)	3639(2)	17(1)
C(17)	3510(3)	2084(3)	2888(2)	13(1)
C(18)	4352(3)	1817(3)	2616(2)	13(1)
C(19)	5979(3)	1314(3)	2472(2)	15(1)
C(20)	5787(3)	1553(3)	1876(2)	15(1)
C(21)	4145(3)	2048(3)	2002(2)	13(1)
C(22)	808(4)	4414(4)	3085(2)	28(1)
C(23)	-22(3)	2813(4)	3134(2)	25(1)
C(24)	3004(4)	3094(4)	4626(2)	31(1)
C(25)	2547(4)	1339(4)	4522(2)	28(1)

C(26)	6888(4)	-143(4)	2906(3)	42(2)
C(27)	7330(4)	1511(5)	3293(2)	39(2)
C(28)	6139(4)	863(4)	904(2)	28(1)
C(29)	6836(4)	2446(4)	1257(3)	37(2)
C(30)	2744(3)	3000(3)	1342(2)	15(1)
C(31)	1641(3)	3014(4)	1275(2)	17(1)
C(32)	1126(4)	2166(4)	1372(2)	21(1)
C(33)	130(4)	2156(4)	1298(2)	28(1)
C(34)	-380(4)	2990(5)	1116(2)	34(2)
C(35)	119(4)	3833(4)	999(2)	31(1)
C(36)	1126(4)	3836(4)	1069(2)	22(1)
C(37)	3031(3)	2539(4)	791(2)	16(1)
C(38)	3089(3)	1524(3)	731(2)	18(1)
C(39)	3293(4)	1100(4)	212(2)	23(1)
C(40)	3422(4)	1676(4)	-261(2)	29(1)
C(41)	3353(4)	2682(4)	-216(2)	27(1)
C(42)	3155(3)	3111(4)	304(2)	20(1)
C(43)	3203(3)	4000(3)	1471(2)	16(1)
C(44)	2889(4)	4708(3)	1858(2)	20(1)
C(45)	3649(4)	5379(4)	2015(2)	23(1)
C(46)	4441(4)	5088(3)	1749(2)	21(1)
C(47)	4188(3)	4230(3)	1423(2)	17(1)
Cl(10)	3763(1)	5127(1)	-651(1)	18(1)
C(110)	4612(5)	5383(6)	-23(3)	21(2)
Cl(11)	3961(1)	5151(1)	5505(1)	39(1)
Cl(12)	4410(1)	8254(1)	5472(1)	34(1)
C(111)	4219(7)	6351(2)	5235(3)	12(3)
C(112)	4250(8)	7034(2)	5767(3)	13(3)
C(114)	4190(9)	7023(3)	5230(4)	17(4)
C(113)	4200(10)	6398(3)	5786(4)	21(4)
H(2A)	1500	3176	2365	18
H(4A)	1377	4044	4148	30
H(4B)	297	3696	4127	30
H(5A)	855	2058	4205	28
H(5B)	1203	2674	4759	28
H(7A)	3770	1752	3743	18
H(8A)	5372	1261	3216	19
H(10A)	7915	1757	2341	46
H(10B)	8299	694	2458	46
H(11A)	7247	133	1704	48
H(11B)	7963	910	1503	48
H(13A)	4785	2082	1267	16
H(22A)	700	4346	2672	34
H(22B)	1400	4766	3191	34
H(22C)	278	4764	3216	34
H(23A)	-18	2705	2726	30
H(23B)	-594	3169	3197	30
H(23C)	-17	2195	3329	30
H(24A)	2850	3740	4484	37
H(24B)	3663	2943	4574	37
H(24C)	2927	3060	5030	37
H(25A)	3233	1223	4556	33
H(25B)	2217	861	4269	33
H(25C)	2329	1292	4897	33

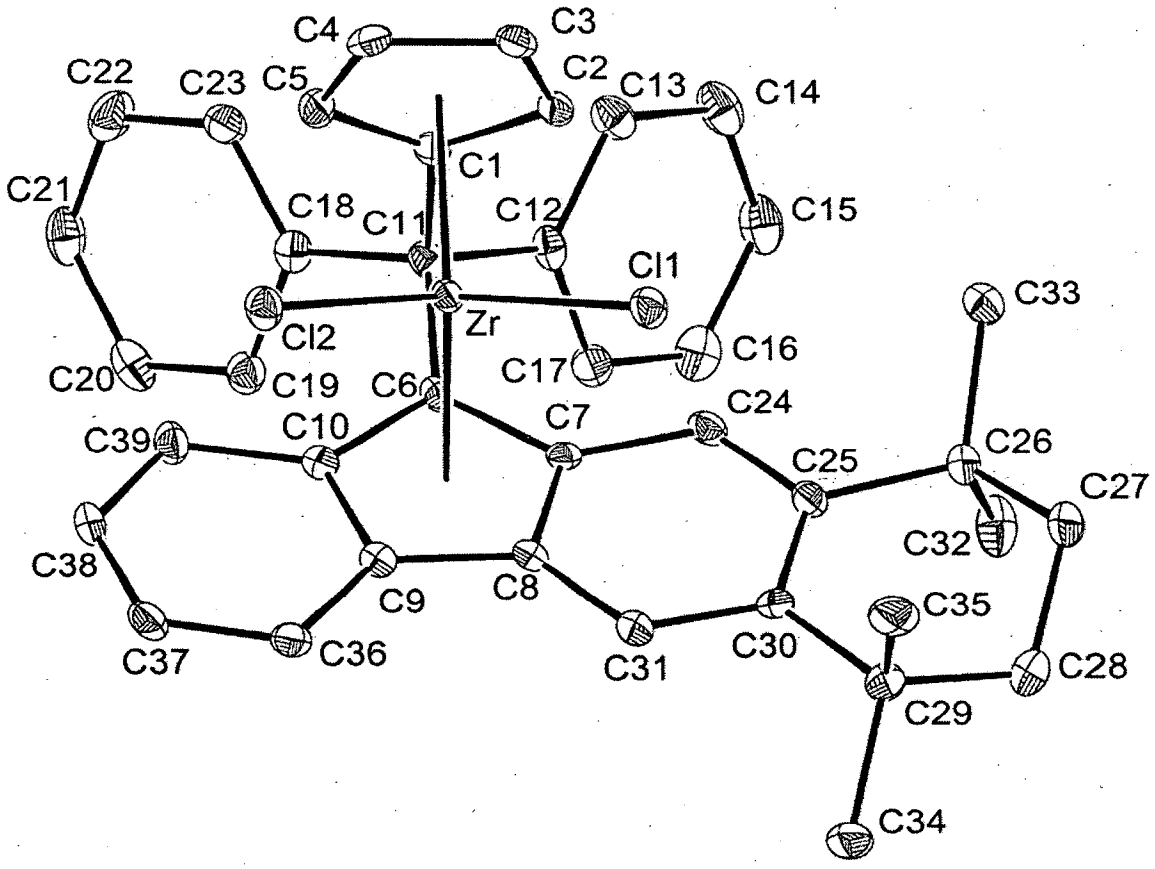
H(26A)	6673	-518	2567	51
H(26B)	6429	-206	3181	51
H(26C)	7509	-378	3075	51
H(27A)	7985	1329	3428	47
H(27B)	6923	1373	3588	47
H(27C)	7303	2196	3206	47
H(28A)	5660	1252	677	34
H(28B)	5847	269	1017	34
H(28C)	6655	711	680	34
H(29A)	6269	2796	1095	45
H(29B)	7273	2378	970	45
H(29C)	7150	2799	1583	45
H(32A)	1459	1598	1489	25
H(33A)	-200	1586	1369	33
H(34A)	-1054	2983	1067	41
H(35A)	-220	4396	878	37
H(36A)	1459	4393	977	27
H(38A)	2987	1124	1041	21
H(39A)	3341	425	186	28
H(40A)	3563	1394	-604	35
H(41A)	3432	3075	-533	32
H(42A)	3101	3786	327	23
H(44A)	2277	4730	1981	23
H(45A)	3623	5917	2257	28
H(46A)	5037	5405	1776	25
H(47A)	4598	3877	1212	21
H(11K)	4897	6024	-58	25
H(11L)	4283	5377	322	25
H(11C)	4835	6354	5079	15
H(11D)	3714	6553	4934	15
H(11E)	4788	6867	6056	16
H(11F)	3652	6994	5942	16
H(11I)	3567	6973	4995	21
H(11J)	4691	6807	5003	21
H(11G)	3700	6609	6015	25
H(11H)	4825	6436	6021	25

Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(Oct)(C_5H_4)ZrCl_2$.

Zr-Cent(1)	2.165(1)	Zr-C(14)	2.508(5)
Zr-Cent(2)	2.238(2)	Zr-C(45)	2.514(5)
Zr-Pln(1)	2.163(3)	Zr-C(46)	2.522(5)
Zr-Pln(2)	2.218(3)	Zr-C(18)	2.666(5)
Zr-Cl(1)	2.4158(19)	Zr-C(17)	2.671(5)
Zr-Cl(2)	2.4371(19)		
Zr-C(1)	2.411(5)	C(43)-C(30)-C(1)	98.4(4)
Zr-C(44)	2.437(5)	Cent(1)-Zr-Cent(2)	117.76(4)
Zr-C(43)	2.458(5)	Pln(1)-Zr-Pln(2)	107.73(17)
Zr-C(47)	2.456(5)	Cl(1)-Zr-Cl(2)	96.79(7)
Zr-C(21)	2.509(5)		

X-ray Crystal Structure Data for $Ph_2C(C_{21}H_{22})(C_5H_4)ZrCl_2$ (10)

Cambridge Database (CCDC) 137697



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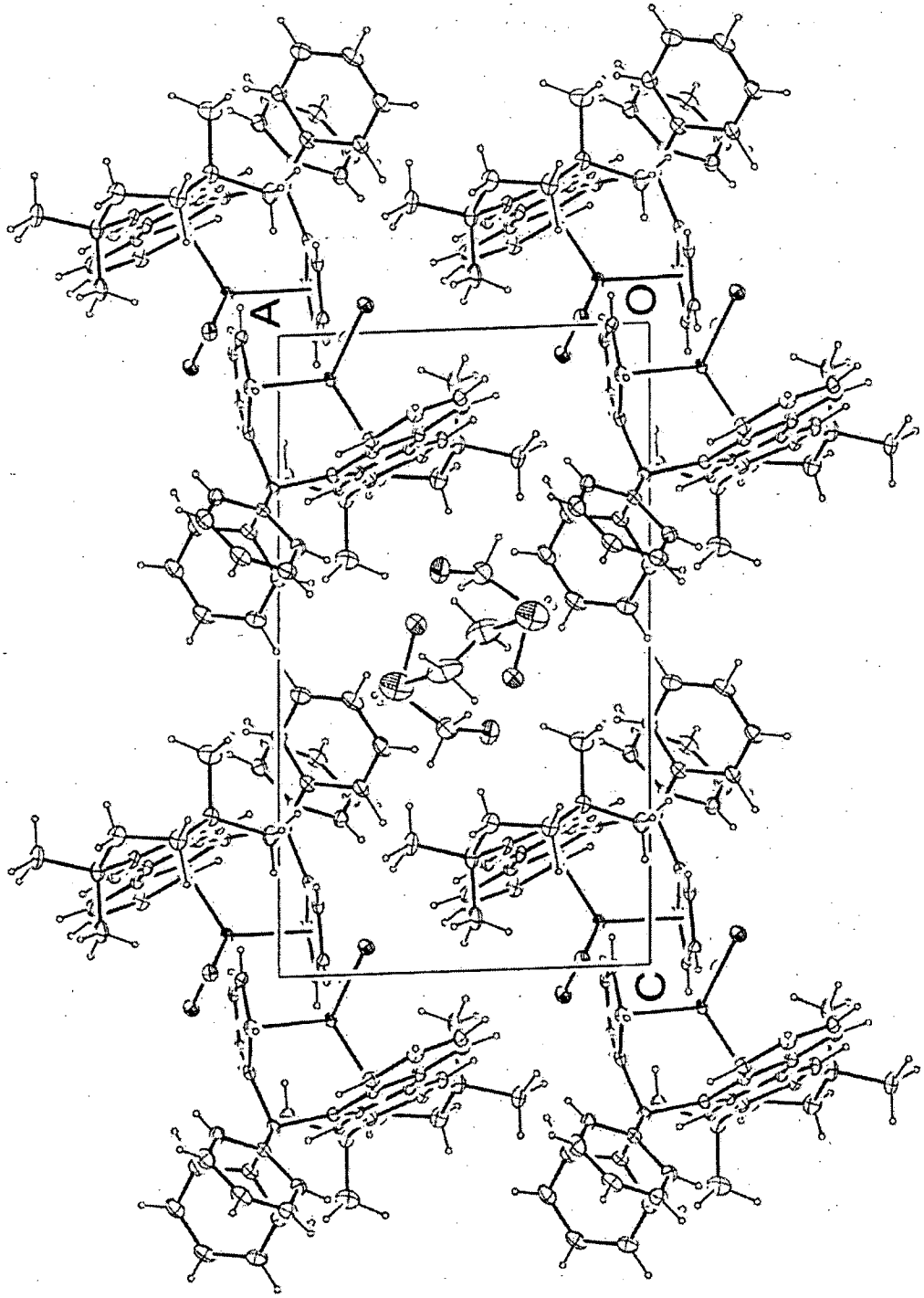

Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $Ph_2C(Tet)(C_5H_4)ZrCl_2$.

Empirical formula	$C_{42}H_{42}Cl_5Zr$ $[C_{39}H_{36}ClZr \cdot 3/2(C_2H_4Cl_2)]$	
Formula weight	815.28 [666.84 · 3/2(98.959)]	
Crystallization solvent	$ClCH_2CH_2Cl$	
Crystal habit	tabular	
Crystal size	0.40 x 0.36 x 0.18 mm^3	
Crystal color	tangerine	
Data Collection		
Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker SMART 1000 ccd	
Wavelength	0.71073 Å MoKα	
Data collection temperature	98 K	
Theta range for 5986 reflections used in lattice determination	2.5 to 28.4°	
Unit cell dimensions	a = 9.1631(10) Å	α= 70.655(2)°
	b = 12.4550(13) Å	β= 87.699(2)°
	c = 16.7351(18) Å	γ = 87.820(2)°
Volume	1800.0(3) $Å^3$	
Z	2	
Crystal system	triclinic	
Space group	P $\bar{1}$ (#2)	
Density (calculated)	1.504 g/cm^3	
F(000)	838	
Theta range for data collection	1.79 to 28.45°	
Completeness to theta = 28.45°	89.6 %	
Index ranges	-11<=h<=11, -16<=k<=16, -21<=l<=21	
Data collection scan type	ω-scans at 3 fixed ϕ values	
Reflections collected	17128	
Independent reflections	8132 [R_{int}= 0.0406]	
Absorption coefficient	0.708 mm^{-1}	
Absorption correction	none	
Number of standards	initial 75 frames recollected at end	
Variation of standards	within counting statistics	
Structure Solution and Refinement		
Structure solution program	SHELXS-97 (Sheldrick, 1990)	
Primary solution method	direct methods	
Secondary solution method	difference map	
Hydrogen placement	geometric	
Structure refinement program	SHELXL-97 (Sheldrick, 1997)	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	8132 / 0 / 559	
Treatment of hydrogen atoms	refine xyz, U_{iso}'s fixed at 120% that of attached atom	
Goodness-of-fit on F^2	2.757	
Final R indices [I>2s(I)]	R1 = 0.0467, wR2 = 0.0847	
R indices (all data)	R1 = 0.0538, wR2 = 0.0855	
Type of weighting scheme used	calculated	
Weighting scheme used	$w=1/\sigma^2(F_o^2)$	
Max shift/error	0.030	
Average shift/error	0.001	
Largest diff. peak and hole	2.114 and -1.154 $e.Å^{-3}$	

Special Details

Several crystals were examined and appeared split, streaky and/or twinned. The crystal used had slightly split peaks. Paratone-N oil was used to mount the crystals on a glass fiber. Three runs of data were collected with 30 second long, –0.3° wide ω-scans at three values of φ (0, 120 and 240°) with the detector 5 cm (nominal) distant at a θ of -28°. The initial cell for data reduction was based on reflections found in the data frames. [The crystal to detector distance was held constant (the value based on other samples) since it decreased with further refinement.] The cell thus obtained was used for another cycle of unrestrained data integration with SAINT v6.02. [For data processing, all SAINT defaults were used, except: box size optimization was enabled, periodic orientation matrix updating was disabled, no Laue class integration restraints were used, the model profiles from all nine areas were blended, and for the post-integration global least squares refinement, no constraints were applied.] The final box sizes were somewhat larger than typical. Absorption correction with SADABS did not improve the data and was not used.

There is one molecule of $phenyl_2C(Tet)(Cp)ZrCl_2$ in the asymmetric unit as well as one and one half (the latter on a center of inversion) molecules of $ClCH_2CH_2Cl$. As seen in the view along the *b*-axis, the solvent molecules lie in a channel parallel to the axis. These solvent molecules are slightly disordered; four of the five peaks over |1| $e.Å^{-3}$ in the final difference map are near the chlorine atoms in the solvent molecules. [The peaks are: 2.11 $e.Å^{-3}$ at 0.86 Å from Cl3, -1.15 $e.Å^{-3}$ at 0.48 Å from Cl5,-1.13 $e.Å^{-3}$ at 0.66 Å from Cl3, -1.06 $e.Å^{-3}$ at 0.55 Å from Cl5, with 1.26 $e.Å^{-3}$ at 0.80 Å from Zr.]

Two outlier reflections (0 1 0 and 2 3 8) were omitted from the final dataset. Refinement of F^2 is against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. The $\sigma^2(F_o^2)$ include the default instrument error constant of 0.005I. SAINT uses model profiles to improve the determination of weak reflections; however, it does not calculate the σ's for these weak reflections properly.

Table 2. Atomic coordinates ($x\ 10^4$) and equivalent isotropic displacement parameters ($Å^2 x\ 10^3$) for $Ph_2C(Tet)(C_5H_4)ZrCl_2$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr	8626(1)	7234(1)	693(1)	11(1)
Cl1	8170(1)	9255(1)	108(1)	16(1)
Cl2	7661(1)	6672(1)	-432(1)	16(1)
C1	10797(3)	6364(2)	1464(2)	12(1)
C2	11047(3)	7543(2)	1104(2)	13(1)
C3	11183(3)	7823(2)	216(2)	15(1)
C4	11004(3)	6839(2)	14(2)	15(1)
C5	10744(3)	5937(2)	777(2)	14(1)
C6	8535(3)	6145(2)	2181(2)	12(1)
C7	7877(3)	7222(2)	2164(2)	11(1)
C8	6482(3)	7360(2)	1789(2)	13(1)
C9	6235(3)	6345(2)	1579(2)	13(1)
C10	7488(3)	5595(2)	1826(2)	13(1)
C11	10151(3)	5786(2)	2349(2)	12(1)
C12	10783(3)	6218(2)	3021(2)	14(1)
C13	12203(3)	6634(2)	2925(2)	18(1)
C14	12775(3)	6982(3)	3547(2)	22(1)

C15	11989(3)	6886(3)	4284(2)	23(1)
C16	10599(3)	6463(3)	4389(2)	22(1)
C17	10004(3)	6127(2)	3765(2)	16(1)
C18	10423(3)	4489(2)	2682(2)	13(1)
C19	9476(3)	3803(2)	3295(2)	16(1)
C20	9767(3)	2652(2)	3650(2)	20(1)
C21	11009(3)	2164(3)	3399(2)	22(1)
C22	11954(3)	2831(3)	2793(2)	23(1)
C23	11664(3)	3986(2)	2445(2)	17(1)
C24	8385(3)	8147(2)	2376(2)	13(1)
C25	7552(3)	9115(2)	2265(2)	14(1)
C26	8188(3)	10060(2)	2544(2)	16(1)
C27	7314(3)	11178(2)	2203(2)	20(1)
C28	5686(3)	11012(3)	2287(2)	21(1)
C29	5173(3)	10306(2)	1761(2)	18(1)
C30	6121(3)	9229(2)	1923(2)	14(1)
C31	5628(3)	8339(2)	1689(2)	14(1)
C32	8164(4)	9652(3)	3514(2)	25(1)
C33	9771(3)	10274(3)	2211(2)	19(1)
C34	3552(3)	10037(3)	2004(2)	22(1)
C35	5269(3)	11002(3)	820(2)	22(1)
C36	5036(3)	6053(2)	1197(2)	15(1)
C37	5104(3)	5030(2)	1048(2)	17(1)
C38	6336(3)	4298(2)	1270(2)	16(1)
C39	7525(3)	4551(2)	1642(2)	15(1)
Cl3	5662(1)	3177(1)	3723(1)	40(1)
Cl4	3698(1)	3272(1)	5447(1)	33(1)
C40	4537(4)	4329(3)	3798(2)	35(1)
C41	3228(4)	3929(3)	4373(2)	28(1)
Cl5	3170(1)	9461(1)	4485(1)	54(1)
C42	4474(6)	10370(4)	4703(3)	56(1)
H2	11010(30)	8120(30)	1387(19)	16
H3	11280(30)	8420(30)	-110(20)	17
H4	11020(30)	6780(30)	-460(20)	19
H5	10620(30)	5170(30)	834(19)	17
H13	12790(30)	6860(30)	2360(20)	21
H14	13650(40)	7350(30)	3480(20)	26
H15	12360(40)	7070(30)	4680(20)	28
H16	10060(40)	6420(30)	4890(20)	26
H17	9130(40)	5880(30)	3850(20)	20
H19	8700(40)	4030(30)	3510(20)	19
H20	9160(40)	2180(30)	4030(20)	24
H21	11250(40)	1500(30)	3660(20)	26
H22	12650(40)	2490(30)	2630(20)	27
H23	12210(40)	4290(30)	2090(20)	20
H24	9210(30)	8060(30)	2570(20)	16
H27A	7580(30)	11780(30)	2510(20)	24
H27B	7550(30)	11570(30)	1500(20)	24
H28A	5210(40)	11720(30)	2120(20)	25
H28B	5430(40)	10750(30)	2800(20)	25
H31	4770(30)	8380(30)	1410(20)	17
H32A	8730(40)	8880(30)	3800(20)	30
H32B	7140(40)	9480(30)	3780(20)	30
H32C	8640(40)	10240(30)	3730(20)	30

H33A	10500(40)	9610(30)	2550(20)	23
H33B	10060(30)	11010(30)	2290(20)	23
H33C	9860(30)	10350(30)	1640(20)	23
H34A	3500(30)	9630(30)	2610(20)	26
H34B	3070(30)	9630(30)	1640(20)	26
H34C	2870(30)	10870(30)	1810(20)	26
H35A	6170(40)	11170(30)	600(20)	26
H35B	4720(40)	11660(30)	710(20)	26
H35C	4980(40)	10540(30)	440(20)	26
H36	4160(30)	6650(30)	1040(19)	18
H37	4460(40)	4870(30)	770(20)	20
H38	6330(30)	3630(30)	1189(19)	19
H39	8390(30)	3930(30)	1861(19)	18
H40A	5090(40)	4730(30)	4010(20)	42
H40B	4080(40)	4740(30)	3250(30)	42
H41A	2740(40)	3360(30)	4240(20)	34
H41B	2580(40)	4500(30)	4360(20)	34
H42A	5270(50)	10810(40)	4220(30)	68
H42B	3850(50)	11140(40)	4960(30)	68

Table 3. Selected bond lengths [Å] and angles [°] for $Ph_2C(Tet)(C_5H_4)ZrCl_2$.

Zr-Cp1	2.158	Cp1-Zr-Cp2	118.1
Zr-Cp2	2.242	Cp1-Zr-Cl1	108.9
Zr-Pln1	2.1551(12)	Cp1-Zr-Cl2	109.1
Zr-Pln2	2.2226(12)	Cp2-Zr-Cl1	109.5
Zr-Cl1	2.4063(7)	Cp2-Zr-Cl2	111.7
Zr-Cl2	2.4229(7)	Cl1-Zr-Cl2	98.84(2)
Zr-C1	2.431(3)	Pln1-Pln2	72.2(1)
Zr-C2	2.430(2)	C1-C11-C6	99.1(2)
Zr-C3	2.502(3)		
Zr-C4	2.524(3)		
Zr-C5	2.455(3)		
Zr-C6	2.408(3)		
Zr-C7	2.524(3)		
Zr-C8	2.669(3)		
Zr-C9	2.657(3)		
Zr-C10	2.507(3)		

Symmetry transformations used to generate equivalent atoms:
(i) -x+1,-y+2,-z+1
Cp1 is the centroid formed by C1, C2, C3, C4, C5
Cp2 is the centroid formed by C6, C7, C8, C9, C10
Pln1 is the plane formed by C1, C2, C3, C4, C5
Pln2 is the plane formed by C6, C7, C8, C9, C10