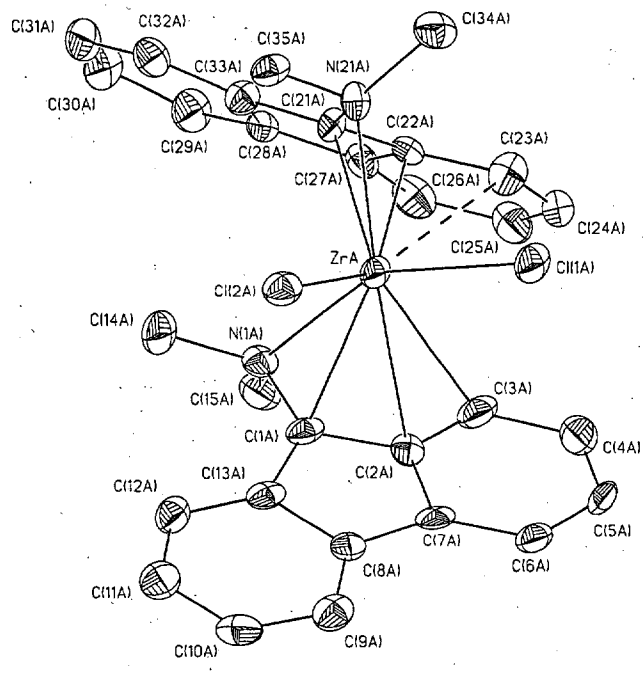
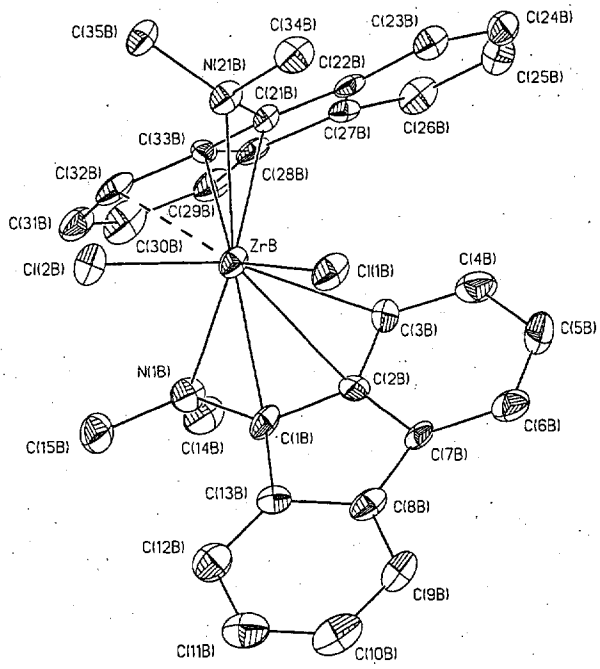
X-ray crystal structure data for $\{9\text{-}(Me_2N)C_{13}H_8\}_2ZrCl_2$ (4)

Cambridge Database

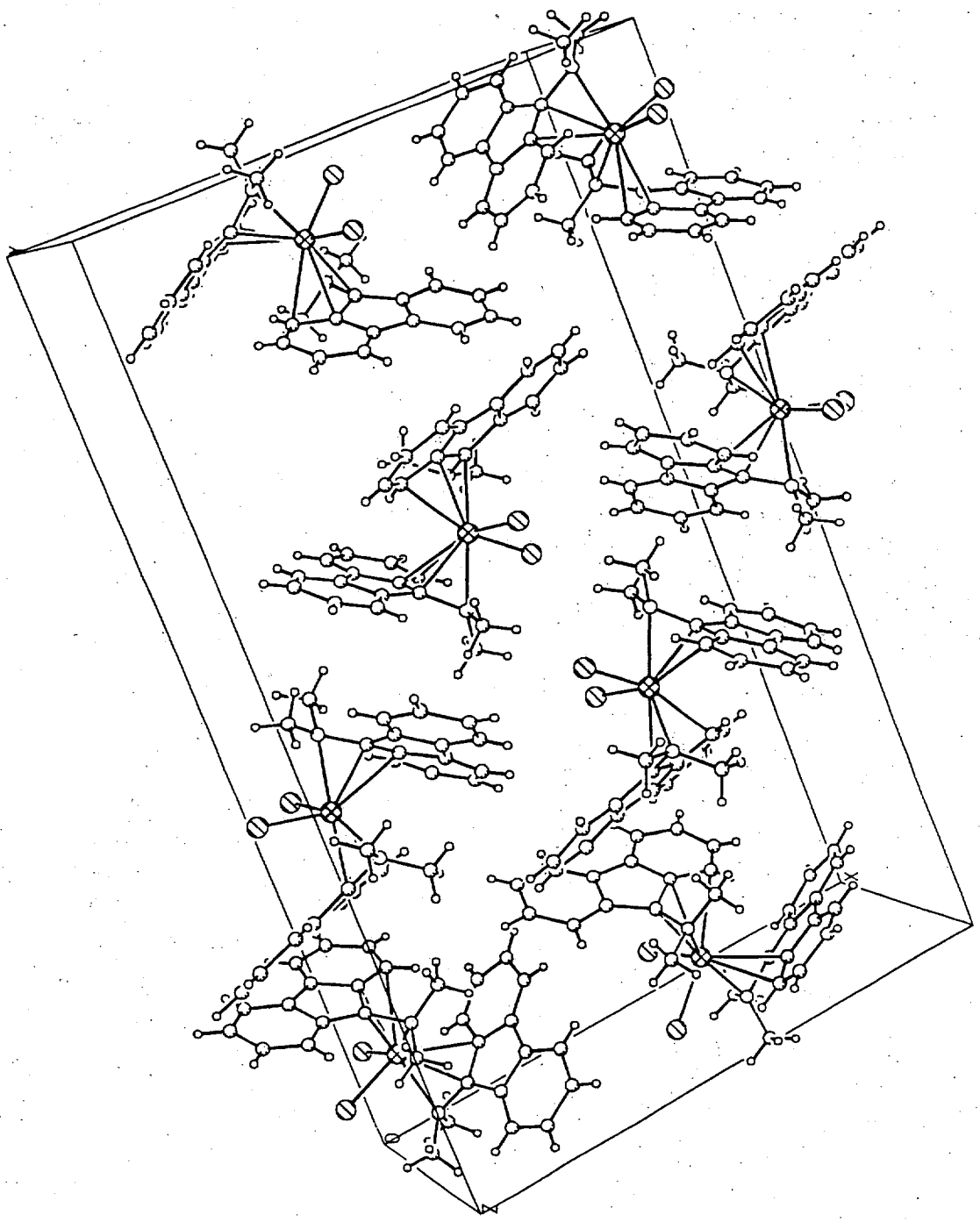
(CCDC) 100582



Labeled view of molecule A with 50% probability ellipsoids



Labeled view of molecule B with 50% probability ellipsoids



Depiction of unit cell contents showing the unit cell boundaries

Table 1. Crystal data and structure refinement for $\{9\text{-}(Me_2N)\text{-}C_{13}H_8\}_2ZrCl_2$.

Empirical formula	$C_{30}\ H_{28}\ Cl_2\ N_2\ Zr$	
Formula weight	578.69	
Crystallization solvent	dichloromethane	
Crystal shape	irregular fragment	
Crystal size	0.37 x 0.29 x 0.08 mm	
Crystal color	almandine	
Data Collection		
Type of diffractometer	CAD-4	
Wavelength	0.71073Å MoK alpha	
Data collection temperature	160 K	
Lattice determination from	25 reflections	
Theta range for reflections used in lattice determination	11.4 to 13.1°	
Unit cell dimensions	a = 18.781(3)Å	alpha = 90°
	b = 30.088(9)Å	beta = 99.17(3)°
	c = 8.994(8)Å	gamma = 90°
Volume	5017(3)Å^3	
Z	8	
Crystal system and space group	Monoclinic P2(1)/n	
Density (calculated)	1.532 g/cm^3	
Absorption coefficient	0.674 mm^{-1}	
F(000)	2368	
Theta range for data collection	1.75 to 25.0°	
Index ranges	-22<=h<=22, -35<=k<=35, 0<=l<=10	
Data collection scan type	Omega-scans	
Reflections collected	19792	
Independent reflections	8829 [R(merge) = 0.08 GOF(merge) = 1.26]	
Absorption correction	None	
Number of standards	3 reflections measured every 60 min.	
Variation of standards	0.9%	
Structure Solution and Refinement		
Structure solution program	SHELXS-86 (Sheldrick, 1990)	
Primary solution method	Direct methods	
Secondary solution method	Difference Fourier map	
Hydrogen placement	Calculated geometric sites	
Structure refinement program	SHELXL-93 (Sheldrick, 1993)	
Refinement method	Full matrix least-squares on F^2	
Data / restraints / parameters	Restrained to calculated geometric sites	
Goodness-of-fit on F^2	1.132	
Final R indices [I>2sigma(I)]	R1 = 0.0747, wR2 = 0.0942	
R indices (all data)	R1 = 0.1487, wR2 = 0.1120	
Max shift/error	-0.001	
Average shift/error	0.000	
Largest diff. peak and hole	0.611 and -0.606 e.Å^{-3}	

Special Notes

These crystals were extremely fragile and were falling apart as they were being removed from the Paratone. Therefore, the data were weak and the refinement statistics were adversely affected.

Refinement on F^2 for ALL reflections except for 3 with very negative F^2 or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating _R_factor_obs, 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 (9-(Me_2N)-$C_{13}H_8$)$_2$$ZrCl_2$. U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
ZrA	620(1)	1008(1)	2018(1)	20(1)
Cl(1A)	362(1)	939(1)	-716(2)	28(1)
Cl(2A)	-599(1)	787(1)	2318(2)	27(1)
N(1A)	817(3)	1454(2)	4230(7)	23(2)
N(21A)	882(3)	249(2)	2181(6)	20(2)
C(1A)	265(4)	1675(2)	3155(8)	23(2)
C(2A)	480(4)	1839(2)	1797(8)	20(2)
C(3A)	1114(5)	1815(2)	1236(9)	30(2)
C(4A)	1140(5)	1956(2)	-267(10)	38(2)
C(5A)	520(5)	2120(2)	-1102(9)	34(2)
C(6A)	-126(5)	2150(2)	-566(8)	29(2)
C(7A)	-165(4)	2022(2)	891(9)	26(2)
C(8A)	-733(4)	2013(2)	1779(8)	22(2)
C(9A)	-1432(4)	2169(2)	1486(9)	29(2)
C(10A)	-1876(5)	2131(2)	2556(10)	32(2)
C(11A)	-1617(5)	1932(2)	3939(9)	31(2)
C(12A)	-932(4)	1776(2)	4259(9)	27(2)
C(13A)	-464(4)	1809(2)	3206(8)	22(2)
C(14A)	534(4)	1229(2)	5468(8)	33(2)
C(15A)	1421(4)	1740(2)	4894(9)	33(2)
C(21A)	1446(4)	486(2)	3166(8)	17(2)
C(22A)	1976(4)	749(2)	2548(8)	22(2)
C(23A)	2044(4)	897(2)	1111(8)	29(2)
C(24A)	2581(4)	1194(2)	933(9)	32(2)
C(25A)	3056(4)	1363(2)	2147(10)	33(2)
C(26A)	3009(4)	1207(2)	3573(10)	32(2)
C(27A)	2494(4)	907(2)	3802(8)	22(2)
C(28A)	2339(4)	684(2)	5129(8)	22(2)
C(29A)	2736(4)	685(2)	6598(9)	32(2)
C(30A)	2535(5)	411(2)	7680(9)	34(2)
C(31A)	1926(4)	132(3)	7329(9)	32(2)
C(32A)	1521(4)	138(2)	5903(8)	28(2)
C(33A)	1730(4)	403(2)	4776(8)	22(2)
C(34A)	1115(4)	-24(2)	982(8)	30(2)
C(35A)	417(4)	-27(2)	2982(8)	24(2)
ZrB	-4496(1)	905(1)	-2308(1)	19(1)
Cl(1B)	-4939(1)	954(1)	-4990(2)	28(1)
Cl(2B)	-5465(1)	416(1)	-1845(2)	29(1)
N(1B)	-4819(3)	1430(2)	-588(7)	25(2)
N(21B)	-3896(3)	237(2)	-2770(6)	20(2)
C(1B)	-4991(4)	1627(2)	-2072(8)	21(2)
C(2B)	-4419(4)	1754(2)	-2834(8)	18(2)
C(3B)	-3687(4)	1645(2)	-2622(9)	23(2)
C(4B)	-3279(4)	1751(2)	-3712(9)	30(2)
C(5B)	-3582(5)	1982(2)	-5004(10)	36(2)
C(6B)	-4300(4)	2100(2)	-5228(9)	29(2)

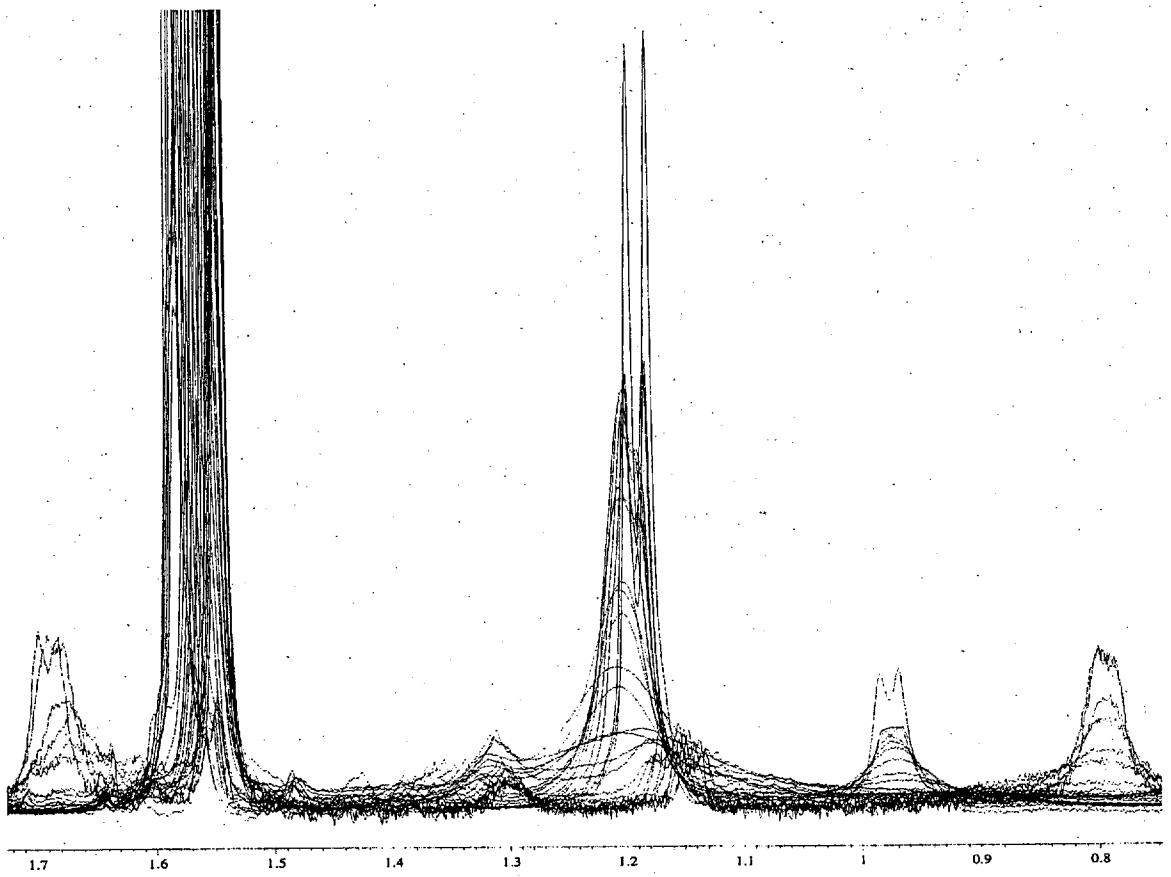
C(7B)	-4736(4)	1991(2)	-4181(8)	20(2)
C(8B)	-5485(4)	2044(2)	-4120(8)	25(2)
C(9B)	-6025(4)	2267(2)	-5101(9)	30(2)
C(10B)	-6702(5)	2294(2)	-4744(10)	38(2)
C(11B)	-6872(5)	2091(2)	-3487(10)	35(2)
C(12B)	-6362(4)	1852(2)	-2529(10)	31(2)
C(13B)	-5662(4)	1833(2)	-2833(9)	20(2)
C(14B)	-4327(4)	1712(2)	489(8)	33(2)
C(15B)	-5424(5)	1315(2)	175(9)	38(2)
C(21B)	-3374(4)	562(2)	-2074(7)	18(2)
C(22B)	-2699(4)	722(2)	-2469(8)	18(2)
C(23B)	-2384(4)	709(2)	-3764(8)	22(2)
C(24B)	-1751(4)	929(2)	-3830(8)	30(2)
C(25B)	-1392(4)	1172(2)	-2607(9)	29(2)
C(26B)	-1683(4)	1181(2)	-1304(9)	27(2)
C(27B)	-2318(4)	959(2)	-1210(7)	15(2)
C(28B)	-2722(4)	913(2)	36(7)	18(2)
C(29B)	-2589(4)	1069(2)	1497(8)	24(2)
C(30B)	-3073(4)	986(2)	2440(8)	33(2)
C(31B)	-3683(4)	742(2)	1974(8)	28(2)
C(32B)	-3830(4)	568(2)	516(8)	25(2)
C(33B)	-3347(4)	654(2)	-467(8)	17(2)
C(34B)	-3817(4)	136(2)	-4368(8)	28(2)
C(35B)	-3913(4)	-194(2)	-1988(8)	24(2)

Table 3. Selected bond lengths [Å] for (9-(Me_2N)-$C_{13}H_8$)$_2$$ZrCl_2$.

ZrA-C(21A)	2.330(7)
ZrA-N(21A)	2.337(5)
ZrA-N(1A)	2.379(6)
ZrA-C(1A)	2.394(7)
ZrA-Cl(1A)	2.438(2)
ZrA-Cl(2A)	2.439(2)
ZrA-C(2A)	2.516(7)
ZrA-C(22A)	2.633(7)
ZrA-C(3A)	2.731(7)
ZrA-C(23A)	2.939(8)
ZrB-C(21B)	2.326(7)
ZrB-N(1B)	2.357(6)
ZrB-N(21B)	2.373(5)
ZrB-C(1B)	2.384(7)
ZrB-Cl(2B)	2.427(2)
ZrB-Cl(1B)	2.428(2)
ZrB-C(2B)	2.605(6)
ZrB-C(33B)	2.614(7)
ZrB-C(3B)	2.736(7)
ZrB-C(32B)	2.834(7)

Determination of the barrier to rotation around the C-N bond of {9-(N,N-diisopropylamino)fluorenyl)(pentamethylcyclopentadienyl}$ZrCl_2$ (9)

An overlay of the ^{1}H NMR (400 MHz) spectra from the variable temperature study of **9** is shown below (in toluene-d_8). Spectra were take at 5°C intervals over the temperature range +65°C to - 65°C. At the high temperature limit, the methyl protons of the isopropyl groups give a doublet centered at δ 1.19. At the low temperature limit, two doublets, separated by 358 Hz, are seen: one at δ 0.79 and the other at δ 1.69. The coalescence temperature is approximately -25°C. Therefore, $k_{rotation}$(-25°C) = 796 s^{-1}, and $\Delta G^{\ddagger}$ (-25°C) is calculated to be 11.1 kcal·mol^{-1} The peak near δ 1.59 is attributed to the protons of the Cp* ligand. The peaks near δ 0.98 and 1.31 are attributed to impurities.



UV-visible electronic spectra of 4 and 5

The UV-visible electronic spectra obtained for **4** (M = Zr) and **5** (M = Hf) are shown below (solvent = toluene).