Supporting material to :

"Pentamethylcyclopentadienyl Zirconium and Hafnium Polyhydride Complexes: Synthesis, structure and reactivity"

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Part I: Crystal structure determination of $Cp^*_3Hf_3H_4Cl_5$ (6).

Abstract. $C_{30}H_{49}Cl_5Hf_3$, M = 1122.45, triclinic, P_{-1}, a = 9.029(1), b = 11.214(1), c = 17.449(2) Å, α = 88.912(95)°, β = 83.370(8)°, γ = 88.690(8)°, V = 1754.2(3) Å^3, Z = 2, D_x = 2.125 g cm^{-3}, λ(MoK$\bar{\alpha}$) = 0.71073 Å, μ = 92.5 cm^{-1}, F(000) = 1060, T = 130 K, $wR(F^2)$ = 0.1557 for 8065 reflections with $F_o^2 \geq 0$ and 358 parameters and $R(F)$ = 0.0589 for 7308 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

A white colored plate-shaped crystal, of approximate size 0.12 x 0.38 x 0.48 mm., used for characterization and data collection was glued on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F*[2] diffractometer, interfaced to a *INDY* (*Silicon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-K$\bar{\alpha}$ radiation, $\Delta\omega = 0.90 + 0.34\ \mathrm{tg}\ \theta$).

Cell constants and orientation matrices[3] for data collection were obtained from systematic searches of limited hemispheres of reciprocal space; sets of diffraction maxima were located whose *SET4*[4] setting angles (22 reflections in the range 18.19° < θ < 20.62°) were refined by least squares. The unit cell was identified as triclinic, space group P_{-1}. Reduced cell calculations did not indicate any higher metric lattice symmetry[5] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. A 360° ψ-scan for a reflections close to axial (1-4-1-) showed variation in intensity of 40% about the mean value. Intensity data were corrected for Lorentz and polarization effects, scale variation and for absorption (Gaussian integration:[8] grid 10 x 10 x 10; max. and min. correction: in the range 17.27 and 2.43) and reduced to F_o^2.[9]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[10] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined.

Refinement was frustrated by a disorder problem: from the solution it was clear that one of the three Cp^* ligands was highly rotational disordered: the electron density of the outer carbon atoms (C26—C30) appeared to be spread out. Attempts to refine a disorder model with discrete C-positions with fractional occupation in this region failed; so in the final refinement these atoms showed unrealistic displacement parameters.

The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using sp^3 hybridization at the C-atom as appropriate with $U_{iso} = c \times U_{equiv}$ of their parent atom, where $c = 1.5$ and where values U_{equiv} are related to the atoms to which the H atoms are bonded. The methyl-groups were refined as rigid groups, which were allowed to rotate free. The missing 4 hydride positions could not be located in the difference Fourier map.

Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.1557$ for 8065 reflections with $F_o^2 \geq 0$ and $R(F) = 0.0589$ for 7308 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 358 parameters. The final difference Fourier map showed all peaks within 1.0 Å from the three Hf positions; these were rejected, being artifacts.

The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \Sigma_h\ [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated

structure factor amplitudes, respectively; *a* and *b* were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables of Crystallography.*[11] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[12] (least-square refinements), *PLATON*[13] (calculation of geometric data and the *ORTEP* illustrations) and a locally modified version of the program *PLUTO*[14] (preparation of illustrations).

Table 1.

a. Crystal data and details of the structure determination.

Moiety_ Formula	$C_{30}H_{49}Cl_5Hf_3$
Formula_Weight, g.mol^{-1}	1122.45
Crystal system	triclinic
Space group	P^{-}
a, Å	9.029(1)
b, Å	11.214(1)
c, Å	17.449(2)
α, deg	88.912(9)
β, deg	83.370(8)
γ, deg	88.690(8)
V, Å^3	1754.2(3)
Formula_*Z*	2
ρ_{calc}, g.cm^{-3}	2.125
F(000), electrons	1060
μ(Mo K$\bar{\alpha}$), cm^{-1}	92.5
color, habit	white, plate
Approx. crystal dimension, mm	0.12 x 0.38 x 0.48

b. Data collection.

Radiation	Mo K$\bar{\alpha}$
Wavelength, Å	0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.47, 27.50
ω/2θ scan, deg	$\Delta\omega = 0.90 + 0.34$ tg θ
Index ranges	h: -11→11; k: -14→0; l: -22→22
Crystal-to-receiving-aperture-distance, mm	173
Horizontal-, vertical-aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	2-22, 2.3
r.m.s. dev. in %	-1-2-2, 2.4
	1-1-2, 1.0
Drift correction	0.954 - 1.014
Min.- max. absorption transmission factor	0.0579-.4111
X-ray exposure time, h	116.9
Total data	8737
Unique data	8065
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	7308
$R_{int} = \Sigma\ [\lvert F_o^2 - F_o^2\ (\text{mean})\rvert] / \Sigma\ [F_o^2]$	0.072
$R_{sig} = \Sigma\ \sigma(F_o^2) / \Sigma\ [F_o^2]$	0.0172

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)	8065
Number of refined parameters	358
Final agreement factors:	
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$	0.1557
for $F_o^2 > 0$	
Weighting scheme: *a, b*	0.0924, 49.26
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \Sigma(\|\|F_o\| - \|F_c\|\|) / \Sigma\|F_o\|$	0.0589
for $F_o > 4.0\ \sigma\ (F_o)$	
GooF = S $=[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.013
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
difference Fourier map, e/Å^3	-4.68, 10.6(4)
Max. (shift/σ) final cycle	< 0.001

Table 2. Final fractional atomic coordinates and equivalent isotropic displacement parameters for non-H atoms with s.u.'s in parentheses.

Atoms of the Asymmetric Unit.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
Hf(1)	0.17630(4)	0.11924(3)	0.27323(2)	0.0193(1)
Hf(2)	0.26690(4)	0.38284(3)	0.32219(2)	0.0183(1)
Hf(3)	0.26939(4)	0.26194(4)	0.12489(2)	0.0202(1)
Cl(1)	0.0898(3)	0.2433(3)	0.39871(14)	0.0309(7)
Cl(2)	0.3916(3)	0.4280(3)	0.18731(14)	0.0315(8)
Cl(3)	-0.0970(3)	0.1228(3)	0.27160(16)	0.0304(7)
Cl(4)	0.0636(3)	0.5184(3)	0.30622(19)	0.0380(9)
Cl(5)	0.5000(3)	0.1878(3)	0.05899(17)	0.0397(9)
C(1)	0.0370(11)	0.3570(9)	0.0903(5)	0.021(3)
C(2)	0.1521(12)	0.4351(10)	0.0577(6)	0.025(3)
C(3)	0.2419(12)	0.3694(10)	0.0000(6)	0.027(3)
C(4)	0.1816(13)	0.2542(11)	-0.0036(7)	0.031(3)
C(5)	0.0535(11)	0.2472(10)	0.0519(7)	0.027(3)
C(6)	-0.0955(12)	0.3916(11)	0.1450(7)	0.031(3)
C(7)	-0.0563(14)	0.1473(12)	0.0596(8)	0.038(4)
C(8)	0.3712(14)	0.4140(13)	-0.0536(7)	0.037(4)
C(9)	0.2350(15)	0.1599(15)	-0.0601(7)	0.045(5)
C(10)	0.1637(16)	0.5635(10)	0.0748(7)	0.037(3)
C(11)	0.2753(15)	-0.0365(10)	0.3560(7)	0.035(3)
C(12)	0.3714(14)	-0.035(1)	0.2858(9)	0.037(4)
C(13)	0.2862(15)	-0.0735(10)	0.2281(7)	0.034(3)
C(14)	0.1403(13)	-0.0991(9)	0.2615(7)	0.029(3)
C(15)	0.1333(13)	-0.0759(10)	0.3408(6)	0.029(3)
C(16)	0.314(3)	-0.0164(15)	0.4361(10)	0.067(7)
C(17)	0.5349(17)	-0.0113(13)	0.2746(13)	0.062(6)
C(18)	0.347(2)	-0.0992(14)	0.1455(9)	0.058(5)
C(19)	0.0207(18)	-0.1529(13)	0.2222(11)	0.053(5)
C(20)	-0.0047(19)	-0.0976(14)	0.3994(9)	0.058(5)
C(21)	0.472(3)	0.3661(13)	0.4061(13)	0.067(7)
C(22)	0.356(3)	0.403(2)	0.4512(10)	0.071(7)
C(23)	0.3133(15)	0.5115(19)	0.4285(10)	0.064(6)
C(24)	0.408(2)	0.5494(12)	0.3651(11)	0.058(6)
C(25)	0.5122(14)	0.4528(18)	0.3500(8)	0.055(5)
C(26)	0.556(4)	0.253(2)	0.419(2)	0.19(2)
C(27)	0.283(5)	0.345(4)	0.5238(13)	0.22(2)
C(28)	0.196(2)	0.588(5)	0.470(2)	0.28(3)
C(29)	0.411(5)	0.666(2)	0.323(3)	0.25(3)

C(30)	0.650(2)	0.439(3)	0.2936(13)	0.124(14)

*) $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i^*\mathbf{a}_j^*\mathbf{a}_i.\mathbf{a}_j$ [20]

Table 3. Thermal Displacement Parameters for non-H atoms with e.s.d.'s in parentheses.

Atoms of the Asymmetric Unit.

	U(1,1) or U	*U(2,2)*	*U(3,3)*	*U(2,3)*	*U(1,3)*	*U(1,2)*
Hf(1)	0.0216(2)	0.0170(2)	0.0187(2)	-0.00394(14)	0.00029(14)	-0.00277(14)
Hf(2)	0.0196(2)	0.0178(2)	0.01776(19)	-0.00472(14)	-0.00269(14)	-0.00101(14)
Hf(3)	0.01562(19)	0.0244(2)	0.0203(2)	-0.00322(15)	0.00030(14)	-0.00192(14)
Cl(1)	0.0367(14)	0.0321(13)	0.0220(11)	-0.0091(10)	0.008(1)	-0.0093(11)
Cl(2)	0.0357(14)	0.0388(14)	0.0209(11)	-0.0038(10)	-0.0026(10)	-0.0197(11)
Cl(3)	0.0199(11)	0.0346(13)	0.0363(13)	-0.0044(10)	0.000(1)	-0.0066(10)
Cl(4)	0.0349(14)	0.0292(13)	0.0524(17)	-0.0137(12)	-0.0154(13)	0.0101(11)
Cl(5)	0.0265(13)	0.0552(18)	0.0346(14)	-0.0076(13)	0.0085(11)	0.0077(12)
C(1)	0.017(4)	0.031(5)	0.018(4)	-0.003(4)	-0.009(3)	0.001(4)
C(2)	0.029(5)	0.027(5)	0.020(5)	0.000(4)	-0.007(4)	0.002(4)
C(3)	0.024(5)	0.034(6)	0.024(5)	-0.002(4)	-0.007(4)	-0.003(4)
C(4)	0.023(5)	0.037(6)	0.033(6)	-0.005(5)	0.004(4)	-0.006(4)
C(5)	0.014(4)	0.035(6)	0.033(5)	-0.008(4)	0.000(4)	-0.005(4)
C(6)	0.023(5)	0.039(6)	0.032(6)	-0.006(5)	-0.008(4)	0.009(4)
C(7)	0.027(6)	0.041(7)	0.047(7)	-0.015(5)	-0.006(5)	-0.016(5)
C(8)	0.032(6)	0.054(8)	0.027(5)	0.001(5)	-0.009(5)	-0.009(5)
C(9)	0.036(7)	0.073(10)	0.026(6)	-0.033(6)	-0.003(5)	-0.008(6)
C(10)	0.049(7)	0.023(5)	0.039(6)	-0.001(5)	-0.013(5)	0.001(5)
C(11)	0.050(7)	0.018(5)	0.038(6)	0.000(4)	-0.014(5)	0.006(5)
C(12)	0.027(6)	0.019(5)	0.066(8)	0.002(5)	-0.006(5)	0.002(4)
C(13)	0.043(7)	0.020(5)	0.036(6)	-0.005(4)	0.005(5)	-0.001(5)
C(14)	0.031(6)	0.016(4)	0.040(6)	-0.007(4)	0.002(5)	-0.005(4)
C(15)	0.035(6)	0.025(5)	0.027(5)	0.002(4)	0.003(4)	-0.007(4)
C(16)	0.112(16)	0.040(8)	0.055(9)	-0.001(7)	-0.042(10)	0.004(9)
C(17)	0.035(7)	0.032(7)	0.117(15)	0.005(8)	-0.004(8)	0.000(6)
C(18)	0.076(11)	0.043(8)	0.047(8)	-0.012(6)	0.033(8)	0.008(7)
C(19)	0.056(9)	0.029(7)	0.079(11)	-0.026(7)	-0.021(8)	-0.003(6)
C(20)	0.065(10)	0.045(8)	0.054(9)	0.022(7)	0.026(8)	0.003(7)
C(21)	0.095(14)	0.030(7)	0.093(14)	-0.006(8)	-0.084(13)	0.001(8)
C(22)	0.096(15)	0.083(14)	0.044(9)	0.014(9)	-0.039(10)	-0.059(13)
C(23)	0.024(6)	0.103(14)	0.069(10)	-0.068(11)	-0.008(6)	-0.002(7)
C(24)	0.076(11)	0.021(6)	0.089(12)	0.017(7)	-0.053(10)	-0.025(7)
C(25)	0.020(6)	0.114(14)	0.032(6)	-0.035(8)	0.000(5)	-0.015(7)

C(26)	0.24(4)	0.044(11)	0.32(5)	-0.054(19)	-0.24(4)	0.050(17)
C(27)	0.31(5)	0.32(5)	0.048(12)	0.07(2)	-0.09(2)	-0.25(5)
C(28)	0.035(11)	0.53(8)	0.28(5)	-0.37(6)	-0.024(18)	0.03(2)
C(29)	0.39(6)	0.048(12)	0.37(6)	0.11(2)	-0.35(5)	-0.12(2)
C(30)	0.038(10)	0.27(4)	0.067(13)	-0.059(19)	-0.008(9)	-

Table 4. Hydrogen parameters.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
H(6)	-0.18373(-)	0.39817(-)	0.11723(-)	0.04653(-)
H(6')	-0.07831(-)	0.46855(-)	0.16777(-)	0.04653(-)
H(6'')	-0.11154(-)	0.33071(-)	0.18601(-)	0.04653(-)
H(7)	-0.10322(-)	0.14185(-)	0.11303(-)	0.05684(-)
H(7')	-0.00408(-)	0.07183(-)	0.04562(-)	0.05684(-)
H(7'')	-0.13313(-)	0.16312(-)	0.02513(-)	0.05684(-)
H(8)	0.45848(-)	0.36171(-)	-0.04952(-)	0.05557(-)
H(8')	0.39383(-)	0.49528(-)	-0.03953(-)	0.05557(-)
H(8'')	0.34586(-)	0.41430(-)	-0.10669(-)	0.05557(-)
H(9)	0.15391(-)	0.13937(-)	-0.08995(-)	0.06697(-)
H(9')	0.26698(-)	0.08878(-)	-0.03241(-)	0.06697(-)
H(9'')	0.31928(-)	0.18967(-)	-0.09519(-)	0.06697(-)
H(10)	0.26637(-)	0.58881(-)	0.06018(-)	0.05504(-)
H(10')	0.13610(-)	0.57591(-)	0.13006(-)	0.05504(-)
H(10'')	0.09613(-)	0.61045(-)	0.04534(-)	0.05504(-)
H(16)	0.26295(-)	0.05634(-)	0.45654(-)	0.09959(-)
H(16')	0.42188(-)	-0.00790(-)	0.43462(-)	0.09959(-)
H(16'')	0.28178(-)	-0.08463(-)	0.46937(-)	0.09959(-)
H(17)	0.59086(-)	-0.08698(-)	0.26791(-)	0.09270(-)
H(17')	0.56289(-)	0.02914(-)	0.31995(-)	0.09270(-)
H(17'')	0.55798(-)	0.03956(-)	0.22868(-)	0.09270(-)
H(18)	0.39124(-)	-0.17991(-)	0.14252(-)	0.08800(-)
H(18')	0.42400(-)	-0.04122(-)	0.12772(-)	0.08800(-)
H(18'')	0.26638(-)	-0.09292(-)	0.11261(-)	0.08800(-)
H(19)	0.05733(-)	-0.16641(-)	0.16793(-)	0.08045(-)
H(19')	-0.06638(-)	-0.09865(-)	0.22537(-)	0.08045(-)
H(19'')	-0.00772(-)	-0.22913(-)	0.24751(-)	0.08045(-)
H(20)	-0.09461(-)	-0.07080(-)	0.37698(-)	0.08646(-)
H(20')	0.00375(-)	-0.05276(-)	0.44636(-)	0.08646(-)
H(20'')	-0.01113(-)	-0.18287(-)	0.41227(-)	0.08646(-)
H(26)	0.59633(-)	0.25614(-)	0.46839(-)	0.27837(-)
H(26')	0.63723(-)	0.24344(-)	0.37716(-)	0.27837(-)
H(26'')	0.48808(-)	0.18606(-)	0.41929(-)	0.27837(-)
H(27)	0.18691(-)	0.31264(-)	0.51411(-)	0.32653(-)

H(27')	0.26620(-)	0.40458(-)	0.56448(-)	0.32653(-)
H(27")	0.34742(-)	0.28037(-)	0.54022(-)	0.32653(-)
H(28)	0.14878(-)	0.54519(-)	0.51557(-)	0.41554(-)
H(28')	0.12039(-)	0.60995(-)	0.43590(-)	0.41554(-)
H(28")	0.24069(-)	0.66110(-)	0.48660(-)	0.41554(-)
H(29)	0.32156(-)	0.67532(-)	0.29604(-)	0.36885(-)
H(29')	0.49995(-)	0.66822(-)	0.28455(-)	0.36885(-)
H(29")	0.41426(-)	0.73093(-)	0.35906(-)	0.36885(-)
H(30)	0.73426(-)	0.41355(-)	0.32127(-)	0.18658(-)
H(30')	0.67221(-)	0.51489(-)	0.26681(-)	0.18658(-)
H(30")	0.63370(-)	0.37813(-)	0.25579(-)	0.18658(-)

Table 5. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

Hf(1)	-Hf(2)	3.241(6)	C(2)	-C(3)	1.423(15)
Hf(1)	-Hf(3)	3.0608(6)	C(2)	-C(10)	1.484(16)
Hf(1)	-Cl(1)	2.648(3)	C(3)	-C(4)	1.419(17)
Hf(1)	-Cl(3)	2.470(3)	C(3)	-C(8)	1.498(17)
Hf(1)	-C(11)	2.463(12)	C(4)	-C(5)	1.423(16)
Hf(1)	-C(12)	2.465(12)	C(4)	-C(9)	1.493(19)
Hf(1)	-C(13)	2.462(12)	C(5)	-C(7)	1.507(17)
Hf(1)	-C(14)	2.493(10)	C(11)	-C(12)	1.417(19)
Hf(1)	-C(15)	2.483(11)	C(11)	-C(15)	1.421(18)
Hf(2)	-Hf(3)	3.721(7)	C(11)	-C(16)	1.50(2)
Hf(2)	-Cl(1)	2.516(3)	C(12)	-C(13)	1.415(19)
Hf(2)	-Cl(2)	2.536(3)	C(12)	-C(17)	1.50(2)
Hf(2)	-Cl(4)	2.394(3)	C(13)	-C(14)	1.411(18)
Hf(2)	-C(21)	2.49(3)	C(13)	-C(18)	1.51(2)
Hf(2)	-C(22)	2.49(2)	C(14)	-C(15)	1.407(16)
Hf(2)	-C(23)	2.451(19)	C(14)	-C(19)	1.49(2)
Hf(2)	-C(24)	2.461(16)	C(15)	-C(20)	1.54(2)
Hf(2)	-C(25)	2.470(14)	C(21)	-C(22)	1.30(3)
Hf(3)	-Cl(2)	2.514(3)	C(21)	-C(25)	1.39(3)
Hf(3)	-Cl(5)	2.399(3)	C(21)	-C(26)	1.49(3)
Hf(3)	-C(1)	2.464(10)	C(22)	-C(23)	1.33(3)
Hf(3)	-C(2)	2.524(11)	C(22)	-C(27)	1.50(4)
Hf(3)	-C(3)	2.505(11)	C(23)	-C(24)	1.38(2)
Hf(3)	-C(4)	2.466(12)	C(23)	-C(28)	1.48(4)
Hf(3)	-C(5)	2.459(11)	C(24)	-C(25)	1.43(2)

C(1)	-C(2)	1.434(15)		C(24)	-C(29)	1.49(4)	
C(1)	-C(5)	1.410(15)		C(25)	-C(30)	1.50(2)	
C(1)	-C(6)	1.491(15)					

Bond angles (deg.)

Hf(3)	-Hf(1)	-Cl(1)	116.81(7)	C(21)	-Hf(2)	-C(25)	32.5(6)
Hf(3)	-Hf(1)	-Cl(3)	99.85(7)	C(22)	-Hf(2)	-C(23)	31.3(7)
Hf(3)	-Hf(1)	-C(11)	140.1(3)	C(22)	-Hf(2)	-C(24)	53.4(7)
Hf(3)	-Hf(1)	-C(12)	107.2(3)	C(22)	-Hf(2)	-C(25)	52.7(7)
Hf(3)	-Hf(1)	-C(13)	96.7(3)	C(23)	-Hf(2)	-C(24)	32.7(6)
Hf(3)	-Hf(1)	-C(14)	117.6(3)	C(23)	-Hf(2)	-C(25)	53.7(5)
Hf(3)	-Hf(1)	-C(15)	149.7(2)	C(24)	-Hf(2)	-C(25)	33.6(6)
Cl(1)	-Hf(1)	-Cl(3)	79.24(9)	Hf(1)	-Hf(3)	-Cl(2)	96.58(6)
Cl(1)	-Hf(1)	-C(11)	88.6(3)	Hf(1)	-Hf(3)	-Cl(5)	111.82(8)
Cl(1)	-Hf(1)	-C(12)	115.9(4)	Hf(1)	-Hf(3)	-C(1)	105.0(2)
Cl(1)	-Hf(1)	-C(13)	143.3(3)	Hf(1)	-Hf(3)	-C(2)	133.5(2)
Cl(1)	-Hf(1)	-C(14)	124.5(3)	Hf(1)	-Hf(3)	-C(3)	158.1(3)
Cl(1)	-Hf(1)	-C(15)	93.5(3)	Hf(1)	-Hf(3)	-C(4)	130.7(3)
Cl(3)	-Hf(1)	-C(11)	115.6(3)	Hf(1)	-Hf(3)	-C(5)	103.4(3)
Cl(3)	-Hf(1)	-C(12)	136.1(3)	Cl(2)	-Hf(3)	-Cl(5)	93.59(10)
Cl(3)	-Hf(1)	-C(13)	110.9(3)	Cl(2)	-Hf(3)	-C(1)	103.0(2)
Cl(3)	-Hf(1)	-C(14)	81.5(3)	Cl(2)	-Hf(3)	-C(2)	81.9(3)
Cl(3)	-Hf(1)	-C(15)	84.1(3)	Cl(2)	-Hf(3)	-C(3)	96.8(3)
C(11)	-Hf(1)	-C(12)	33.4(5)	Cl(2)	-Hf(3)	-C(4)	129.9(3)
C(11)	-Hf(1)	-C(13)	54.8(4)	Cl(2)	-Hf(3)	-C(5)	135.2(3)
C(11)	-Hf(1)	-C(14)	55.0(4)	Cl(5)	-Hf(3)	-C(1)	137.4(2)
C(11)	-Hf(1)	-C(15)	33.4(4)	Cl(5)	-Hf(3)	-C(2)	114.6(3)
C(12)	-Hf(1)	-C(13)	33.4(4)	Cl(5)	-Hf(3)	-C(3)	84.6(3)
C(12)	-Hf(1)	-C(14)	55.5(4)	Cl(5)	-Hf(3)	-C(4)	84.0(3)
C(12)	-Hf(1)	-C(15)	55.5(4)	Cl(5)	-Hf(3)	-C(5)	114.6(3)
C(13)	-Hf(1)	-C(14)	33.1(4)	C(1)	-Hf(3)	-C(2)	33.4(3)
C(13)	-Hf(1)	-C(15)	54.6(4)	C(1)	-Hf(3)	-C(3)	54.9(3)
C(14)	-Hf(1)	-C(15)	32.8(4)	C(1)	-Hf(3)	-C(4)	55.3(3)
Cl(1)	-Hf(2)	-Cl(2)	143.11(9)	C(1)	-Hf(3)	-C(5)	33.3(3)
Cl(1)	-Hf(2)	-Cl(4)	89.91(10)	C(2)	-Hf(3)	-C(3)	32.9(3)
Cl(1)	-Hf(2)	-C(21)	97.4(5)	C(2)	-Hf(3)	-C(4)	55.0(4)
Cl(1)	-Hf(2)	-C(22)	81.0(6)	C(2)	-Hf(3)	-C(5)	55.3(4)
Cl(1)	-Hf(2)	-C(23)	97.6(4)	C(3)	-Hf(3)	-C(4)	33.1(4)
Cl(1)	-Hf(2)	-C(24)	130.1(4)	C(3)	-Hf(3)	-C(5)	55.2(4)
Cl(1)	-Hf(2)	-C(25)	129.7(4)	C(4)	-Hf(3)	-C(5)	33.6(4)
Cl(2)	-Hf(2)	-Cl(4)	92.18(10)	Hf(1)	-Cl(1)	-Hf(2)	77.71(7)
Cl(2)	-Hf(2)	-C(21)	105.9(6)	Hf(2)	-Cl(2)	-Hf(3)	94.93(10)

Cl(2)	-Hf(2)	-C(22)	131.4(6)	Hf(3)	-C(1)	-C(2)	75.6(6)
Cl(2)	-Hf(2)	-C(23)	119.3(4)	Hf(3)	-C(1)	-C(5)	73.2(6)
Cl(2)	-Hf(2)	-C(24)	86.7(4)	Hf(3)	-C(1)	-C(6)	126.2(7)
Cl(2)	-Hf(2)	-C(25)	78.7(3)	C(2)	-C(1)	-C(5)	109.0(9)
Cl(4)	-Hf(2)	-C(21)	136.8(4)	C(2)	-C(1)	-C(6)	126.0(9)
Cl(4)	-Hf(2)	-C(22)	111.4(6)	C(5)	-C(1)	-C(6)	124.1(9)
Cl(4)	-Hf(2)	-C(23)	85.1(4)	Hf(3)	-C(2)	-C(1)	71.0(6)
Cl(4)	-Hf(2)	-C(24)	89.3(4)	Hf(3)	-C(2)	-C(3)	72.8(6)
Cl(4)	-Hf(2)	-C(25)	121.9(5)	Hf(3)	-C(2)	-C(10)	126.6(8)
C(21)	-Hf(2)	-C(22)	30.2(8)	C(1)	-C(2)	-C(3)	106.7(9)
C(21)	-Hf(2)	-C(23)	51.7(6)	C(1)	-C(2)	-C(10)	126.1(10)
C(21)	-Hf(2)	-C(24)	54.0(5)	C(3)	-C(2)	-C(10)	126.9(10)
Hf(3)	-C(3)	-C(2)	74.3(6)	C(13)	-C(14)	-C(15)	107.2(10)
Hf(3)	-C(3)	-C(4)	71.9(6)	C(13)	-C(14)	-C(19)	126.5(12)
Hf(3)	-C(3)	-C(8)	123.5(8)	C(15)	-C(14)	-C(19)	126.0(12)
C(2)	-C(3)	-C(4)	108.5(10)	Hf(1)	-C(15)	-C(11)	72.5(6)
C(2)	-C(3)	-C(8)	127.2(11)	Hf(1)	-C(15)	-C(14)	74.0(6)
C(4)	-C(3)	-C(8)	124.1(10)	Hf(1)	-C(15)	-C(20)	122.0(8)
Hf(3)	-C(4)	-C(3)	74.9(7)	C(11)	-C(15)	-C(14)	108.2(10)
Hf(3)	-C(4)	-C(5)	72.9(7)	C(11)	-C(15)	-C(20)	127.6(11)
Hf(3)	-C(4)	-C(9)	122.0(8)	C(14)	-C(15)	-C(20)	124.2(11)
C(3)	-C(4)	-C(5)	108.2(10)	Hf(2)	-C(21)	-C(22)	74.9(15)
C(3)	-C(4)	-C(9)	126.1(11)	Hf(2)	-C(21)	-C(25)	72.9(11)
C(5)	-C(4)	-C(9)	125.5(11)	Hf(2)	-C(21)	-C(26)	123.6(17)
Hf(3)	-C(5)	-C(1)	73.5(6)	C(22)	-C(21)	-C(25)	109.7(17)
Hf(3)	-C(5)	-C(4)	73.5(6)	C(22)	-C(21)	-C(26)	124.(2)
Hf(3)	-C(5)	-C(7)	125.3(8)	C(25)	-C(21)	-C(26)	126.(2)
C(1)	-C(5)	-C(4)	107.6(9)	Hf(2)	-C(22)	-C(21)	74.9(13)
C(1)	-C(5)	-C(7)	126.2(10)	Hf(2)	-C(22)	-C(23)	72.6(11)
C(4)	-C(5)	-C(7)	125.6(11)	Hf(2)	-C(22)	-C(27)	124.(2)
Hf(1)	-C(11)	-C(12)	73.4(7)	C(21)	-C(22)	-C(23)	109.9(18)
Hf(1)	-C(11)	-C(15)	74.1(7)	C(21)	-C(22)	-C(27)	128.(3)
Hf(1)	-C(11)	-C(16)	124.4(9)	C(23)	-C(22)	-C(27)	121.(2)
C(12)	-C(11)	-C(15)	108.5(11)	Hf(2)	-C(23)	-C(22)	76.1(12)
C(12)	-C(11)	-C(16)	128.2(15)	Hf(2)	-C(23)	-C(24)	74.(1)
C(15)	-C(11)	-C(16)	122.9(14)	Hf(2)	-C(23)	-C(28)	122.9(14)
Hf(1)	-C(12)	-C(11)	73.2(7)	C(22)	-C(23)	-C(24)	109.8(16)
Hf(1)	-C(12)	-C(13)	73.2(7)	C(22)	-C(23)	-C(28)	126.(2)
Hf(1)	-C(12)	-C(17)	123.9(9)	C(24)	-C(23)	-C(28)	124.(2)
C(11)	-C(12)	-C(13)	106.4(11)	Hf(2)	-C(24)	-C(23)	73.2(10)
C(11)	-C(12)	-C(17)	127.7(14)	Hf(2)	-C(24)	-C(25)	73.5(9)
C(13)	-C(12)	-C(17)	125.5(15)	Hf(2)	-C(24)	-C(29)	120.(2)
Hf(1)	-C(13)	-C(12)	73.4(7)	C(23)	-C(24)	-C(25)	104.6(14)
Hf(1)	-C(13)	-C(14)	74.6(7)	C(23)	-C(24)	-C(29)	129.(2)
Hf(1)	-C(13)	-C(18)	124.7(9)	C(25)	-C(24)	-C(29)	126.(2)

C(12)	-C(13)	-C(14)	109.6(11)	Hf(2)	-C(25)	-C(21)	74.6(13)
C(12)	-C(13)	-C(18)	125.2(13)	Hf(2)	-C(25)	-C(24)	72.8(9)
C(14)	-C(13)	-C(18)	124.7(12)	Hf(2)	-C(25)	-C(30)	122.1(12)
Hf(1)	-C(14)	-C(13)	72.3(6)	C(21)	-C(25)	-C(24)	105.9(15)
Hf(1)	-C(14)	-C(15)	73.2(6)	C(21)	-C(25)	-C(30)	122.(2)
Hf(1)	-C(14)	-C(19)	124.8(8)	C(24)	-C(25)	-C(30)	132.2(19)

Part II: Structure determination of $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$ (7).

Abstract. $C_{23}H_{42}Cl_3PZr_2$, M_r = 638.36, monoclinic, $P2_1/c$, a = 15.599(3), b = 11.203(3), c = 16.862(4) Å, β = 103.27(2) °, V = 2868(1) Å^3, Z = 4, D_x = 1.478 gcm^{-3}, λ(MoK$\bar{\alpha}$) = 0.71073 Å, μ = 10.6 cm^{-3}, F(000) = 1304, T = 130 K, R_F = 0.034 for 5557 unique observed reflections with I = 2.5 σ(I) and 432 parameters. The crystal structure was solved by standard Patterson methods and subsequent partial structure expansion and difference Fourier techniques.

Experimental.

X-ray diffraction: Crystal and Molecular Structure.

A suitable transparant coloured parallelepiped shaped crystal, 0.18 x 0.25 x 0.30 mm, obtained by recrystallisation from Et_2O, was glued on the top of a glass fiber and transferred into the cold nitrogen stream of the low temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Data were obtained at 130 K. Precise lattice parameters and their standard deviation were derived from the angular settings of 22 reflections in the range 16.58° < θ < 19.27°. Space group $P2_1/c$ was determined from the observed systematic extinctions; h0l: l=2n+1 and 0k0: k=2n+1 and checked for the presence of higher metrical symmetry[21]. This choice was confirmed by the solution and the successful refinement in this space group of the structure. Three reference reflections measured every three hours of X-ray exposure indicated a small linear decay of 6.5% over 138 h of X-ray exposure time. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects. The correction for absorption was judged to be not necessary in view of the observed small intensity variation (7%) for an 360° ψ-scan of the reflection (131) close to axial. Variance in the intensities based on counting statistics were increased according to an analysis of the excess variance[21] of the three reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.027I)^2$[21] and equivalent reflections were averaged resulting in 5557 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability.

The structure was solved by Patterson methods and subsequent partial structure expansion

(SHELXS86[22]) and from subsequent difference Fourier syntheses. Refinement of the positions and anisotropic thermal parameters for the non-hydrogen atoms followed by difference Fourier synthesis resulted in the location of all the hydrogen atoms. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged at R_F = 0.034 (wR = 0.039). Weights were introduced in the final refinement cycles.The quantity minimized by the least-squares procedure was: $Q = \Sigma_h [w(|F_o| - |F_c|)^2]$. The crystal exhibited some secondary extinction for which the F values were corrected by refinement of an empirical isotropic extinction parameter[23]. The final difference Fourier map was essentially featureless with the minimum and maximum residual densities map of -1.03 and 1.09 e/ Å^3 in the neighbourhood of the Cl1 atom. Scattering factors were taken from Cromer & Mann[24]. Anomalous dispersion factors are those given by Cromer & Liberman[25]. All calculations carried out on the CDCCyber 170/760 computer of the University of Groningen with the program packages XTAL[26], EUCLID[27] (calculations of geometric data) and a locally modified version of the program PLUTO[28] (preparation of illustrations).

Table 1.

a. Crystal data and details of the structure determination.

Moiety_ Formula	$C_{23}H_{42}Cl_3PZr_2$
Formula_Weight, g.mol^{-1}	638.36
Crystal system	monoclinic
Space group	$P2_1/c$, 14
a, Å	15.599(3)
b, Å	11.203(3)
c, Å	16.862(4)
β, deg	103.27(2)
V, Å^3	2868(1)
Formula_*Z*	4
ρ_{calc}, g.cm^{-3}	1.478
F(000), electrons	1304
μ(Mo K$\bar{\alpha}$), cm^{-1}	10.6
color, habit	white plate
Approx. crystal dimension, mm	0.18 x 0.25 x 0.30

b. Data collection.

Diffractometer	Enraf-Nonius CAD-4F
Radiation	Mo K$\bar{\alpha}$, 0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.24, 28.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 1.05 + 0.35$ tg θ
Index ranges	h: -20→20; k: -1→14; l: 0→22
Crystal-to-receiving-aperture-distance, mm	173
Horizontal-, vertical-aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	224, 1.7
r.m.s. dev. in %	216, 1.6
	420, 1.3
Instability constant *P*	0.027
Drift correction	1.000-1.065
Min.- max. absorption transmission factor	0.0579-.4111
X-ray exposure time, h	138
Total data	8206
Unique data	6899
Data with criterion: ($I \geq 2.5\sigma(I)$)	5557
$R_1 = \Sigma [I-I] / \Sigma I$	0.020
$R_2 = \Sigma\sigma / \Sigma I$	0.035
Number of equivalent reflections	1858

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)	5557
Number of refined parameters	432
Isotropic secondary-extinction coefficient, g	$0.71(3)*10^{-4}$
Final agreement factors:	
$R_F = \Sigma(\|\|F_o\| - \|F_c\|\|) / \Sigma\|F_o\|$	0.034
$wR = [\Sigma[w(\|F_o\| - \|F_c\|)^2] / \Sigma w\|F_o\|^2]^{1/2}$	0.039
Weighting scheme:	$1/\sigma^2(F)$
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2] / (m-n)]^{1/2}$	2.045
m = number of reflections	
n = number of parameters refined	
Residual electron density in final	
difference Fourier map, e/Å^3	-1.03, 1.09
Max. (shift/σ) final cycle	0.044
Average (shift/σ) final cycle	0.003

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms, with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
Zr(1)	0.31241(2)	0.03409(3)	0.18013(2)	0.0149(1)
Zr(2)	0.16663(2)	-0.02374(2)	0.27432(2)	0.0146(1)
Cl(1)	0.38097(5)	-0.14226(7)	0.13204(5)	0.0225(2)
Cl(2)	0.16848(5)	0.15186(6)	0.36187(4)	0.0196(2)
Cl(3)	0.02544(4)	0.00053(7)	0.17562(4)	0.0216(2)
P(1)	0.19892(5)	0.03390(7)	0.02942(5)	0.0189(2)
C(1)	0.3440(2)	0.2506(3)	0.2112(2)	0.0220(9)
C(2)	0.3674(2)	0.2302(3)	0.1362(2)	0.0235(9)
C(3)	0.4402(2)	0.1499(3)	0.1500(2)	0.0235(9)
C(4)	0.4610(2)	0.1205(3)	0.2349(2)	0.0225(9)
C(5)	0.4018(2)	0.1844(3)	0.2722(2)	0.0224(9)
C(6)	0.2750(2)	0.3398(3)	0.2245(2)	0.036(1)
C(7)	0.3350(2)	0.3018(4)	0.0599(2)	0.038(1)
C(8)	0.4877(2)	0.1092(4)	0.0872(2)	0.040(1)
C(9)	0.5337(2)	0.0404(4)	0.2782(2)	0.037(1)
C(10)	0.4078(2)	0.1919(4)	0.3627(2)	0.034(1)
C(11)	0.2289(2)	-0.1585(3)	0.3915(2)	0.027(1)
C(12)	0.2185(2)	-0.2281(3)	0.3193(2)	0.0227(9)
C(13)	0.1266(2)	-0.2381(3)	0.2830(2)	0.0215(9)
C(14)	0.0801(2)	-0.1772(3)	0.3343(2)	0.026(1)
C(15)	0.1426(2)	-0.1282(3)	0.4009(2)	0.027(1)
C(16)	0.3145(3)	-0.1291(4)	0.4503(2)	0.042(1)
C(17)	0.2906(2)	-0.2900(3)	0.2894(2)	0.030(1)
C(18)	0.0881(2)	-0.3065(3)	0.2074(2)	0.032(1)
C(19)	-0.0183(2)	-0.1705(3)	0.3231(2)	0.037(1)
C(20)	0.1213(3)	-0.0664(4)	0.4731(2)	0.042(1)
C(21)	0.2471(2)	0.0375(3)	-0.0597(2)	0.031(1)
C(22)	0.1400(2)	-0.1072(3)	0.0140(2)	0.0255(9)
C(23)	0.1119(2)	0.1450(3)	0.0086(2)	0.0245(9)

*) $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ [20]

Table 3. Thermal Displacement Parameters for non-H atoms with e.s.d.'s in parentheses.

Residue 1.

	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Zr(1)	0.01580(13)	0.01583(14)	0.01367(14)	-0.00011(12)	0.0044(1)	-0.00013(11)
Cl(1)	0.0216(3)	0.0174(3)	0.0308(4)	-0.0045(3)	0.0110(3)	0.0041(3)
P(1)	0.0215(4)	0.0195(4)	0.0161(3)	-0.0015(3)	0.0053(3)	-0.0015(3)
C(1)	0.0188(13)	0.0191(15)	0.0278(17)	-0.0039(14)	0.0047(13)	-0.0082(13)
C(2)	0.0239(15)	0.0222(16)	0.0233(16)	0.0028(14)	0.0030(13)	-0.0090(13)
C(3)	0.0236(15)	0.0272(17)	0.0217(16)	-0.0043(14)	0.0095(13)	-0.0088(14)
C(4)	0.0149(13)	0.0288(17)	0.0231(16)	-0.0015(14)	0.0031(12)	-0.0038(13)
C(5)	0.0195(14)	0.0271(17)	0.0209(16)	-0.0041(14)	0.0051(12)	-0.0075(13)
C(6)	0.0324(18)	0.0202(17)	0.061(3)	-0.0072(18)	0.0201(18)	-0.0033(15)
C(7)	0.042(2)	0.038(2)	0.0286(19)	0.0118(18)	-0.0039(16)	-0.0145(18)
C(8)	0.0362(19)	0.054(3)	0.037(2)	-0.013(2)	0.0226(17)	-0.0144(19)
C(9)	0.0206(16)	0.046(2)	0.043(2)	0.006(2)	0.0022(15)	0.0056(16)
C(10)	0.0311(17)	0.051(2)	0.0207(17)	-0.0106(17)	0.0101(14)	-0.0169(17)
C(21)	0.0347(18)	0.039(2)	0.0206(16)	-0.0031(16)	0.0108(14)	-0.0035(16)
C(22)	0.0303(16)	0.0201(16)	0.0239(16)	-0.0043(14)	0.0018(13)	-0.0035(13)
C(23)	0.0269(16)	0.0222(16)	0.0231(16)	0.0004(14)	0.0032(13)	0.0004(14)

Residue 2.

	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Zr(2)	0.01728(13)	0.01269(14)	0.01461(14)	-0.00010(12)	0.00531(10)	-0.00092(11)
Cl(2)	0.0235(3)	0.0162(3)	0.0202(3)	-0.0048(3)	0.0073(3)	-0.0015(3)
Cl(3)	0.0181(3)	0.0258(4)	0.0195(3)	-0.0001(3)	0.0017(3)	-0.0017(3)
C(11)	0.0394(19)	0.0174(15)	0.0231(16)	0.0068(14)	0.0059(14)	0.0003(14)
C(12)	0.0306(16)	0.0132(14)	0.0268(17)	0.0058(13)	0.0119(14)	0.0030(12)
C(13)	0.0284(15)	0.0142(14)	0.0253(16)	0.0010(13)	0.0132(14)	-0.0035(13)
C(14)	0.0353(17)	0.0153(15)	0.0329(18)	0.0055(14)	0.0201(15)	-0.0002(13)
C(15)	0.047(2)	0.0141(15)	0.0258(17)	0.0070(14)	0.0185(15)	0.0027(14)
C(16)	0.052(2)	0.036(2)	0.0297(19)	0.0085(18)	-0.0074(17)	0.0006(19)
C(17)	0.0328(17)	0.0212(16)	0.038(2)	0.0066(16)	0.0119(16)	0.0073(14)
C(18)	0.0383(19)	0.0222(17)	0.037(2)	-0.0075(16)	0.0141(16)	-0.0093(15)
C(19)	0.0393(19)	0.0242(18)	0.058(3)	0.0038(18)	0.0336(19)	-0.0030(16)
C(20)	0.075(3)	0.031(2)	0.0288(19)	0.0023(17)	0.030(2)	0.006(2)

Table 4. Hydrogen parameters.

Residue 1.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
H(1)	0.200(2)	0.091(4)	0.192(2)	0.056(12)
H(2)	0.2188(17)	-0.086(3)	0.1857(17)	0.013(7)

H(3)	0.321(3)	-0.010(4)	0.311(3)	0.066(14)
H(61)	0.224(2)	0.335(4)	0.165(2)	0.069(14)
H(62)	0.306(3)	0.432(4)	0.238(3)	0.083(15)
H(63)	0.243(2)	0.318(4)	0.262(3)	0.076(15)
H(71)	0.279(2)	0.309(4)	0.044(2)	0.054(12)
H(72)	0.357(2)	0.262(4)	0.015(2)	0.057(12)
H(73)	0.3737(18)	0.377(3)	0.0556(19)	0.025(9)
H(81)	0.447(2)	0.097(4)	0.046(2)	0.058(13)
H(82)	0.532(3)	0.039(4)	0.110(3)	0.075(15)
H(83)	0.528(2)	0.177(4)	0.089(2)	0.054(12)
H(91)	0.591(2)	0.102(4)	0.308(2)	0.060(13)
H(92)	0.551(3)	-0.023(4)	0.240(3)	0.067(14)
H(93)	0.508(3)	-0.013(5)	0.306(4)	0.12(2)
H(101)	0.451(2)	0.267(4)	0.386(2)	0.051(11)
H(102)	0.437(2)	0.104(4)	0.398(2)	0.063(13)
H(103)	0.351(2)	0.200(3)	0.375(2)	0.045(11)
H(211)	0.307(3)	-0.040(4)	-0.043(3)	0.072(15)
H(212)	0.275(2)	0.110(4)	-0.063(2)	0.066(13)
H(213)	0.204(2)	0.023(3)	-0.110(2)	0.042(11)
H(221)	0.179(2)	-0.167(3)	0.023(2)	0.041(10)
H(222)	0.098(2)	-0.109(4)	0.060(2)	0.062(13)
H(223)	0.103(2)	-0.108(3)	-0.0413(19)	0.033(10)
H(231)	0.0710(19)	0.134(3)	0.044(2)	0.035(10)
H(232)	0.134(2)	0.225(4)	0.008(2)	0.047(11)
H(233)	0.0713(19)	0.135(3)	-0.0478(19)	0.034(10)

Residue 2.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
H(161)	0.369(2)	-0.145(4)	0.418(2)	0.058(13)
H(162)	0.329(3)	-0.190(4)	0.496(2)	0.082(15)
H(163)	0.314(2)	-0.043(3)	0.476(2)	0.054(12)
H(171)	0.273(2)	-0.300(3)	0.228(2)	0.055(12)
H(172)	0.3451(18)	-0.243(3)	0.3048(19)	0.030(9)
H(173)	0.297(2)	-0.367(3)	0.310(2)	0.051(12)
H(181)	0.129(2)	-0.292(3)	0.170(2)	0.048(11)
H(182)	0.027(2)	-0.282(4)	0.178(2)	0.052(12)
H(183)	0.089(3)	-0.391(5)	0.222(3)	0.108(19)
H(191)	-0.035(2)	-0.096(4)	0.348(2)	0.048(11)
H(192)	-0.036(2)	-0.229(4)	0.354(2)	0.058(12)
H(193)	-0.043(2)	-0.186(4)	0.263(2)	0.052(12)
H(201)	0.181(3)	-0.036(4)	0.507(3)	0.064(14)
H(202)	0.071(3)	-0.003(5)	0.458(3)	0.10(2)
H(203)	0.090(2)	-0.123(4)	0.504(2)	0.056(12)

Table 5. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Bond distances (Å)

Zr(1)	-Zr(2)	3.126(1)	C(1)	-C(5)	1.412(4)
Zr(1)	-Cl(1)	2.470(1)	C(1)	-C(6)	1.523(5)
Zr(1)	-P(1)	2.744(1)	C(2)	-C(3)	1.425(5)
Zr(1)	-C(1)	2.506(3)	C(2)	-C(7)	1.501(5)
Zr(1)	-C(2)	2.531(3)	C(3)	-C(4)	1.431(4)
Zr(1)	-C(3)	2.526(3)	C(3)	-C(8)	1.496(5)
Zr(1)	-C(4)	2.486(3)	C(4)	-C(5)	1.424(4)
Zr(1)	-C(5)	2.489(3)	C(4)	-C(9)	1.498(5)
Zr(2)	-Cl(2)	2.456(1)	C(5)	-C(10)	1.510(4)
Zr(2)	-Cl(3)	2.452(1)	C(11)	-C(12)	1.424(5)
Zr(2)	-C(11)	2.499(3)	C(11)	-C(15)	1.432(5)
Zr(2)	-C(12)	2.488(3)	C(11)	-C(16)	1.506(5)
Zr(2)	-C(13)	2.494(3)	C(12)	-C(13)	1.427(4)
Zr(2)	-C(14)	2.535(3)	C(12)	-C(17)	1.503(5)
Zr(2)	-C(15)	2.536(3)	C(13)	-C(14)	1.424(5)
P(1)	-C(21)	1.828(3)	C(13)	-C(18)	1.491(5)
P(1)	-C(22)	1.817(3)	C(14)	-C(15)	1.418(5)
P(1)	-C(23)	1.816(3)	C(14)	-C(19)	1.505(5)
C(1)	-C(2)	1.414(4)	C(15)	-C(20)	1.503(5)

Bond angles (deg.).

Zr(2)	-Zr(1)	-Cl(1)	114.91(3)
Zr(2)	-Zr(1)	-P(1)	94.62(3)
Zr(2)	-Zr(1)	-C(1)	103.04(7)
Zr(2)	-Zr(1)	-C(2)	131.60(8)
Zr(2)	-Zr(1)	-C(3)	155.29(7)
Zr(2)	-Zr(1)	-C(4)	128.11(7)
Zr(2)	-Zr(1)	-C(5)	101.09(7)
Cl(1)	-Zr(1)	-P(1)	86.06(3)
Cl(1)	-Zr(1)	-C(1)	139.75(7)
Cl(1)	-Zr(1)	-C(2)	113.36(8)
Cl(1)	-Zr(1)	-C(3)	85.62(8)
Cl(1)	-Zr(1)	-C(4)	89.78(8)

Cl(1)	-Zr(1)	-C(5)	121.53(8)
P(1)	-Zr(1)	-C(1)	104.38(8)
P(1)	-Zr(1)	-C(2)	85.38(8)
P(1)	-Zr(1)	-C(3)	100.67(7)
P(1)	-Zr(1)	-C(4)	133.84(8)
P(1)	-Zr(1)	-C(5)	136.73(8)
C(1)	-Zr(1)	-C(2)	32.6(1)
C(1)	-Zr(1)	-C(3)	54.4(1)
C(1)	-Zr(1)	-C(4)	54.8(1)
C(1)	-Zr(1)	-C(5)	32.8(1)
C(2)	-Zr(1)	-C(3)	32.7(1)
C(2)	-Zr(1)	-C(4)	54.6(1)
C(2)	-Zr(1)	-C(5)	54.3(1)
C(3)	-Zr(1)	-C(4)	33.2(1)
C(3)	-Zr(1)	-C(5)	54.8(1)
C(4)	-Zr(1)	-C(5)	33.3(1)
Zr(1)	-Zr(2)	-Cl(2)	103.29(3)
Zr(1)	-Zr(2)	-Cl(3)	106.08(3)
Zr(1)	-Zr(2)	-C(11)	109.32(8)
Zr(1)	-Zr(2)	-C(12)	97.00(8)
Zr(1)	-Zr(2)	-C(13)	116.76(7)
Zr(1)	-Zr(2)	-C(14)	149.23(8)
Cl(2)	-Zr(2)	-Cl(3)	101.77(3)
Cl(2)	-Zr(2)	-C(11)	93.44(8)
Cl(2)	-Zr(2)	-C(12)	126.59(8)
Cl(2)	-Zr(2)	-C(13)	134.80(8)
Cl(2)	-Zr(2)	-C(14)	103.73(8)
Cl(3)	-Zr(2)	-C(11)	136.82(8)
Cl(3)	-Zr(2)	-C(12)	119.17(8)
Cl(3)	-Zr(2)	-C(13)	87.07(8)
Cl(3)	-Zr(2)	-C(14)	82.44(8)
C(11)	-Zr(2)	-C(12)	33.2(1)
C(11)	-Zr(2)	-C(13)	55.2(1)
C(11)	-Zr(2)	-C(14)	54.6(1)
C(12)	-Zr(2)	-C(13)	33.3(1)
C(12)	-Zr(2)	-C(14)	54.6(1)
C(13)	-Zr(2)	-C(14)	32.9(1)
Zr(1)	-P(1)	-C(21)	117.5(1)
Zr(1)	-P(1)	-C(22)	109.3(1)
Zr(1)	-P(1)	-C(23)	118.3(1)
C(21)	-P(1)	-C(22)	101.0(1)
C(21)	-P(1)	-C(23)	104.8(1)
C(22)	-P(1)	-C(23)	103.7(1)
Zr(1)	-C(1)	-C(2)	74.7(2)
Zr(1)	-C(1)	-C(5)	72.9(2)

Zr(1)	-C(1)	-C(6)	123.6(2)
C(2)	-C(1)	-C(5)	108.3(3)
C(2)	-C(1)	-C(6)	125.1(3)
C(5)	-C(1)	-C(6)	126.3(3)
Zr(1)	-C(2)	-C(1)	72.8(2)
Zr(1)	-C(2)	-C(3)	73.4(2)
Zr(1)	-C(2)	-C(7)	130.1(2)
C(1)	-C(2)	-C(3)	108.4(3)
C(1)	-C(2)	-C(7)	125.1(3)
C(3)	-C(2)	-C(7)	125.2(3)
Zr(1)	-C(3)	-C(2)	73.9(2)
Zr(1)	-C(3)	-C(4)	71.9(2)
Zr(1)	-C(3)	-C(8)	121.9(2)
C(2)	-C(3)	-C(4)	107.4(3)
C(2)	-C(3)	-C(8)	125.6(3)
C(4)	-C(3)	-C(8)	127.0(3)
Zr(1)	-C(4)	-C(3)	74.9(2)
Zr(1)	-C(4)	-C(5)	73.5(2)
Zr(1)	-C(4)	-C(9)	119.0(2)
C(3)	-C(4)	-C(5)	107.7(3)
C(3)	-C(4)	-C(9)	126.8(3)
C(5)	-C(4)	-C(9)	125.5(3)
Zr(1)	-C(5)	-C(1)	74.3(2)
Zr(1)	-C(5)	-C(4)	73.3(2)
Zr(1)	-C(5)	-C(10)	124.3(2)
C(1)	-C(5)	-C(4)	108.2(3)
C(1)	-C(5)	-C(10)	126.0(3)
C(4)	-C(5)	-C(10)	125.3(3)
Zr(2)	-C(11)	-C(12)	73.0(2)
Zr(2)	-C(11)	-C(15)	74.9(2)
Zr(2)	-C(11)	-C(16)	120.9(2)
C(12)	-C(11)	-C(15)	107.4(3)
C(12)	-C(11)	-C(16)	126.4(3)
C(15)	-C(11)	-C(16)	126.1(3)
Zr(2)	-C(12)	-C(11)	73.8(2)
Zr(2)	-C(12)	-C(13)	73.6(2)
Zr(2)	-C(12)	-C(17)	122.6(2)
C(11)	-C(12)	-C(13)	108.4(3)
C(11)	-C(12)	-C(17)	126.3(3)
C(13)	-C(12)	-C(17)	125.1(3)
Zr(2)	-C(13)	-C(12)	73.1(2)
Zr(2)	-C(13)	-C(14)	75.2(2)
Zr(2)	-C(13)	-C(18)	120.1(2)
C(12)	-C(13)	-C(14)	107.7(3)
C(12)	-C(13)	-C(18)	125.1(3)

C(14)	-C(13)	-C(18)	127.1(3)
Zr(2)	-C(14)	-C(13)	72.0(2)
Zr(2)	-C(14)	-C(15)	73.8(2)
Zr(2)	-C(14)	-C(19)	122.5(2)
C(13)	-C(14)	-C(15)	108.2(3)
C(13)	-C(14)	-C(19)	126.5(3)
C(15)	-C(14)	-C(19)	125.2(3)
Zr(2)	-C(15)	-C(11)	72.1(2)
Zr(2)	-C(15)	-C(14)	73.7(2)
Zr(2)	-C(15)	-C(20)	124.9(2)
C(11)	-C(15)	-C(14)	108.3(3)
C(11)	-C(15)	-C(20)	126.0(3)
C(14)	-C(15)	-C(20)	125.5(3)

Part III: Structure determination of $[Cp^*HfCl_2]_2\{\mu\text{-xy-NCH=CHN-xy}\}$ (11).

Abstract. $(C_{19}H_{25}Cl_2HfN)_2$, M = 1033.62, triclinic, P_{-1}, a = 9.451(1), b = 10.885(1), c = 11.774(1) Å, α = 116.363(6) °, β = 92.371(8) °, γ = 113.232(8) °, V = 962.17(19) Å^3, Z = 1, D_x = 1.784 g cm^{-3}, λ(MoK$\bar{\alpha}$) = 0.71073 Å, μ = 57 cm^{-1}, F(000) = 504, T = 130 K, $wR(F^2)$ = 0.0561 for 4181 reflections and 308 parameters and $R(F)$ = 0.0218 for 3865 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.

The asymmetric unit consists of a half of the dimer molecule of the title compound, which has a crystallographic imposed inversion center.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

Suitable orange colored plate-shaped crystals were obtained by crystallisation from C_6D_6. The crystal, of approximate size 0.06 x 0.24 x 0.56 mm., used for characterization and data collection was glued on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F*[2] diffractometer, interfaced to a *INDY* (*Silicon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-K$\bar{\alpha}$ radiation, $\Delta\omega = 0.95 + 0.34$ tg θ). Unit cell parameters[3] and orientation matrix were determined from a least-squares treatment of the *SET4*[4] setting angles of 22 reflections in the range $16.65° < \theta < 21.69°$.

The unit cell was identified as triclinic, space group group P_{-1}. Reduced cell calculations did not indicate any higher metric lattice symmetry[5] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. 360° ψ-scans for reflections close to axial showed variation in intensity of 27% about the mean value. Intensity data were corrected for Lorentz and polarization effects, scale variation, for absorption and reduced to F_o^2.[29] By the special form of the crystal

(large thin plate) an empirical absorption correction was applied: *DIFABS* method,[9] as implemented in *PLATON*. The calculated virtual transmission-factor range was: 0.264-0.717. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[10] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined.

A subsequent difference Fourier synthesis, before the empirical absorption correction was applied, resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.0561$ for 4181 reflections and 308 parameters and $R(F) = 0.0218$ for 3865 reflections with $F_o \geq 4.0\ \sigma(F_o)$.

The final difference Fourier map was essentially featureless with a few peaks of max. 1.36(12) e/Å^3 within 1.0 Å from Hf, but were neglected/rejected, being artefacts. No other significant peaks having chemical meaning above the general background were observed in the final difference Fourier syntheses.

The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \Sigma_h\ [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined.

Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables for Crystallography*.[11] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[12] (least-square refinements), *PLATON*[13] (calculation of geometric data and the *ORTEP* illustrations) and a locally modified version of the program *PLUTO*[14] (preparation of illustrations).

Table 1.

a. Crystal data and details of the structure determination.

Moiety_ Formula	$(C_{19}H_{25}Cl_2HfN)_2$
Formula_Weight, g.mol^{-1}	1033.62
Crystal system	Triclinic
Space group	P^-
a, Å	9.451(1)
b, Å	10.885(1)
c, Å	11.774(1)
α, deg	116.363(6)
β, deg	92.371(8)
γ, deg	113.232(8)
V, Å^3	962.17(19)
Formula_*Z*	1
SpaceGroup_*Z*	2
Z' (= Formula_Z / SpaceGroup-*Z*)	0.5
ρ_{calc}, g.cm^{-3}	1.784
F(000), electrons	504
μ(Mo K$\bar{\alpha}$), cm^{-1}	57.0
color, habit	Orange, plate-shaped
Approx. crystal dimension, mm	0.06 x 0.24 x 0.56

b. Data collection.

Radiation	Mo K$\bar{\alpha}$
Wavelength, Å	0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	2.00, 27.0
ω/2θ scan, deg	$\Delta\omega = 0.95 + 0.34$ tg θ
Index ranges	h: 0→12; k: -13→12; l: -15→15
Crystal-to-receiving-aperture-distance, mm	173
Horizontal-, vertical-aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	2-1-1, 2.0
r.m.s. dev. in %	02-2, 0.8
	121, 1.0
Drift correction	1.000 - 1.053
Min.- max. absorption transmission factor	0.264 - 0.717
X-ray exposure time, h	81.5
Total data	4442
Unique data	4183
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	3865
$R_{int} = \Sigma\ [\lvert F_o^2 - F_o^2\ (\text{mean})\rvert] / \Sigma\ [F_o^2]$	0.0279
$R_{sig} = \Sigma\ \sigma(F_o^2) / \Sigma\ [F_o^2]$	0.0174

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)	4181
Number of refined parameters	308
Final agreement factors:	
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$	0.0561
Weighting scheme: *a, b*	0.0409, 0.585
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \Sigma(\|\|F_o\| - \|F_c\|\|) / \Sigma\|F_o\|$	0.0218
for $F_o > 4.0\ \sigma\ (F_o)$	
GooF = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.046
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
difference Fourier map, e/Å^3	-1.40, 1.36(12)
Max. (shift/σ) final cycle	< 0.001

Table 2. Final fractional atomic coordinates and equivalent isotropic displacement parameters for non-H atoms with s.u.'s in parentheses.

Atoms of the Asymmetric Unit.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
Hf	0.22794(1)	-0.02503(1)	0.23321(1)	0.0151(1)
Cl(1)	0.34472(11)	0.09819(11)	0.11345(9)	0.0284(3)
Cl(2)	0.08115(11)	0.10870(11)	0.33325(10)	0.0305(3)
N	0.4021(3)	0.0378(3)	0.3851(3)	0.0162(8)
C(1)	0.1655(4)	-0.2767(4)	0.0401(3)	0.0196(9)
C(2)	0.0313(4)	-0.2509(4)	0.0274(3)	0.0206(9)
C(3)	-0.0395(4)	-0.2540(4)	0.1301(3)	0.0212(9)
C(4)	0.0522(4)	-0.2810(4)	0.2076(3)	0.0208(9)
C(5)	0.1779(4)	-0.2967(4)	0.1500(3)	0.0197(9)
C(6)	0.2714(5)	-0.2915(5)	-0.0525(4)	0.0297(11)
C(7)	-0.0281(5)	-0.2314(5)	-0.0810(4)	0.0313(12)
C(8)	-0.1934(5)	-0.2467(5)	0.1479(5)	0.0352(13)
C(9)	0.0135(6)	-0.2973(5)	0.3246(4)	0.0343(12)
C(10)	0.2904(5)	-0.3489(5)	0.1835(4)	0.0268(11)
C(11)	0.5301(4)	0.1882(4)	0.4224(3)	0.0159(9)
C(12)	0.6551(4)	0.1988(4)	0.3603(3)	0.0180(9)
C(13)	0.7767(4)	0.3444(5)	0.3963(4)	0.0236(10)
C(14)	0.7751(5)	0.4766(4)	0.4919(4)	0.0265(11)
C(15)	0.6549(5)	0.4657(4)	0.5555(4)	0.0247(10)
C(16)	0.5314(4)	0.3221(4)	0.5235(3)	0.0194(9)
C(17)	0.6597(5)	0.0564(5)	0.2581(4)	0.0251(11)
C(18)	0.4079(5)	0.3140(5)	0.6000(4)	0.0242(11)
C(19)	0.4310(4)	-0.0295(4)	0.4567(3)	0.0173(9)

*) $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ [20]

Table 3. Thermal Displacement Parameters for non-H atoms with e.s.d.'s in parentheses.

Atoms of the Asymmetric Unit.

	U(1,1)	*U(2,2)*	*U(3,3)*	*U(2,3)*	*U(1,3)*	*U(1,2)*
Hf	0.01498(8)	0.01527(8)	0.01505(8)	0.00771(6)	0.00362(5)	0.00693(6)
Cl(1)	0.0255(4)	0.0327(5)	0.0290(5)	0.0223(4)	0.0057(4)	0.0075(4)
Cl(2)	0.0241(4)	0.0261(4)	0.0344(5)	0.0061(4)	0.0041(4)	0.0161(4)

N	0.0177(13)	0.0167(13)	0.0174(14)	0.0096(12)	0.0043(11)	0.0095(11)
C(1)	0.0230(16)	0.0150(15)	0.0129(15)	0.0030(13)	0.0037(13)	0.0063(14)
C(2)	0.0188(16)	0.0181(16)	0.0181(17)	0.0064(14)	0.0018(13)	0.0058(14)
C(3)	0.0166(15)	0.0171(16)	0.0220(17)	0.0058(14)	0.0044(14)	0.0055(14)
C(4)	0.0222(16)	0.0142(15)	0.0188(17)	0.0076(14)	0.0077(14)	0.0026(13)
C(5)	0.0218(16)	0.0163(15)	0.0168(16)	0.0063(14)	0.0044(13)	0.0074(14)
C(6)	0.034(2)	0.030(2)	0.0224(19)	0.0088(18)	0.0138(17)	0.0167(18)
C(7)	0.030(2)	0.032(2)	0.024(2)	0.0129(19)	-0.0050(17)	0.0098(19)
C(8)	0.0207(18)	0.032(2)	0.040(3)	0.009(2)	0.0115(18)	0.0108(18)
C(9)	0.037(2)	0.031(2)	0.023(2)	0.0133(18)	0.0105(18)	0.0052(19)
C(10)	0.032(2)	0.0213(19)	0.026(2)	0.0097(17)	0.0021(17)	0.0142(18)
C(11)	0.0175(15)	0.0180(15)	0.0150(15)	0.0094(13)	0.0041(12)	0.0094(13)
C(12)	0.0174(15)	0.0205(16)	0.0183(16)	0.0107(14)	0.0038(13)	0.0096(14)
C(13)	0.0174(16)	0.0288(19)	0.0275(19)	0.0189(17)	0.0064(15)	0.0077(15)
C(14)	0.0249(18)	0.0196(18)	0.031(2)	0.0152(16)	0.0004(16)	0.0044(16)
C(15)	0.0286(18)	0.0191(17)	0.0230(18)	0.0081(16)	0.0005(15)	0.0115(16)
C(16)	0.0228(16)	0.0204(16)	0.0183(16)	0.0104(14)	0.0039(14)	0.0121(14)
C(17)	0.0212(17)	0.031(2)	0.026(2)	0.0133(17)	0.0104(16)	0.0154(16)
C(18)	0.0283(19)	0.028(2)	0.0191(18)	0.0104(17)	0.0097(15)	0.0167(17)
C(19)	0.0185(15)	0.0164(15)	0.0173(16)	0.0092(13)	0.0062(13)	0.0073(13)

Table 4. Hydrogen parameters.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
H(6)	0.370(7)	-0.273(7)	-0.011(6)	0.057(17)
H(6')	0.275(8)	-0.244(8)	-0.095(6)	0.067(19)
H(6")	0.236(8)	-0.396(8)	-0.114(7)	0.071(19)
H(7)	-0.084(7)	-0.321(7)	-0.148(6)	0.056(17)
H(7')	0.054(7)	-0.164(6)	-0.107(5)	0.047(14)
H(7")	-0.090(6)	-0.173(6)	-0.050(5)	0.047(14)
H(8)	-0.212(7)	-0.182(7)	0.103(6)	0.067(18)
H(8')	-0.195(6)	-0.197(6)	0.237(6)	0.043(14)
H(8")	-0.290(8)	-0.358(8)	0.121(6)	0.069(19)
H(9)	0.075(8)	-0.337(7)	0.350(6)	0.067(19)
H(9')	-0.088(9)	-0.342(9)	0.317(7)	0.09(2)
H(9")	0.035(7)	-0.202(7)	0.403(6)	0.054(16)
H(10)	0.266(6)	-0.446(6)	0.111(5)	0.036(13)
H(10')	0.279(6)	-0.362(5)	0.251(5)	0.033(12)
H(10")	0.382(7)	-0.282(7)	0.204(6)	0.054(17)
H(13)	0.863(5)	0.357(5)	0.355(4)	0.021(10)
H(14)	0.853(5)	0.571(5)	0.521(4)	0.02(1)
H(15)	0.653(5)	0.554(6)	0.627(5)	0.029(11)
H(17)	0.597(6)	0.014(6)	0.179(5)	0.041(14)

H(17')	0.643(8)	-0.019(8)	0.289(7)	0.08(2)
H(17")	0.759(7)	0.076(7)	0.245(5)	0.049(15)
H(18)	0.456(7)	0.402(8)	0.684(6)	0.063(18)
H(18')	0.368(7)	0.237(7)	0.600(6)	0.050(16)
H(18")	0.319(7)	0.332(6)	0.566(5)	0.050(15)
H(19)	0.338(5)	-0.130(5)	0.436(4)	0.02(1)

Table 5. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

Hf	-Cl(1)	2.3761(12)	C(3)	-C(4)	1.430(6)
Hf	-Cl(2)	2.3741(12)	C(3)	-C(8)	1.506(7)
Hf	-N	2.039(3)	C(4)	-C(5)	1.423(6)
Hf	-C(1)	2.471(4)	C(4)	-C(9)	1.507(6)
Hf	-C(2)	2.470(3)	C(5)	-C(10)	1.500(7)
Hf	-C(3)	2.483(4)	C(11)	-C(12)	1.408(6)
Hf	-C(4)	2.485(4)	C(11)	-C(16)	1.409(5)
Hf	-C(5)	2.493(4)	C(12)	-C(13)	1.392(7)
N	-C(11)	1.446(5)	C(12)	-C(17)	1.501(6)
N	-C(19)	1.417(5)	C(13)	-C(14)	1.385(6)
C(1)	-C(2)	1.419(6)	C(14)	-C(15)	1.381(7)
C(1)	-C(5)	1.412(5)	C(15)	-C(16)	1.396(6)
C(1)	-C(6)	1.509(6)	C(16)	-C(18)	1.503(6)
C(2)	-C(3)	1.413(5)	C(19)	-C(19)a	1.343(5)
C(2)	-C(7)	1.505(6)			

Bond angles (deg.)

Cl(1)	-Hf	-Cl(2)	100.87(4)	Hf	-C(2)	-C(1)	73.3(2)
Cl(1)	-Hf	-N	109.02(10)	Hf	-C(2)	-C(3)	73.9(2)
Cl(1)	-Hf	-C(1)	89.09(10)	Hf	-C(2)	-C(7)	120.8(3)
Cl(1)	-Hf	-C(2)	89.73(10)	C(1)	-C(2)	-C(3)	108.1(3)
Cl(1)	-Hf	-C(3)	119.76(9)	C(1)	-C(2)	-C(7)	125.3(4)
Cl(1)	-Hf	-C(4)	142.78(8)	C(3)	-C(2)	-C(7)	126.6(4)
Cl(1)	-Hf	-C(5)	118.43(9)	Hf	-C(3)	-C(2)	72.9(2)
Cl(2)	-Hf	-N	104.89(9)	Hf	-C(3)	-C(4)	73.4(2)
Cl(2)	-Hf	-C(1)	135.82(10)	Hf	-C(3)	-C(8)	124.1(3)
Cl(2)	-Hf	-C(2)	103.1(1)	C(2)	-C(3)	-C(4)	107.9(4)
Cl(2)	-Hf	-C(3)	83.4(1)	C(2)	-C(3)	-C(8)	126.5(4)

Cl(2)	-Hf	-C(4)	99.38(10)	C(4)	-C(3)	-C(8)	125.4(4)
Cl(2)	-Hf	-C(5)	132.55(10)	Hf	-C(4)	-C(3)	73.2(2)
N	-Hf	-C(1)	112.27(13)	Hf	-C(4)	-C(5)	73.7(2)
N	-Hf	-C(2)	142.31(14)	Hf	-C(4)	-C(9)	121.2(3)
N	-Hf	-C(3)	128.03(13)	C(3)	-C(4)	-C(5)	107.7(3)
N	-Hf	-C(4)	95.37(13)	C(3)	-C(4)	-C(9)	124.7(4)
N	-Hf	-C(5)	87.27(13)	C(5)	-C(4)	-C(9)	127.6(4)
C(1)	-Hf	-C(2)	33.37(13)	Hf	-C(5)	-C(1)	72.6(2)
C(1)	-Hf	-C(3)	55.12(13)	Hf	-C(5)	-C(4)	73.1(2)
C(1)	-Hf	-C(4)	55.11(12)	Hf	-C(5)	-C(10)	126.9(3)
C(1)	-Hf	-C(5)	33.05(12)	C(1)	-C(5)	-C(4)	107.9(3)
C(2)	-Hf	-C(3)	33.15(12)	C(1)	-C(5)	-C(10)	123.9(4)
C(2)	-Hf	-C(4)	55.26(12)	C(4)	-C(5)	-C(10)	127.5(4)
C(2)	-Hf	-C(5)	55.10(13)	N	-C(11)	-C(12)	119.5(3)
C(3)	-Hf	-C(4)	33.45(13)	N	-C(11)	-C(16)	119.7(3)
C(3)	-Hf	-C(5)	55.14(14)	C(12)	-C(11)	-C(16)	120.7(4)
C(4)	-Hf	-C(5)	33.22(13)	C(11)	-C(12)	-C(13)	118.9(4)
Hf	-N	-C(11)	108.9(2)	C(11)	-C(12)	-C(17)	121.1(4)
Hf	-N	-C(19)	136.8(3)	C(13)	-C(12)	-C(17)	120.0(4)
C(11)	-N	-C(19)	114.3(3)	C(12)	-C(13)	-C(14)	120.6(4)
Hf	-C(1)	-C(2)	73.3(2)	C(13)	-C(14)	-C(15)	120.4(4)
Hf	-C(1)	-C(5)	74.3(2)	C(14)	-C(15)	-C(16)	121.0(4)
Hf	-C(1)	-C(6)	121.6(3)	C(11)	-C(16)	-C(15)	118.4(4)
C(2)	-C(1)	-C(5)	108.4(3)	C(11)	-C(16)	-C(18)	122.0(4)
C(2)	-C(1)	-C(6)	126.3(3)	C(15)	-C(16)	-C(18)	119.6(4)
C(5)	-C(1)	-C(6)	125.1(4)	N	-C(19)	-C(19)a	124.9(4)

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