Crystal structure of [1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]-chloro-[η^2-*N,C*-3,4,5,6-tetrafluoropyridyl]zirconium(IV), $ZrCl(C_5F_4N)(C_{20}H_{24})$

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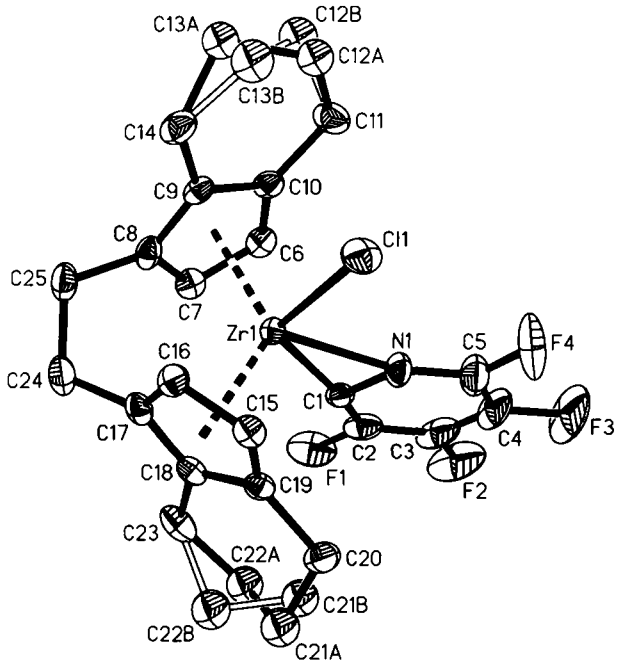
Received March 21, 2005, accepted and available on-line April 8, 2005; CCDC no. 1267/1513



Abstract

$C_{25}H_{24}ClF_4NZr$, monoclinic, $P12_1/n1$ (no. 14), $a = 9.903(2)$ Å, $b = 11.279(2)$ Å, $c = 20.231(4)$ Å, $\beta = 92.43(3)°$, $V = 2257.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.035$, $wR_{obs}(F^2) = 0.076$, $T = 200$ K.

Source of material

The complex *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (1.0 g, 1.9 mmol; ebthi = 1,2-ethylene-1,1′-bis(tetrahydroindenyl)) was dissolved in 10 ml of toluene under Ar and treated under stirring with pentafluoropyridine (0.8 ml, 7.3 mmol). Traces of 2-chloro-3,4,5,6-tetrafluoropyridine contained in the batch of pentafluoropyridine reacted with *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$). After 15 min at 353 K the green solution became green-brownish and a light brown precipitate had formed. The solvent was removed in vacuum, and the residue was dissolved in [D_6]-benzene for NMR measurements. From this solution a few beige crystals were obtained.

Experimental details

Both anellated cyclohexyl rings of the ebthi ligand are disordered. The corresponding atoms were refined using split positions.

Discussion

The activation of several types of C–F bonds by many transition metal complexes was summarized in many reviews [1-6]. Beckhaus and coworkers observed the C–F bond cleavage reaction of pentafluoropyridine with Cp$_2$Ti(η^2-$Me_3SiC_2SiMe_3$) under formation of a F-bridged dinuclear Ti(III) complex [7]. In the corresponding reaction with Cp$_2$Zr(*L*)(η^2-$Me_3SiC_2SiMe_3$) (*L* = pyridine), a C–F activation took place and the formed Cp$_2$Zr(4-C_5NF_4)F was confirmed by crystal structure analysis [8].

The crystal structure of *rac*-(ebthi)Zr(η^2-N,C-3,4,5,6-NC_5F_4)Cl, reveals C–Cl activation in 2-position instead of C–F activation of the 2-chloro-3,4,5,6-tetrafluoropyridine. The molecular structure of *rac*-(ebthi)Zr(η^2-*N,C*-3,4,5,6-NC_5F_4)Cl (d(Zr1—C1) = 2.241(3) Å, d(Zr1—N1) = 2.289(3) Å, d(C1—N1) = 1.348(5) Å, d(Zr1—Cl1) = 2.519(1) Å, ∠N1–Zr–C1 = 34.6(1)°) is comparable with the cationic zirconocene complex [Cp$_2$Zr(η^2-N,C-picolyl)(PMe_3)]$^+$ (d(Zr—C1) = 2.29(2) Å, d(Zr—N) = 2.21(1) Å, d(C1—N) = 1.32(2) Å, ∠N–Zr–C1 = 34.2(2)°) [9]. The Zr—Cl bond distance in the title compound is longer than that found for the corresponding *rac*-(ebthi)$ZrCl_2$ [10], but similar to the Zr—Cl bond length in [$SiMe_2(C_5H_4)_2$][(η^5-C_5H_5)ZrCl(μ-H)]$_2$ (d(Zr1—Cl1) = 2.526(1) Å, d(Zr2—Cl2) = 2.521(1) Å) [11].

Table 1. Data collection and handling.

Crystal:	beige prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.51 cm^{-1}
Diffractometer, scan mode:	STOE IPDS I, φ
$2\theta_{max}$:	48.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6533, 3561
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2716
$N(param)_{refined}$:	285
Programs:	SHELXS-86 [12], SHELXL-97 [13]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(6)	4*e*		0.9427	0.3627	0.7328	0.049
H(7)	4*e*		1.1826	0.2874	0.7346	0.049
H(11A)	4*e*		0.7494	0.3509	0.6145	0.071
H(11B)	4*e*		0.6979	0.2500	0.6632	0.071
C(12A)	4*e*	0.73(1)	0.7249(5)	0.1870(6)	0.5678(3)	0.061(2)
H(12A)	4*e*	0.73	0.6922	0.1099	0.5842	0.074
H(12B)	4*e*	0.73	0.6496	0.2241	0.5416	0.074
C(13A)	4*e*	0.73	0.8416(5)	0.1636(6)	0.5219(3)	0.061(2)
H(13A)	4*e*	0.73	0.8093	0.1151	0.4836	0.073
H(13B)	4*e*	0.73	0.8764	0.2396	0.5050	0.073
C(12B)	4*e*	0.27	0.744(2)	0.242(1)	0.5531(3)	0.056(5)
H(12C)	4*e*	0.27	0.7920	0.3023	0.5275	0.068
H(12D)	4*e*	0.27	0.6467	0.2433	0.5387	0.068
C(13B)	4*e*	0.27	0.8041(7)	0.118(1)	0.543(1)	0.067(6)

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Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(13C)	4e	0.27	0.7894	0.0980	0.4953	0.081
H(13D)	4e	0.27	0.7511	0.0612	0.5682	0.081
H(14A)	4e		0.9220	0.0182	0.5741	0.064
H(14B)	4e		1.0334	0.0873	0.5336	0.064
H(15)	4e		0.9693	−0.1768	0.7645	0.046
H(16)	4e		1.1014	−0.1044	0.6679	0.049
H(20A)	4e		1.0194	−0.1613	0.9004	0.062
H(20B)	4e		0.9867	−0.0227	0.9069	0.062
C(21A)	4e	0.55(1)	1.1815(6)	−0.0651(6)	0.9401(4)	0.059(3)
H(21A)	4e	0.55	1.2495	−0.1266	0.9311	0.070
H(21B)	4e	0.55	1.1577	−0.0710	0.9870	0.070
C(22A)	4e	0.55	1.2362(9)	0.0575(6)	0.9254(3)	0.057(3)
H(22A)	4e	0.55	1.3111	0.0749	0.9578	0.068

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(22B)	4e	0.55	1.1638	0.1162	0.9323	0.068
C(21B)	4e	0.45	1.1466(8)	−0.005(1)	0.9404(5)	0.068(4)
H(21C)	4e	0.45	1.1052	0.0749	0.9428	0.082
H(21D)	4e	0.45	1.1462	−0.0397	0.9853	0.082
C(22B)	4e	0.45	1.2929(9)	0.011(1)	0.9223(4)	0.080(4)
H(22C)	4e	0.45	1.3433	0.0581	0.9564	0.096
H(22D)	4e	0.45	1.3377	−0.0672	0.9182	0.096
H(23A)	4e		1.2893	0.1611	0.8460	0.070
H(23B)	4e		1.3807	0.0444	0.8546	0.070
H(24A)	4e		1.3612	0.1269	0.7244	0.066
H(24B)	4e		1.3884	0.0065	0.6850	0.066
H(25A)	4e		1.2275	0.0512	0.6043	0.063
H(25B)	4e		1.3133	0.1706	0.6153	0.063

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr(1)	4e	0.98432(3)	0.09263(3)	0.74117(2)	0.0293(2)	0.0286(2)	0.0293(2)	−0.0012(2)	0.0027(1)	−0.0022(2)
Cl(1)	4e	0.7775(1)	−0.0151(1)	0.69600(5)	0.0529(6)	0.0627(7)	0.0576(7)	−0.0214(5)	−0.0135(5)	0.0028(5)
C(1)	4e	0.9641(4)	0.1951(3)	0.8351(2)	0.041(2)	0.043(2)	0.028(2)	0.009(2)	−0.000(2)	0.000(2)
C(2)	4e	0.9748(5)	0.2742(4)	0.8868(2)	0.084(3)	0.043(2)	0.039(2)	0.019(2)	−0.006(2)	−0.001(2)
C(3)	4e	0.8680(7)	0.2955(4)	0.9255(2)	0.129(5)	0.064(3)	0.035(2)	0.044(3)	0.017(3)	−0.002(2)
C(4)	4e	0.7494(6)	0.2401(5)	0.9126(3)	0.103(4)	0.090(4)	0.065(4)	0.047(4)	0.053(4)	0.012(3)
C(5)	4e	0.7398(5)	0.1627(5)	0.8601(3)	0.054(3)	0.081(4)	0.082(4)	0.011(3)	0.027(3)	0.013(3)
C(6)	4e	0.9774(4)	0.3049(3)	0.7039(2)	0.055(2)	0.024(2)	0.043(2)	0.003(2)	0.008(2)	0.000(2)
C(7)	4e	1.1116(4)	0.2635(3)	0.7045(2)	0.045(2)	0.031(2)	0.047(2)	−0.009(2)	0.003(2)	0.002(2)
C(8)	4e	1.1231(4)	0.1808(3)	0.6530(2)	0.045(2)	0.031(2)	0.047(2)	−0.001(2)	0.018(2)	0.009(2)
C(9)	4e	0.9941(4)	0.1682(3)	0.6223(2)	0.053(2)	0.029(2)	0.029(2)	0.005(2)	0.008(2)	0.003(2)
C(10)	4e	0.9042(4)	0.2461(3)	0.6531(2)	0.049(2)	0.034(2)	0.036(2)	0.008(2)	0.003(2)	0.005(2)
C(11)	4e	0.7606(4)	0.2667(4)	0.6276(2)	0.059(3)	0.063(3)	0.056(3)	0.025(2)	−0.007(2)	−0.004(2)
C(14)	4e	0.9542(4)	0.0977(4)	0.5613(2)	0.069(3)	0.056(2)	0.035(2)	0.008(2)	0.006(2)	−0.006(2)
C(15)	4e	1.0407(4)	−0.1205(3)	0.7667(2)	0.040(2)	0.025(2)	0.051(2)	−0.001(2)	0.001(2)	0.002(2)
C(16)	4e	1.1153(4)	−0.0807(3)	0.7127(2)	0.051(2)	0.034(2)	0.039(2)	0.013(2)	0.008(2)	−0.003(2)
C(17)	4e	1.2140(3)	0.0004(3)	0.7372(2)	0.033(2)	0.028(2)	0.056(2)	0.006(2)	0.007(2)	0.006(2)
C(18)	4e	1.1976(3)	0.0122(3)	0.8054(2)	0.033(2)	0.032(2)	0.047(2)	0.007(2)	−0.005(2)	−0.001(2)
C(19)	4e	1.0904(3)	−0.0625(3)	0.8236(2)	0.039(2)	0.029(2)	0.039(2)	0.004(2)	−0.001(2)	0.004(2)
C(20)	4e	1.0565(4)	−0.0806(4)	0.8948(2)	0.062(2)	0.052(2)	0.040(2)	0.005(2)	0.003(2)	0.005(2)
C(23)	4e	1.2873(4)	0.0753(4)	0.8563(2)	0.038(2)	0.050(3)	0.086(3)	0.003(2)	−0.015(2)	−0.006(2)
C(24)	4e	1.3176(4)	0.0632(4)	0.6974(2)	0.041(2)	0.050(3)	0.075(3)	0.008(2)	0.022(2)	0.009(2)
C(25)	4e	1.2503(4)	0.1153(3)	0.6363(2)	0.045(2)	0.049(3)	0.066(3)	0.007(2)	0.027(2)	0.014(2)
N(1)	4e	0.8439(3)	0.1410(3)	0.8241(2)	0.043(2)	0.053(2)	0.048(2)	0.008(2)	0.015(2)	−0.002(2)
F(1)	4e	1.0920(3)	0.3329(2)	0.9001(1)	0.114(2)	0.065(2)	0.070(2)	0.001(2)	−0.032(2)	−0.024(1)
F(2)	4e	0.8788(4)	0.3726(3)	0.9759(1)	0.233(4)	0.103(2)	0.047(2)	0.065(3)	0.018(2)	−0.026(2)
F(3)	4e	0.6410(4)	0.2596(4)	0.9491(2)	0.163(3)	0.157(4)	0.133(3)	0.068(3)	0.112(3)	0.016(3)
F(4)	4e	0.6256(3)	0.1064(4)	0.8446(2)	0.055(2)	0.153(3)	0.184(4)	−0.011(2)	0.059(2)	−0.011(3)

Acknowledgment. The work was supported by the Deutsche Forschungsgemeinschaft (project code SPP 1118).

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