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Synthesis and Characterization of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ and $\{[(\eta^5\text{-}C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$.

Synthesis of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$.

A 0.250-g (0.674) sample of freshly sublimed $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$, which was prepared by the alkylation of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrCl_2$ with 2 eq. of LiMe, was placed in a 100 mL solv-seal flask which was attached through a solv-seal joint to a calibrated gas bulb equipped with high vacuum Teflon stopcocks. The reaction assembly was evacuated and toluene (*ca.* 30 mL) was introduced by vacuum distillation. The calibrated bulb was charged with 2 eq. of CO_2. The CO_2 was condensed into the reaction flask and the valve to the calibrated bulb was closed. The reaction mixture was stirred overnight at ambient temperature. Following the removal of the volatiles, the product residue was washed with 10 mL of cold pentane. The white powder was recrystallized by slow removal of pentane from a saturated solution to afford suitable crystals for the X-ray diffraction analysis. Overall isolated yield: 0.21 g (68%). ^{1}H NMR spectrum ($CDCl_3$, 270MHz): δ 2.12, 1.85 (s, C_5Me_4), 2.05 (s, O_2CMe), 1.17 (s, $NCMe_3$), 0.57 (s, $SiMe_2$). $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 67.8 MHz): 189.4 (O_2**C**Me), 131.2, 129.7 (distal and proximal ring carbons of C_5Me_4), 104.7 (bridgehead C of C_5Me_4), 57.2 (N**C**Me_3), 33.9 (NC**Me**$_3$), 23.2 (η^2-O_2C**Me**), 13.5, 10.4 (C_5**Me**$_4$), 7.7 ($SiMe_2$). IR (Nujol, cm^{-1}): ν(OCO-bridging) 1603 (s), 1444 (m); ν(OCO-chelating) 1534 (m), 1466 (m). IR (toluene, cm^{-1}): ν(OCO-chelating) 1536 (s), 1474 (m). Anal. Calcd. for $C_{19}H_{33}O_4NSiZr$ (emp. form): C, 49.76; H, 7.25; N, 3.05. Found: C, 49.74; H, 7.32; N, 2.84.

Synthesis of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$.

Initially the reaction $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ with

a large excess (20-fold) of CO_2 was carried out on an NMR scale. From this reaction, a sparingly soluble compound, $\{[(\eta^5\text{-}C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2 \cdot C_6D_6$ was isolated as well-formed single crystals. Following the identification of this dinuclear species, a larger scale reaction of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$ under an atmosphere of CO_2 was performed. A 0.197-g sample (0.531 mmol) of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$ was placed in a 100 mL solv-seal flask which was attached to a high vacuum adapter equipped with a high vacuum Teflon stopcock. After the addition of *ca.* 15 mL of toluene, the reaction flask was pressurized to 1 atmosphere of CO_2 and stirred for several days. Following the removal of the volatiles, the product residue was washed several times with 10 mL portions of cold pentane to yield $\{[(\eta^5\text{-}C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2$ as a white powder. Overall isolated yield: 0.15 (70%). ^1H NMR spectrum ($CDCl_3$, 270MHz): δ 2.18, 2.11 (s, O_2CMe), 2.01, 1.84 (s, C_5Me_4), 0.31 (s, $SiMe_2$). $^{13}C\{^1H\}$ spectrum ($CDCl_3$, 67.8 MHz): 187.5 ($\eta^2\text{-}O_2\mathbf{C}Me$), 177.4 ($\mu\text{-}O_2\mathbf{C}Me$), 131.5, 128.0 (distal and proximal ring carbons of C_5Me_4), 105.5 (bridgehead C of C_5Me_4), 26.4 ($\mu\text{-}O_2C\mathbf{Me}$), 23.2 ($\eta^2\text{-}O_2C\mathbf{Me}$), 14.7, 10.9 ($C_5\mathbf{Me}_4$), 3.9 ($SiMe_2$). IR (Nujol, cm^{-1}): ν(OCO-bridging) 1577 (s), 1449 (m); ν(OCO-chelating) 1535 (sh), 1476.1 (m). Anal. Calcd. for $C_{15}H_{24}O_5SiZr$ (emp. form): C, 44.63; H, 5.99; N, 0.0. Found: C, 44.61; H, 6.09; N, 0.0.

The corresponding carboxylation reactions of $[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)]ZrMe_2$ with CO_2 and $^{13}CO_2$ at 60 psi were performed at the Union Carbide Tech Center in S. Charleston, WV by Dr. Greg T. Whiteker. The only volatile organic product detected by GC/MS and IR measurements after each reaction was OCN-t-Bu (ν_{CO} = 2262 cm^{-1}) and $O^{13}CN$-t-Bu ($\nu_{^{13}CO}$ = 2202 cm^{-1}), respectively. The MS spectrum of OCN-t-Bu is identical to that measured under the same conditions for an authentic sample of t-butylisocyanate purchased from Aldrich. The primary ion peak in the MS spectrum of OCN-t-Bu is not due to the parent ion (m/z = 99) but is located at m/z = 84 (parent ion - CH_3). The

primary ion peak in the MS spectrum of $O^{13}CN$-t-Bu is not the parent ion peak at m/z = 100 but is found at m/z = 85 (parent ion - CH_3).

X-ray Structural Analyses of {[(η^5-C_5Me_4)$SiMe_2$(N-t-Bu)]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$ and {[(η^5-C_5Me_4)$SiMe_2O$]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$·C_6D_6.

The X-ray structural analyses of {[(η^5-C_5Me_4)$SiMe_2$(N-t-Bu)]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$, **2**, and {[(η^5-C_5Me_4)$SiMe_2O$]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$·C_6D_6, **3·C_6D_6**, were performed by following the same general procedures. A single crystal of each compound was sealed in a capillary tube under a nitrogen atmosphere and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The corresponding lattice parameters and orientation matrix for the respective unit cells were determined from a least-squares fit of the orientation angles of at least 20 higher order reflections at 22 °C. The systematic absences observed for **2** of {h k l}, h + k + l = 2n +1, {h 0 l}, h = 2n + 1 are consistent with the monoclinic space groups Ia, non-standard setting of Cc (C_s^4, No. 9), and I2/a, nonstandard setting of C2/c (C_{2h}^6, No.15). The I-centered cell with lattice parameters of a = 20.498(2) Å, b = 9.157(3) Å, c = 23.677(3) Å, β = 92.23(2)° was used for data collection and latter transformed to the standard C-centered cell. The centrosymmetric space group was confirmed as the correct one for **2** on the basis of the structural analysis. No systematic absences were observed for **3·C_6D_6**, which crystallizes in the centrosymmetric space group $P\bar{1}$ (C_i^1, No. 2). The refined lattice parameters and other pertinent crystallographic information are summarized in TablesS1 and S6.

Intensity data were measured at 22 ± 1 °C with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and ω scans with variable scan rates (2 - 10 °/min). Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections during data collection and showed no

evidence of sample decomposition. The intensity data were corrected for Lorentz-polarization and merged.

The structure solutions of **2** and **3·C$_6$D$_6$** were carried out with the heavy-atom and direct methods algorithms available with SHELXTL IRIS. In both dinuclear compounds the two Zr centers are related by a crystallogaphic center of inversion. The approximate coordinates of the independent non-hydrogen atoms were revealed by Fourier methods and then refined anisotropically. The hydrogen atom positions were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of all the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinements, based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2(F_o^2) + (aP)^2 + b\,P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2\,F_c^2)/3$, were performed with SHELXL-93 operating on a Silicon Graphics Iris Indigo workstation. The values of the weighting parameters, a and b, were 0.0346, 0.4584 and 0.0371, 0.2608 for **2** and **3·C$_6$D$_6$**, respectively. The final discrepancy indices for **2** are R1 = 0.0395, wR2 = 0.0726 for 1964 reflections with $I > 2\,\sigma(I)$ with the overall GOF = 1.013, whereas their corresponding values for **3·C$_6$D$_6$** are R1 = 0.0264, wR2 = 0.0681 for 4108 reflections with $I > 2\,\sigma(I)$ with the overall GOF = 1.054. The values of the discrepancy indices were calculated from the expressions $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum(w_i(F_o^2 - F_c^2)^2)/\sum(w_i(F_o^2)^2)]^{1/2}$ and the standard deviation of an observation of unit weight σ_1 is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.

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Table S1. Crystal data and structure refinement for

$\{[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)Zr(O_2CMe)_2]\}_2$.

Identification code	lmko2cme
Empirical formula	$C_{19}H_{33}NO_4SiZr$
Formula weight	458.77
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a = 30.710(5) Å α = 90° b = 9.157(2) Å β = 129.61(1)° c = 20.498(2) Å γ = 90°
Volume	4441(2) Å^3
Z	8
Density (calculated)	1.372 g/cm^3
Absorption coefficient	5.71 mm^{-1}
F(000)	1920
Crystal size	0.04 x 0.14 x 0.56 mm
θ range for data collection	1.99 to 22.51°
Index ranges	$-32 \le h \le 32$, $-9 \le k \le 9$, $-22 \le \ell \le 21$
Reflections collected	8194
Independent reflections	2899 (R_{int} = 0.0614)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2607 / 0 / 246
Goodness-of-fit on F^2	1.013
Final R indices [I>2σ(I)]	R1 = 0.0395, wR2 = 0.0726
R indices (all data)	R1 = 0.0806, wR2 = 0.0852
Largest diff. peak and hole	0.314 and -0.265 eÅ^{-3}

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Table S2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for {[(C_5Me_4)$SiMe_2$(N-t-Bu)Zr(O_2CMe)$_2$}$_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zr	3435(1)	2847(1)	165(1)	34(1)
Si	4110(1)	2905(2)	-467(1)	49(1)
O(1)	3536(2)	790(4)	889(2)	45(1)
O(2)	4175(1)	2494(4)	1522(2)	50(1)
O(3)	2594(1)	2208(4)	-890(2)	41(1)
O(4)	3009(1)	3395(4)	686(2)	44(1)
N	3771(2)	1621(4)	-315(2)	36(1)
C(1)	3822(2)	4506(6)	-282(3)	41(1)
C(2)	3227(2)	4789(5)	-839(3)	42(1)
C(3)	3092(2)	5448(6)	-376(4)	52(2)
C(4)	3588(2)	5627(6)	458(4)	52(2)
C(5)	4040(2)	5054(6)	515(3)	46(1)
C(6)	2808(2)	4481(6)	-1774(3)	67(2)
C(7)	2512(2)	5983(6)	-730(4)	79(2)
C(8)	3634(3)	6384(7)	1150(4)	87(2)
C(9)	4654(2)	5132(6)	1304(3)	73(2)
C(10)	4899(2)	2783(7)	302(4)	86(2)
C(11)	3943(3)	3039(7)	-1518(4)	91(2)
C(12)	3793(2)	27(6)	-419(3)	44(1)
C(13)	4288(2)	-691(6)	408(3)	60(2)
C(14)	3857(2)	-288(6)	-1091(3)	60(2)
C(15)	3241(2)	-708(6)	-734(4)	61(2)
C(16)	3988(2)	1270(7)	1547(3)	45(1)
C(17)	4317(3)	435(7)	2359(4)	77(2)
C(18)	2109(2)	1862(5)	-1157(3)	36(1)
C(19)	1660(2)	1710(7)	-2095(3)	69(2)

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Table S3. Interatomic distances [Å] and bond angles [°]

for $\{[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)Zr(O_2CMe)_2]_2$.

Zr-O(1)	2.293(3)	Zr-O(2)	2.224(3)
Zr-O(3)	2.137(3)	Zr-O(4)	2.211(3)
Zr-N	2.140(4)	Zr-Cp(c)	2.213
Zr-C(1)	2.438(5)	Zr-C(2)	2.477(5)
Zr-C(3)	2.554(5)	Zr-C(4)	2.589(5)
Zr-C(5)	2.520(5)	Si-N	1.725(4)
Si-C(1)	1.871(5)	Si-C(10)	1.871(6)
Si-C(11)	1.875(6)	O(1)-C(16)	1.246(6)
O(2)-C(16)	1.276(6)	O(3)-C(18)	1.258(5)
O(4)-C(18)'	1.251(5)	N-C(12)	1.483(6)
C(1)-C(2)	1.430(6)	C(2)-C(3)	1.393(7)
C(2)-C(6)	1.504(7)	C(3)-C(4)	1.397(7)
C(3)-C(7)	1.515(7)	C(4)-C(5)	1.417(7)
C(4)-C(8)	1.501(7)	C(5)-C(1)	1.404(7)
C(5)-C(9)	1.514(7)	C(12)-C(13)	1.527(7)
C(12)-C(14)	1.538(6)	C(12)-C(15)	1.533(7)
C(16)-C(17)	1.495(7)	C(18)-C(19)	1.495(6)

O(1)-Zr-O(2)	57.51(12)	O(1)-Zr-O(3)	90.42(13)
O(1)-Zr-O(4)	75.59(12)	O(1)-Zr-N	87.77(13)
O(1)-Zr-Cp(c)	161.2	O(2)-Zr-O(3)	146.93(13)
O(2)-Zr-O(4)	82.87(12)	O(2)-Zr-N	95.26(13)
O(2)-Zr-Cp(c)	104.3	O(3)-Zr-O(4)	81.12(11)
O(3)-Zr-N	90.94(13)	O(3)-Zr-Cp(c)	106.6
O(4)-Zr-N	161.41(13)	O(4)-Zr-Cp(c)	98.8
N-Zr-Cp(c)	99.6	N-Si-C(1)	94.6(2)
N-Si-C(10)	114.5(2)	N-Si-C(11)	119.9(3)
C(1)-Si-C(10)	113.7(3)	C(1)-Si-C(11)	111.3(3)
C(10)-Si-C(11)	103.2(3)	C(16)-O(1)-Zr	90.5(3)
C(16)-O(2)-Zr	92.9(3)	C(18)-O(3)-Zr	147.3(3)
C(18)'-O(4)-Zr	151.9(3)	C(12)-N-Si	123.8(3)
C(12)-N-Zr	131.5(3)	Si-N-Zr	104.4(2)
C(5)-C(1)-C(2)	106.5(4)	C(2)-C(1)-Si	120.5(4)

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C(5)-C(1)-Si	125.4(4)	C(1)-C(2)-C(3)	108.5(5)
C(1)-C(2)-C(6)	127.1(5)	C(3)-C(2)-C(6)	124.3(5)
C(2)-C(3)-C(4)	108.6(5)	C(2)-C(3)-C(7)	125.8(6)
C(4)-C(3)-C(7)	125.4(6)	C(3)-C(4)-C(5)	107.6(5)
C(3)-C(4)-C(8)	125.6(6)	C(5)-C(4)-C(8)	126.6(6)
C(1)-C(5)-C(4)	108.7(5)	C(1)-C(5)-C(9)	127.2(5)
C(4)-C(5)-C(9)	123.9(5)	N-C(12)-C(13)	111.6(4)
N-C(12)-C(14)	111.0(4)	N-C(12)-C(15)	110.6(4)
C(13)-C(12)-C(14)	107.9(4)	C(13)-C(12)-C(15)	109.2(5)
C(14)-C(12)-C(15)	106.2(4)	O(1)-C(16)-O(2)	119.1(5)
O(1)-C(16)-C(17)	121.4(6)	O(2)-C(16)-C(17)	119.5(5)
O(3)-C(18)-O(4)'	123.9(4)	O(3)-C(18)-C(19)	116.7(4)
O(4)'-C(18)-C(19)	119.4(4)		

Symmetry transformations used to generate equivalent atoms:

(') -x+1/2,-y+1/2,-z

Cp(c) corresponds to the centroid of the cyclopentadienyl ring.

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Table S4. Anisotropic displacement parameters [$Å^2$ x 10^3] for $\{[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)Zr(O_2CMe)_2]_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$.

	U11	U22	U33	U23	U13	U12
Zr	34(1)	36(1)	38(1)	2(1)	27(1)	1(1)
Si	55(1)	51(1)	65(1)	11(1)	49(1)	10(1)
O(1)	48(2)	47(2)	43(2)	3(2)	31(2)	-2(2)
O(2)	44(2)	60(3)	43(2)	1(2)	27(2)	0(2)
O(3)	32(2)	56(2)	41(2)	-2(2)	26(2)	-4(2)
O(4)	48(2)	51(2)	49(2)	-4(2)	39(2)	-4(2)
N	35(2)	38(3)	42(3)	5(2)	28(2)	8(2)
C(1)	45(3)	36(4)	55(4)	13(3)	38(3)	5(3)
C(2)	41(3)	41(3)	47(4)	12(3)	30(3)	3(3)
C(3)	50(4)	39(4)	79(5)	12(3)	46(4)	6(3)
C(4)	71(4)	33(3)	75(5)	-2(3)	58(4)	-9(3)
C(5)	44(3)	40(4)	55(4)	2(3)	32(3)	-5(3)
C(6)	58(4)	77(5)	56(4)	30(3)	33(4)	8(3)
C(7)	69(4)	58(4)	136(6)	26(4)	77(5)	24(3)
C(8)	130(6)	54(4)	123(6)	-41(4)	102(6)	-31(4)
C(9)	70(4)	77(5)	67(5)	-6(4)	41(4)	-25(4)
C(10)	60(4)	73(4)	137(6)	14(5)	68(4)	9(4)
C(11)	140(6)	85(5)	109(5)	26(4)	108(5)	23(5)
C(12)	48(3)	46(4)	38(3)	2(3)	28(3)	11(3)
C(13)	69(4)	50(4)	65(4)	8(3)	44(4)	17(3)
C(14)	64(4)	64(4)	55(4)	-2(3)	38(4)	18(3)
C(15)	69(4)	45(4)	69(4)	-6(3)	44(4)	-5(3)
C(16)	53(4)	51(4)	46(4)	11(3)	38(3)	14(3)
C(17)	87(5)	79(5)	62(4)	23(4)	47(4)	20(4)
C(18)	40(3)	31(4)	38(3)	-1(2)	26(3)	6(2)
C(19)	49(3)	115(6)	46(4)	-16(3)	32(3)	-9(3)

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Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $\{[(C_5Me_4)SiMe_2(N\text{-}t\text{-}Bu)Zr(O_2CMe)_2]_2$.

	x	y	z	U(eq)
H(6A)	2857(10)	5179(23)	-2073(4)	80
H(6B)	2432(2)	4554(36)	-1963(5)	80
H(6C)	2869(9)	3514(15)	-1883(4)	80
H(7A)	2441(7)	6917(20)	-994(21)	95
H(7B)	2496(5)	6075(39)	-278(5)	95
H(7C)	2231(3)	5298(22)	-1141(17)	95
H(8A)	3676(16)	7415(8)	1122(15)	105
H(8B)	3957(10)	6016(29)	1690(4)	105
H(8C)	3298(7)	6203(35)	1079(14)	105
H(9A)	4873(3)	5554(35)	1166(5)	88
H(9B)	4791(5)	4166(7)	1525(13)	88
H(9C)	4689(3)	5724(31)	1721(9)	88
H(10A)	5018(2)	1937(23)	176(15)	103
H(10B)	5027(2)	2708(42)	867(5)	103
H(10C)	5057(2)	3643(19)	256(17)	103
H(11A)	4182(12)	2383(31)	-1528(10)	109
H(11B)	4008(16)	4021(12)	-1603(11)	109
H(11C)	3555(5)	2783(41)	-1960(4)	109
H(13A)	4251(7)	-536(29)	833(6)	72
H(13B)	4636(2)	-269(24)	591(11)	72
H(13C)	4289(8)	-1720(8)	319(6)	72
H(14A)	4210(6)	102(30)	-907(9)	72
H(14B)	3551(8)	160(29)	-1617(6)	72
H(14C)	3850(13)	-1324(6)	-1170(14)	72
H(15A)	3198(7)	-619(30)	-310(9)	73
H(15B)	3251(6)	-1723(9)	-842(19)	73
H(15C)	2928(2)	-244(23)	-1247(11)	73
H(17A)	4409(13)	-513(15)	2278(7)	92
H(17B)	4094(6)	330(35)	2536(12)	92
H(17C)	4658(8)	953(20)	2787(7)	92
H(19A)	1306(4)	1478(36)	-2227(3)	82
H(19B)	1761(7)	942(24)	-2295(4)	82
H(19C)	1624(10)	2611(13)	-2364(3)	82

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Table S6. Crystal data and structure refinement for

$\{[(C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2 \cdot C_6D_6$.

Identification code	lmkacet
Empirical formula	$C_{18}H_{24}D_3O_5SiZr$
Formula weight	445.73
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 9.3277(4) Å α = 73.545(3)° b = 10.0887(5) Å β = 72.236(4)° c = 12.0840(5) Å γ = 73.818(5)°
Volume	1015.31(8) Å^3
Z	2
Density (calculated)	1.458 g/cm^3
Absorption coefficient	6.23 cm^{-1}
F(000)	458
Crystal size	0.30 x 0.24 x 0.52 mm
θ range for data collection	2.59 to 27.50°
Index ranges	$0 \le h \le 11$, $-12 \le k \le 12$, $-14 \le \ell \le 15$
Reflections collected	4838
Independent reflections	4556 (R_{int} = 0.0145)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4436 / 0 / 244
Goodness-of-fit on F^2	1.054
Final R indices [I>2σ(I)]	R1 = 0.0264, wR2 = 0.0681
R indices (all data)	R1 = 0.0317, wR2 = 0.0711
Extinction coefficient	0.0066(10)
Largest diff. peak and hole	0.339 and -0.222 eÅ^{-3}

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Table S7. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for {[$(C_5Me_4)SiMe_2O$]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$ · C_6D_6. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zr	320(1)	4354(1)	1407(1)	25(1)
Si	-2090(1)	7204(1)	1182(1)	34(1)
O(1)	504(2)	1990(2)	2229(1)	42(1)
O(2)	2564(2)	2840(2)	1653(2)	42(1)
O(3)	-1819(2)	3774(2)	1473(1)	33(1)
O(4)	2181(2)	5469(2)	370(1)	32(1)
O(5)	-884(2)	6241(1)	252(1)	28(1)
C(1)	-1283(2)	6231(2)	2503(2)	32(1)
C(2)	-1646(2)	4960(2)	3309(2)	38(1)
C(3)	-333(3)	4166(3)	3717(2)	43(1)
C(4)	844(3)	4947(3)	3212(2)	41(1)
C(5)	264(2)	6218(2)	2489(2)	36(1)
C(6)	-3184(3)	4555(3)	3769(2)	55(1)
C(7)	-230(4)	2797(3)	4634(2)	67(1)
C(8)	2397(3)	4518(4)	3493(3)	64(1)
C(9)	1078(3)	7425(3)	1896(2)	54(1)
C(10)	-1968(4)	9100(3)	646(3)	65(1)
C(11)	-4136(3)	7156(3)	1381(3)	56(1)
C(12)	1926(3)	1790(2)	2116(2)	42(1)
C(13)	2855(4)	359(3)	2532(3)	73(1)
C(14)	-2519(2)	3884(2)	703(2)	31(1)
C(15)	-3878(3)	3197(3)	1083(2)	49(1)
C(16)	-6221(6)	761(6)	5679(4)	100(2)
C(17)	-5027(7)	1354(5)	4985(5)	99(2)
C(18)	-3799(7)	639(6)	4299(5)	104(2)

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Table S8. Interatomic distances [Å] and bond angles [°] for

{[(C_5Me_4)$SiMe_2$O]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$· C_6D_6.

Zr-O(1)	2.289(2)	Zr-O(2)	2.268(2)
Zr-O(3)	2.2042(14)	Zr-O(4)	2.1929(14)
Zr-O(5)	2.2570(13)	Zr-O(5)'	2.1260(13)
Zr-C(1)	2.492(2)	Zr-C(2)	2.572(2)
Zr-C(3)	2.631(2)	Zr-C(4)	2.628(2)
Zr-C(5)	2.557(2)	Cp(c)-Zr	2.277
Si-O(5)	1.6462(14)	Si-C(1)	1.875(2)
Si-C(10)	1.861(3)	Si-C(11)	1.863(3)
O(1)-C(12)	1.255(3)	O(2)-C(12)	1.265(3)
O(3)-C(14)	1.256(2)	O(4)-C(14)'	1.261(2)
C(5)-C(1)	1.435(3)	C(1)-C(2)	1.428(3)
C(2)-C(3)	1.408(3)	C(2)-C(6)	1.500(3)
C(3)-C(4)	1.415(3)	C(3)-C(7)	1.506(3)
C(4)-C(5)	1.403(3)	C(4)-C(8)	1.506(3)
C(5)-C(9)	1.504(3)	C(12)-C(13)	1.499(3)
C(14)-C(15)	1.501(3)	C(16)-C(17)	1.349(8)
C(16)-C(18)"	1.400(7)	C(17)-C(18)	1.348(7)
C(18)-C(16)"	1.400(7)		

O(1)-Zr-O(2)	56.66(6)	O(1)-Zr-O(3)	71.35(6)
O(1)-Zr-O(4)	128.23(6)	O(1)-Zr-O(5)	144.69(5)
O(1)-Zr-O(5)'	85.36(6)	O(2)-Zr-O(3)	126.36(6)
O(2)-Zr-O(4)	73.02(6)	O(2)-Zr-O(5)	147.46(5)
O(2)-Zr-O(5)'	84.84(5)	O(3)-Zr-O(4)	147.81(5)
O(3)-Zr-O(5)	75.58(5)	O(3)-Zr-O(5)'	78.41(5)
O(4)-Zr-O(5)	77.41(5)	O(4)-Zr-O(5)'	78.39(5)
O(5)-Zr-O(5)'	76.11(5)	Cp(c)-Zr-O(1)	102.2
Cp(c)-Zr-O(2)	101.9	Cp(c)-Zr-O(3)	100.9
Cp(c)-Zr-O(4)	98.9	Cp(c)-Zr-O(5)	95.8
Cp(c)-Zr-O(5)'	171.8	O(5)-Si-C(1)	96.36(8)
O(5)-Si-C(10)	111.59(12)	O(5)-Si-C(11)	112.65(10)
C(10)-Si-C(1)	115.55(12)	C(11)-Si-C(1)	114.63(12)
C(10)-Si-C(11)	106.1(2)	C(12)-O(1)-Zr	92.24(14)

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C(12)-O(2)-Zr	92.92(13)	C(14)-O(3)-Zr	133.79(13)
C(14)'-O(4)-Zr	132.52(13)	Si-O(5)-Zr	104.97(7)
Si-O(5)-Zr'	148.12(8)	Zr-O(5)-Zr'	103.89(5)
C(5)-C(1)-C(2)	106.1(2)	C(5)-C(1)-Si	120.6(2)
C(2)-C(1)-Si	126.5(2)	C(1)-C(2)-C(3)	108.7(2)
C(1)-C(2)-C(6)	127.5(2)	C(3)-C(2)-C(6)	123.5(2)
C(2)-C(3)-C(4)	108.2(2)	C(2)-C(3)-C(7)	126.6(2)
C(4)-C(3)-C(7)	125.0(2)	C(3)-C(4)-C(5)	108.0(2)
C(3)-C(4)-C(8)	125.0(2)	C(5)-C(4)-C(8)	126.8(2)
C(4)-C(5)-C(1)	108.8(2)	C(1)-C(5)-C(9)	125.6(2)
C(4)-C(5)-C(9)	125.3(2)	O(1)-C(12)-O(2)	118.2(2)
O(1)-C(12)-C(13)	121.6(2)	O(2)-C(12)-C(13)	120.2(2)
C(13)-C(12)...Zr	178.4(2)	O(3)-C(14)-O(4)'	125.5(2)
O(3)-C(14)-C(15)	117.7(2)	O(4)'-C(14)-C(15)	116.9(2)
C(17)-C(16)-C(18)"	119.8(5)	C(18)-C(17)-C(16)	121.9(5)
C(17)-C(18)-C(16)"	118.3(5)		

Symmetry transformations used to generate equivalent atoms:

(') -x,-y+1,-z (") -1-x,-y,1-z

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Table S9. Anisotropic displacement parameters [$Å^2$ x 10^3] for

{[$(C_5Me_4)SiMe_2O$]Zr(η^2-O_2CMe)(μ-O_2CMe)}$_2$· C_6D_6.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + $2hka^*b^*U_{12}$].

	U11	U22	U33	U23	U13	U12
Zr	22(1)	29(1)	25(1)	-8(1)	-5(1)	-5(1)
Si	34(1)	32(1)	37(1)	-16(1)	-9(1)	2(1)
O(1)	45(1)	37(1)	45(1)	-4(1)	-14(1)	-9(1)
O(2)	33(1)	43(1)	49(1)	-11(1)	-15(1)	0(1)
O(3)	28(1)	41(1)	32(1)	-8(1)	-4(1)	-12(1)
O(4)	28(1)	39(1)	33(1)	-10(1)	-7(1)	-11(1)
O(5)	25(1)	29(1)	29(1)	-10(1)	-6(1)	-4(1)
C(1)	32(1)	36(1)	31(1)	-16(1)	-4(1)	-5(1)
C(2)	37(1)	46(1)	29(1)	-16(1)	2(1)	-11(1)
C(3)	51(1)	47(1)	25(1)	-12(1)	-6(1)	-3(1)
C(4)	38(1)	58(1)	32(1)	-22(1)	-11(1)	-3(1)
C(5)	38(1)	45(1)	33(1)	-20(1)	-4(1)	-12(1)
C(6)	46(1)	72(2)	45(1)	-21(1)	11(1)	-25(1)
C(7)	95(2)	57(2)	36(1)	-5(1)	-13(1)	-5(2)
C(8)	50(2)	90(2)	65(2)	-39(2)	-30(1)	5(1)
C(9)	54(2)	59(2)	60(2)	-28(1)	-3(1)	-28(1)
C(10)	100(2)	33(1)	66(2)	-13(1)	-33(2)	-4(1)
C(11)	32(1)	71(2)	62(2)	-30(1)	-12(1)	8(1)
C(12)	49(1)	38(1)	41(1)	-11(1)	-19(1)	0(1)
C(13)	77(2)	45(2)	96(2)	-9(2)	-46(2)	10(1)
C(14)	25(1)	34(1)	36(1)	-11(1)	-5(1)	-7(1)
C(15)	41(1)	64(2)	48(1)	-8(1)	-7(1)	-30(1)
C(16)	120(4)	92(3)	89(3)	-7(2)	-51(3)	-6(3)
C(17)	127(4)	63(2)	121(4)	-2(2)	-65(3)	-21(3)
C(18)	113(4)	97(3)	103(4)	16(3)	-51(3)	-35(3)

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Table S10. Hydrogen atom coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $\{[(C_5Me_4)SiMe_2O]Zr(\eta^2\text{-}O_2CMe)(\mu\text{-}O_2CMe)\}_2 \cdot C_6D_6$.

	x	y	z	U(eq)
H(6A)	-3429(10)	4308(19)	4623(2)	66
H(6B)	-3152(7)	3759(13)	3469(13)	66
H(6C)	-3958(4)	5337(7)	3510(14)	66
H(7A)	-858(19)	2238(10)	4551(12)	80
H(7B)	-587(24)	2994(3)	5416(2)	80
H(7C)	821(5)	2285(11)	4519(12)	80
H(8A)	3037(8)	5155(13)	2970(12)	77
H(8B)	2870(10)	3574(8)	3384(17)	77
H(8C)	2273(4)	4553(21)	4303(6)	77
H(9A)	2157(5)	7094(5)	1862(15)	65
H(9B)	660(15)	8153(9)	2344(9)	65
H(9C)	938(18)	7799(13)	1103(6)	65
H(10A)	-2668(18)	9576(6)	148(16)	78
H(10B)	-937(7)	9170(3)	199(16)	78
H(10C)	-2236(24)	9530(6)	1316(3)	78
H(11A)	-4436(7)	7611(17)	648(5)	67
H(11B)	-4780(4)	7640(17)	1996(12)	67
H(11C)	-4247(5)	6191(3)	1601(16)	67
H(13A)	3707(15)	108(10)	1888(6)	88
H(13B)	2218(8)	-327(5)	2794(19)	88
H(13C)	3236(22)	378(7)	3180(13)	88
H(15A)	-3723(9)	2550(14)	587(10)	58
H(15B)	-4793(4)	3909(3)	1008(15)	58
H(15C)	-3988(12)	2692(15)	1897(5)	58
H(16A)	-6897(60)	1068(57)	6064(47)	121
H(17A)	-5116(54)	2161(49)	5146(41)	118
H(18A)	-3037(56)	1071(52)	3862(42)	124