Inorg. Chem. **1994,** *33,* 6289−6292

Influence of the Alkoxide Moiety on Heterometallic Compound Formation: Structure and Dynamics of $KZr_2(O^tBu)_9$ and $K_2Zr_2(O^tBu)_{10}$

Daniel J. Teff, John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405-4001

Received July 12, 1994⊗

$KZr_2(O^tBu)_9$ was prepared by reaction of KO^tBu with $Zr(O^tBu)_4$ in a 1:2 molar ratio. Attempted sublimation results in dissociation of $Zr(O^tBu)_4$, affording $[KZr(O^tBu)_5]_n$, which can also be synthesized using equimolar KO^tBu and $Zr(O^tBu)_4$. Single-crystal X-ray diffraction revealed that $n = 2$; $K_2Zr_2(O^tBu)_{10}$ crystallizes from pentane at −20 °C in the monoclinic space group $P2_1/c$, with the unit cell dimensions $a = 10.532(1)$ Å, $b = 18.057(3)$ Å, $c = 27.618(5)$ Å, $\beta = 95.54(1)°$, and $Z = 4$. The dimer is composed of two five-coordinate Zr centers, each having trigonal bipyramidal geometry; the axes of the trigonal bipyramids are orthogonal, and the $Zr(O^tBu)_5^-$ units encapsulate both potassiums. Due to fluxionality, this species appears as a singlet in ^1H NMR in d_8-toluene even at −75 °C. Interconversions between and possible dissociative reactions of $KZr_2(O^tBu)_9$ and $[KZr(O^tBu)_5]_2$ are also tested experimentally.

Introduction

We have reported on heterometallic compounds[1] containing the $Zr_2(O^iPr)_9^-$ face-shared bioctahedral subunit interacting with Li^+,[2] K^+,[3] Cu^I,[4] Cu^{II},[3] and Ba^{II}.[2] Certain of these compounds were then studied for their mechanism of thermal transformation to oxide solids. Bulk thermolysis of the solid mono- and divalent copper compounds invariably led to reduction of copper to the metallic state, via β-hydrogen migration from isopropoxide.[4] We were therefore interested in the impact (on volatility, solid-state reactivity, and redox properties) of altering the alkoxide substituent to one devoid of hydrogens β to the metal. The obvious close analog to O^iPr is O^tBu. We report here the results of this study.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using oven-dried glassware. Solvents were freshly distilled from appropriate drying agents and stored under nitrogen. KO^tBu was purchased from Alfa/Aesar and used as received. $Zr(O^tBu)_4$ was prepared according to a literature method.[5] NMR spectra were run on a Varian XL-300 spectrometer (^1H and ^{13}C spectra at 300 and 75 MHz, respectively). Samples were run in C_6D_6 and referenced to appropriate solvent peaks (C_6D_5H: $^1H = 7.15$ ppm; $^{13}C = 128.0$ ppm). Low-temperature spectra were run in d_8-toluene and referenced to residual solvent methyl protons (2.09 ppm). Elemental analyses for carbon and hydrogen of $KZr_2(O^tBu)_9$ and $K_2Zr_2(O^tBu)_{10}$ were performed by Desert Analytics and Oneida Research Services, respectively. Potassium elemental analysis was performed on a Varian AA6 spectrophotometer using a sodium lamp with the selected frequency at 766.6 nm and an air/acetylene flame. Thermogravimetric analysis was performed on a DuPont 951 thermogravimetric analyzer at 1 atm under a helium flow.

Synthesis of $KZr_2(O^tBu)_9$ (Method 1). $Zr(O^tBu)_4$ (0.700 g, 1.82 mmol) and KO^tBu (0.102 g, 0.912 mmol) were suspended in 25 mL of pentane and stirred for 6 h. The resulting clear, colorless solution was concentrated to 15 mL and cooled to −20 °C, producing white powder. Recrystallization from a minimum volume of toluene gave colorless needless. The solvent was removed by cannula transfer and the crystals were dried *in vacuo*. Yield: 0.491 g (61%). ^1H NMR (C_6D_6, 25 °C): δ 1.86 (s, 9H), 1.68 (s, 36H), 1.67 (s, 18H), 1.31 (s, 18H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 75.2 (s, 4C), 73.6 (s, 2C), 73.2 (s, 1C), 72.9 (s, 2C), 35.6 (s, 3C), 35.5 (s, 6C), 34.6 (s, 6C), 34.4 (s, 12C). Anal. Calc for $C_{36}H_{81}O_9Zr_2K$: C, 49.16; H, 9.28; K, 4.45. Found: C, 49.04; H, 9.16; K, 3.92.

Loss of $Zr(O^tBu)_4$ from $KZr_2(O^tBu)_9$ was established by thermogravimetric analysis. There are two mass losses experienced at 1 atm of flowing helium. The dissociation of $Zr(O^tBu)_4$ (44%) begins at 100 °C and is complete by 135 °C. Almost immediately, a second mass loss, corresponding to sublimation of $K_2Zr_2(O^tBu)_{10}$, results, leaving only 1.6% of the original sample by 350 °C.

Synthesis of $K_2Zr_2(O^tBu)_{10}$ (Method 1). $Zr(O^tBu)_4$ (0.600 g, 1.56 mmol) and KO^tBu (0.176 g, 1.56 mmol) were suspended in 25 mL pentane and stirred for 6 h. The resulting clear, colorless solution was concentrated *in vacuo* to 15 mL and cooled to -20 °C, producing clear, well-formed crystals (many morphologies). The solvent was removed by cannula transfer, and the crystals were dried *in vacuo*. Yield: 0.519 g (67%). ^1H NMR (C_6D_6, 25 °C): δ 1.51 (s, 90H). ^1H NMR (d_8-toluene): 25 °C, δ 1.48 (s, 90H); −15 °C, δ 1.53 (s, 90H); −75 °C, δ 1.64 (s, 90H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 71.9 (s, 10C), 33.7 (s, 30C). Anal. Calc for $C_{40}H_{90}O_{10}Zr_2K_2$: C, 48.44; H, 9.15; K, 7.88. Found: C, 47.72; H, 9.29; K, 7.42.

Synthesis of $KZr_2(O^tBu)_9$ (Method 2). $Zr(O^tBu)_4$ (0.0268 g, 69.9 μmol) was mixed with 0.5 mL of C_6D_6, and the mixture was added to $K_2Zr_2(O^tBu)_{10}$ (0.0346 g, 34.9 μmol). The resulting homogeneous solution was agitated for 5 min and then transferred to an NMR tube. ^1H NMR (C_6D_6, 25 °C): δ 1.84 (s, 9H), 1.67 (s, 54H), 1.31 (s, 18H).

Synthesis of $K_2Zr_2(O^tBu)_{10}$ (Method 2). $KZr_2(O^tBu)_9$ (0.0400 g, 45.4 μmol) was dissolved in 0.5 mL of C_6D_6, and the solution was added to KO^tBu (0.0051 g, 45.4 μmol). The inhomogeneous (some KO^tBu remained undissolved) solution was agitated for 5 min and transferred to an NMR tube. The tube was capped and placed in a warm water bath. After 1 h, no solid remained. ^1H NMR (C_6D_6, 25 °C): δ 1.50 (s, 90H).

Test for Interaction between $^1/_2K_2Zr_2(O^tBu)_{10}$ and $KZr_2(O^tBu)_9$. $K_2Zr_2(O^tBu)_{10}$ (0.0150 g, 15.1 μmol) was dissolved in 0.75 mL of C_6D_6, and the solution was added to $KZr_2(O^tBu)_9$ (0.0266 g, 30.2 μmol). The homogeneous solution was agitated for 5 min and was transferred to an NMR tube. ^1H NMR (C_6D_6, 25 °C): δ 1.85 (s, 9H), 1.67 (s, 36H), 1.66 (s, 18H), 1.50 (s, 45H), 1.31 (s, 18H).

X-ray Structure Determination of $K_2Zr_2(O^tBu)_{10}$. A small, well-formed crystal was cleaved from a larger sample and affixed to the

---

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1994.

(1) For a review of heterometallic alkoxides, see: Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978; Chapter 5. Hubert-Pfalzgraf, L. G. *Polyhedron* **1994**, *13*, 1181 and references therein.

(2) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *J. Chem. Soc., Chem. Commun.* **1990**, 1750.

(3) Vaartstra, B. A.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 8593.

(4) Vaartstra, B. A.; Samuels, J. A.; Barash, E. H.; Martin, J. D.; Streib, W. E.; Gasser, C.; Caulton, K. G. *J. Organomet. Chem.* **1993**, *449*, 191.

(5) Thomas, I. M. *Can. J. Chem.* **1961**, *39*, 1386.

0020-1669/94/1333-6289$04.50/0

Table 1. Crystallographic Data for $K_2Zr_2(O^tBu)_{10}$

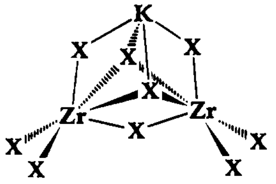
chem formula	$Zr_2C_{40}H_{90}K_2O_{10}$	space group	$P2_1/c$
a, Å	10.532(1)	T, °C	−173
b, Å	18.057(3)	λ, Å	0.710 69
c, Å	27.618(5)	ϱ_{calcd}, g cm^{-3}	1.260
β, deg	95.54(1)	μ(Mo Kα), cm^{-1}	5.9
V, Å^3	5227.98	R^a	0.0393
Z	4	$R_w{}^b$	0.0399
fw	991.78		

[a] $R = \Sigma||F_o| - |F_c||\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

end of a glass fiber using silicone grease, and the mounted sample was then transferred to the goniostat where it was cooled to −173 °C for characterization and data collection. Standard inert-atmosphere handling techniques were used throughout the investigation. A systematic search of a limited hemisphere of reciprocal space located a set of reflections with monoclinic symmetry and systematic absences corresponding to the unique space group $P2_1/c$ (Table 1). Subsequent solution and refinement of the structure confirmed this to be the proper space group. Data were collected ($6 \leq 2\theta \leq 45°$) using a standard moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms. The structure was solved by direct methods (MULTAN78) and Fourier techniques. A difference Fourier map phased on the non-hydrogen atoms clearly located all hydrogen atoms, and these were refined isotropically in the subsequent least squares refinement. A final difference Fourier map was essentially featureless, the largest peak being 0.24 e/Å^3. The results of the structure determination are shown in Tables 2 and 3 and Figure 1.

Results

Reaction of $Zr(O^tBu)_4$ with KO^tBu (2:1 mole ratio) in *pentane*, followed by crystallization in toluene at −20 °C, gives a product whose ^1H NMR is sufficiently complex to be structurally diagnostic. The methyl intensities are 1:2:2:4, whose relative and *total* intensities are consistent with C_{2v} symmetry of KZr_2X_9 (**I**, X = O^tBu). This is exactly the stoichiometry and structure of $KZr_2(O^iPr)_9$ (**I**, X = O^iPr).[3] Both molecules are stereochemically rigid at 25 °C. The $^{13}C\{^1H\}$ NMR spectrum at 25 °C shows four resonances (approximate intensities 1:2:2:4) each for the quaternary and for the methyl carbon regions.



I

Attempted vacuum sublimation of $KZr_2(O^tBu)_9$ at 115 °C and 10^{-2} Torr first results in reflux of a clear, colorless liquid onto the cold finger. Further pumping at an elevated temperature removes this liquid and gives a new deposit on the cold finger. This material has ^1H and $^{13}C\{^1H\}$ NMR spectra completely different from those of $KZr_2(O^tBu)_9$: each methyl signal is a singlet. Even down to −75 °C in d_8-toluene, the ^1H NMR spectrum remains a singlet. The elemental analysis of this new material is consistent with the empirical formula $KZr(O^tBu)_5$ (eq 1), and its spectral properties are identical to those of an

$$KZr_2(O^tBu)_9 \xrightarrow[\text{vacuum}]{\Delta} (1/n)[KZr(O^tBu)_5]_n + Zr(O^tBu)_4 \quad (1)$$

authentic sample of $[KZr(O^tBu)_5]_n$[6] synthesized from equimolar KO^tBu and $Zr(O^tBu)_4$ in pentane. Attempted vacuum sublimation thus causes loss of volatile $Zr(O^tBu)_4$. An earlier attempted synthesis[6] of $KZr_2(O^tBu)_9$, involving a sublimation step, yielded $[KZr(O^tBu)_5]_n$. Also reported there was a direct synthesis of $[KZr(O^tBu)_5]_n$ and *ebullioscopic* (77 °C) molecular weight measurements which gave a molecularity of 1.4 in benzene. This is hard to reconcile with our very simple ^1H and $^{13}C\{^1H\}$ NMR spectra of $[KZr(O^tBu)_5]_n$. We sought to resolve this difficulty by single-crystal X-ray diffraction.

Table 2. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $K_2Zr_2(O^tBu)_{10}$

	x	y	z	$10B_{iso}$
Zr(1)	5364.1(5)	1454.8(3)	1641.1(2)	12
Zr(2)	8010.5(5)	1692.5(3)	3784.2(2)	12
K(3)	8291(1)	1428(1)	2401.9(4)	18
K(4)	5718(1)	2503(1)	2732.7(5)	19
O(5)	4379(4)	946(2)	1109(1)	24
C(6)	3572(5)	666(3)	709(2)	17
C(7)	2205(6)	684(4)	830(2)	28
C(8)	3730(6)	1127(3)	268(2)	24
C(9)	3937(6)	−136(3)	627(2)	24
O(10)	7046(4)	968(2)	1497(1)	24
C(11)	7743(5)	468(3)	1232(2)	19
C(12)	9138(6)	518(4)	1420(3)	32
C(13)	7581(6)	667(3)	696(2)	26
C(14)	7271(6)	−324(3)	1303(3)	30
O(15)	3852(4)	2032(2)	1837(2)	27
C(16)	2688(5)	2403(3)	1843(2)	18
C(17)	1646(6)	1853(4)	1932(2)	27
C(18)	2356(6)	2798(4)	1365(2)	30
C(19)	2789(6)	2961(3)	2260(2)	27
O(20)	5657(3)	1056(2)	2325(1)	16
C(21)	5117(5)	450(3)	2571(2)	19
C(22)	6209(6)	−32(3)	2780(2)	27
C(23)	4228(6)	17(4)	2209(2)	27
C(24)	4382(6)	758(4)	2966(2)	25
O(25)	6420(4)	2407(2)	1743(1)	19
C(26)	6659(5)	2907(3)	1363(2)	18
C(27)	6254(6)	3681(3)	1495(2)	27
C(28)	8077(6)	2884(4)	1294(2)	24
C(29)	5885(6)	2670(3)	892(2)	23
O(30)	8229(3)	2394(2)	3165(1)	16
C(31)	8908(6)	3073(3)	3122(2)	21
C(32)	8801(6)	3304(4)	2590(2)	29
C(33)	8313(7)	3671(3)	3417(2)	30
C(34)	10313(6)	2962(4)	3298(2)	27
O(35)	9130(3)	2268(2)	4239(1)	17
C(36)	9837(5)	2513(3)	4675(2)	20
C(37)	9331(7)	2143(5)	5106(2)	43
C(38)	9705(7)	3352(4)	4711(3)	36
C(39)	11245(6)	2313(4)	4656(2)	26
O(40)	7559(3)	923(2)	4244(1)	18
C(41)	7185(5)	328(3)	4538(2)	20
C(42)	6262(6)	−170(3)	4232(2)	24
C(43)	8363(6)	−110(4)	4738(2)	28
C(44)	6547(6)	633(4)	4970(2)	25
O(45)	6163(3)	2072(3)	3673(1)	16
C(46)	5251(5)	2341(3)	3980(2)	20
C(47)	4292(6)	1740(4)	4070(2)	26
C(48)	5943(6)	2611(4)	4457(2)	25
C(49)	4542(6)	2996(4)	3728(2)	30
O(50)	8860(3)	956(2)	3352(1)	17
C(51)	9885(5)	434(3)	3400(2)	18
C(52)	9345(6)	−355(3)	3406(2)	24
C(53)	10670(6)	510(4)	2966(2)	25
C(54)	10733(6)	592(4)	3867(2)	27

[a] Fractional coordinates are $\times 10^4$. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Solid-State Structure. Single crystals, grown from pentane solution at −20 °C, gave diffraction intensities which led to the structure shown in Figure 1. The molecule is a dimer, K_2-

---

(6) Mehrotra, R. C.; Agrawal, M. M. *J. Chem. Soc. A* **1967**, 1026.

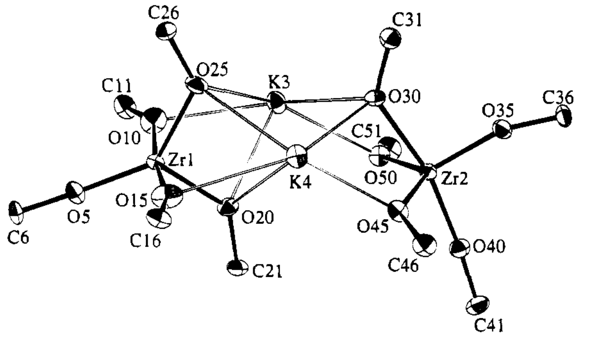


Figure 1. ORTEP view of $\mathrm{K_2Zr_2(O^tBu)_{10}}$, omitting the methyl groups for clarity.

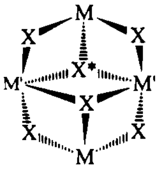
Table 3. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{K_2Zr_2(O^tBu)_{10}}$

K(3)–O(30)	2.742(6)	Zr(2)–O(30)	2.158(3)
K(3)–O(50)	2.770(8)	Zr(2)–O(35)	1.939(4)
K(3)–O(10)	2.832(8)	Zr(2)–O(40)	1.971(4)
K(3)–O(20)	2.843(6)	Zr(2)–O(45)	2.057(3)
K(3)–O(25)	3.103(6)	Zr(2)–O(50)	2.049(4)
K(4)–O(45)	2.708(8)	O(5)–C(6)	1.421(6)
K(4)–O(30)	2.802(6)	O(10)–C(11)	1.413(7)
K(4)–O(20)	2.843(6)	O(15)–C(16)	1.399(6)
K(4)–O(25)	2.904(6)	O(20)–C(21)	1.433(6)
K(4)–O(15)	3.124(8)	O(25)–C(26)	1.426(6)
Zr(1)–O(5)	1.946(4)	O(30)–C(31)	1.429(6)
Zr(1)–O(10)	2.050(4)	O(35)–C(36)	1.425(6)
Zr(1)–O(15)	2.020(4)	O(40)–C(41)	1.426(7)
Zr(1)–O(20)	2.018(4)	O(45)–C(46)	1.426(9)
Zr(1)–O(25)	2.053(4)	O(50)–C(51)	1.429(6)

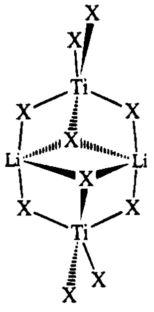
O(5)–Zr(1)–O(10)	93.39(17)	O(35)–Zr(2)–O(45)	115.18(14)
O(5)–Zr(1)–O(15)	93.98(17)	O(35)–Zr(2)–O(50)	116.88(14)
O(5)–Zr(1)–O(20)	124.14(15)	O(40)–Zr(2)–O(45)	92.71(15)
O(5)–Zr(1)–O(25)	137.86(16)	O(40)–Zr(2)–O(50)	93.65(15)
O(10)–Zr(1)–O(15)	172.33(17)	O(45)–Zr(2)–O(50)	126.09(14)
O(10)–Zr(1)–O(20)	88.41(15)	Zr(1)–O(5)–C(6)	172.3(4)
O(10)–Zr(1)–O(25)	85.34(16)	Zr(1)–O(10)–C(11)	151.2(4)
O(15)–Zr(1)–O(20)	89.22(16)	Zr(1)–O(15)–C(16)	164.7(4)
O(15)–Zr(1)–O(25)	87.76(16)	Zr(1)–O(20)–C(21)	133.1(3)
O(20)–Zr(1)–O(25)	97.96(15)	Zr(1)–O(25)–C(26)	124.1(3)
O(30)–Zr(2)–O(35)	95.40(14)	Zr(2)–O(30)–C(31)	131.4(3)
O(30)–Zr(2)–O(40)	167.15(14)	Zr(2)–O(35)–C(36)	161.8(3)
O(30)–Zr(2)–O(45)	81.82(14)	Zr(2)–O(40)–C(41)	174.7(4)
O(30)–Zr(2)–O(50)	80.44(14)	Zr(2)–O(45)–C(46)	135.0(3)
O(35)–Zr(2)–O(40)	97.45(15)	Zr(2)–O(50)–C(51)	137.9(3)

$\mathrm{Zr_2(O^tBu)_{10}}$, with an idealized mirror plane of symmetry containing both Zr, three μ_3-$\mathrm{O^tBu}$ groups, and three terminal $\mathrm{O^tBu}$ groups. The idealized mirror plane contains O(5), Zr(1), O(25), O(20), O(30), Zr(2), O(35), and O(40). This makes the K centers equivalent (both five-coordinate). The five alkoxy ligands attached to each K are associated with an asymmetric disposition of the two $\mathrm{Zr(O^tBu)_5^-}$ units (i.e., the zirconium centers are inequivalent): one (Zr(1)) shares four of its $\mathrm{O^tBu}$ groups, while one shares only three. Thus, Zr(1) has only one terminal alkoxide, while Zr(2) has two.

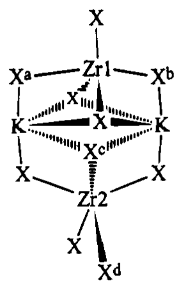
The overall molecular structure can be described in two ways. From the standpoint of the full unit, the structure is related to the more symmetric $\mathrm{M_2M'_2(\mu_3\text{-}X)_2(\mu_2\text{-}X)_4}$ moiety shown in **II**. This has a nearly planar $\mathrm{M_2M'_2}$ array with four μ_2-X nearly in this plane and two μ_3-X groups lying on opposite sides of this plane. M and M′ can then have varying numbers of terminal ligands either on M, M′, or both. For example, $\mathrm{Li_2Ti_2(O^iPr)_{10}}$[7] adopts structure **II**, with two terminal $\mathrm{O^iPr}$ groups on each Ti (at site M) and no terminal ligands on Li (at site M′), as in **III**. This is clearly not the structure of $\mathrm{K_2Zr_2(O^tBu)_{10}}$ since this molecule has *three* μ_3-$\mathrm{O^tBu}$ groups. It is derived from **II** by adding a second μ_3-$\mathrm{O^tBu}$ group toward the reader from X*, as in **IV**. The second important difference between **III** and **IV** is that the idealized C_3 axes of the two trigonal bipyramidal zirconium metals are orthogonal (compare $\mathrm{X^a{-}Zr{-}X^b}$ and $\mathrm{X^c{-}Zr{-}X^d}$). Thus, there is a mirror plane aligned vertically and perpendicular to the page in **IV**, but the zirconium centers are *inequivalent* (although both are five-coordinate). While structure **III** leaves $\mathrm{Li^+}$ four-coordinate, the larger $\mathrm{K^+}$ in **IV** is five-coordinate. The Zr–O distances are longest to the μ_3-O atoms and shortest to the terminal O atoms. While the O(equatorial)–Zr–O(equatorial) angles at Zr(2) are all within 6° of 120°, one of these angles at Zr(1) is compressed to 98.0° in order to allow two equatorial alkoxides to assume μ_3 roles. The O(axial)–Zr–O(axial) angles are 172.3° at Zr(1) and 167.2° at Zr(2). Zr–O–C angles involving terminal alkoxides range from 161.8(3) to 174.7(4)°, and are the largest in the molecule.



II



III



IV

Efficient encapsulation of the two K centers by the bulky $\mathrm{O^tBu}$ ligands creates a hydrocarbon periphery which enhances solubility. This (and the absence of a molecular dipole moment) explains its fairly high solubility in many common solvents, including pentane.

Solution NMR Studies. In contrast to stereochemically-rigid $\mathrm{KZr_2(O^tBu)_9}$, it is apparent from the single $\mathrm{O^tBu}$ environment observed for $\mathrm{K_2Zr_2(O^tBu)_{10}}$ in d_8-toluene from 25 to −75 °C that this is a rapidly fluxional molecule: terminal, μ_2- and μ_3-$\mathrm{O^tBu}$ groups all interconvert rapidly. We suggest that this difference is associated with the higher coordination number (i.e., 6) of Zr in $\mathrm{KZr_2(O^tBu)_9}$ hindering rearrangement. Five-coordinate Zr in $\mathrm{K_2Zr_2(O^tBu)_{10}}$ can initiate rearrangement by bonding to an additional $\mathrm{O^tBu}$ group and becoming six-coordinate in a transition state.

We have done several control experiments to test the alternative hypothesis that fluxionality is due to a dissociative process. For example, we attempted to test for dissociation of $\mathrm{Zr(O^tBu)_4}$ from $\mathrm{K_2Zr_2(O^tBu)_{10}}$ by seeking NMR coalescence of $\mathrm{K_2Zr_2(O^tBu)_{10}}$ with $\mathrm{Zr(O^tBu)_4}$ (eq 2). Instead, a net reaction

$$\mathrm{K_2Zr_2(O^tBu)_{10}} + 2\mathrm{Zr(O^tBu)_4} \xrightarrow{\mathrm{C_6D_6}} 2\mathrm{KZr_2(O^tBu)_9} \quad (2)$$

occurs to form the more zirconium-rich $\mathrm{KZr_2(O^tBu)_9}$. This is the reverse of eq 1. This also implicates a stepwise process for formation of $\mathrm{KZr_2(O^tBu)_9}$ when $\mathrm{Zr(O^tBu)_4}$ is added to $\mathrm{KO^tBu}$.

We have therefore tested for dissociation of $\mathrm{Zr(O^tBu)_4}$ from $\mathrm{K_2Zr_2(O^tBu)_{10}}$ by a second method, that of using $\mathrm{KZr_2(O^tBu)_9}$ as a "buffered" source (see eq 1) of $\mathrm{Zr(O^tBu)_4}$. Combination of $\mathrm{K_2Zr_2(O^tBu)_{10}}$ and $\mathrm{KZr_2(O^tBu)_9}$ (in a 1:2 mole ratio) in $\mathrm{C_6D_6}$ might give ^{1}H NMR line broadening if a $\mathrm{Zr(O^tBu)_4}$ subunit exchanges between these molecules. In fact, the ^{1}H NMR spectrum at 25 °C is simply the superposition of the spectra of the two components; no interaction is detectable, consistent with the fluxionality of $\mathrm{K_2Zr_2(O^tBu)_{10}}$ being intramolecular.

---

[7] Hampden-Smith, M. J.; Williams, D. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4076.

Finally, addition of equimolar KO^{t}Bu to KZr$_2$(O^{t}Bu)$_9$ in C_6D_6 yields (in time of mixing) K$_2$Zr$_2$(O^{t}Bu)$_{10}$, eq 3. This indicates how K$_2$Zr$_2$(O^{t}Bu)$_{10}$ can be formed when KO^{t}Bu is added to Zr(O^{t}Bu)$_4$.

$$\mathrm{KO^tBu + KZr_2(O^tBu)_9 \rightarrow K_2Zr_2(O^tBu)_{10}} \qquad (3)$$

Conclusions

KZr$_2$(O^{t}Bu)$_9$ can be isolated from reaction of Zr(O^{t}Bu)$_4$ and KO^{t}Bu. KZr$_2$(O^{t}Bu)$_9$ dissociates upon attempted sublimation; however, K$_2$Zr$_2$(O^{t}Bu)$_{10}$ sublimes intact. Apparently, the six-coordinate zirconium surrounded by *tert*-butoxide ligands is electronically satisfied. However, dissociation of Zr(O^{t}Bu)$_4$ at 100 °C relieves steric strain at both Zr metal centers, and the coordination number at zirconium decreases from 6 in KZr$_2$(O^{t}Bu)$_9$ to 5 in K$_2$Zr$_2$(O^{t}Bu)$_{10}$. Also, an idealized coordination of 4 at potassium increases to 5 in the formation of K$_2$Zr$_2$(O^{t}Bu)$_{10}$. Apparently, there is a balancing of steric and electronic effects in formation of this dimer.

Acknowledgment. This work was supported by the Department of Energy. We also thank John Samuels and Marco Leite for technical assistance.

Supplementary Material Available: Tables listing full crystallographic details, hydrogen positional and thermal parameters, anisotropic thermal parameters, and complete interatomic distances and angles and a drawing showing atom labeling (10 pages). Ordering information is available on any current masthead page.