Inorg. Chem. **1986**, *25*, 1803–1805

(II)–thioether interaction has been found, namely a thioether bridging two Cu(II) ions through axial sites.

Acknowledgment. We thank the National Science Foundation for support of this research through Grant PCM 79-04915 and R. Baar and Dr. F. Anson for providing the thiobis(ethylenenitrilo)tetraacetic acid used in this study.

Note Added in Proof. The structure of $(Cu_2((O_2CCH_2)_2NCH_2CH_2S)_2)\cdot 4H_2O$ has recently been reported (Dung, P. N.-H.; Viossat, B.; Busnot, A.; Gonzalez-Perez, J. M.; Niclos-Gutierrez, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1739–1742). The solid-state structure of this material is closely related to that reported herein with a bridging *disulfide* in place of the bridging sulfide.

Registry No. $Cu_2(TEDTA)\cdot 5H_2O$, 101348-83-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, positional parameters for hydrogen atoms, bond distances and angles, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Soluble Zinc Bis(aryloxides)

Rolf L. Geerts, John C. Huffman, and Kenneth G. Caulton*

Received October 21, 1985

Alcoholysis of $ZnEt_2$ with HOAr (Ar = 2,6-di-*tert*-butylphenyl) proceeds no further than $(EtZnOAr)_4$. Treatment of $ZnBr_2$ with KOAr gives the adduct $KZn(OAr)_2Br$. However, alcoholysis of $Zn[N(SiMe_3)_2]_2$ yields, in benzene, dimeric $[Zn(OAr)_2]_2$. Treatment of HOAr′ (Ar′ = 2,4,6-tri-*tert*-butylphenyl) with the zinc amide in THF yields $Zn(OAr')_2(THF)$, which may be recrystallized in the presence of excess THF to produce a solid shown by X-ray diffraction to be $Zn(OAr')_2(THF)_2$, containing quasi-tetrahedral Zn(II). This solid dissolves in benzene with liberation of 1 mol of THF. Crystal data (−161 °C): space group $P2_1/c$ with $Z = 4$ and $a = 17.604$ (9) Å, $b = 15.607$ (8) Å, $c = 17.679$ (8) Å, and $\beta = 114.19$ (2)°.

Introduction

The known zinc(II) bis(alkoxides) are all insoluble and presumably polymeric.[1] As such, they are difficult to purify and characterize and thus lack appeal for studies of their reaction chemistry. Our particular objective in zinc alkoxide chemistry is to utilize soluble examples as an entry into mixed-metal chemistry bearing on the conversion of CO and H_2 to methanol, currently catalyzed by oxides of copper and zinc.[2] We report here the use of bulky aryloxide ligands to furnish the first soluble zinc alkoxide.

Experimental Section

General Considerations. All manipulations were carried out with use of standard Schlenk procedures under prepurified nitrogen. Solvents (toluene, THF, hexanes) were dried and deoxygenated by distillation in the presence of sodium/benzophenone. Anhydrous $ZnBr_2$ (Fisher Scientific) was purified by sublimation under vacuum. The alcohols 2,6-di-*tert*-butylphenol (HOAr) and 2,4,6-tri-*tert*-butylphenol (HOAr′) (Aldrich) were purified by crystallization from hexanes. Commercial KH dispersion was washed free of oil with hexanes. $ZnEt_2$[3] (1 M THF solution) and $Zn[N(SiMe_3)_2]_2$[4] were prepared by literature methods. ^1H NMR spectra were recorded on a Varian HR 220-MHz spectrometer at 16 °C and referenced to Me_4Si. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

KOAr. To a THF slurry of KH (0.1 g, 2.5 mmol) was slowly added HOAr (0.5 g, 2.5 mmol) with concomitant production of H_2. After being stirred for 1 h, the solution was filtered to remove any excess KH and the solvent removed to yield an off-white solid. ^1H NMR (CD_3CN): δ 1.34 (s, *tert*-butyl, 18 H); 5.77, (t, *p*-H, 1 H); 7.15 (d, *m*-H, 2 H).

$KZn(OAr)_2Br$. To a THF suspension of $ZnBr_2$ (1.12 g, 5 mmol) was added KOAr (2.44 g, 10 mmol), and the solution was stirred at room temperature for 4 h. After removal of THF in vacuo, the residue was extracted with toluene and filtered through a fine-porosity filter. Addition of hexanes and cooling to −20 °C yielded colorless microcrystals. ^1H NMR (CD_3CN): δ 1.50 (s, *tert*-butyl, 18 H); 6.44 (t, *p*-H 1 H); 7.07 (d, *m*-H, 2 H). Anal. Calcd for $C_{28}H_{42}O_2BrKZn$: C, 56.52; H, 7.11; Zn, 10.98. Found: C, 56.50; H, 6.90, Zn, 10.05.

$(EtZnOAr)_4$. To 5 mL of a 1 M THF solution of $ZnEt_2$ (5 mmol) was added 50 mL of THF and 2.06 g (10 mmol) of HOAr, resulting in immediate gas evolution. Stirring of the solution for 1 h followed by removal of THF under vacuum showed (by ^1H NMR) complete conversion to $(EtZnOAr)_4$; unreacted alcohol was also evident. $(EtZnOAr)_4$ is unchanged in the presence of excess HOAr even after 18 h in refluxing toluene. $(EtZnOAr)_4$ can be isolated by sublimation at 170 °C under vacuum as a colorless powder. ^1H NMR (C_6D_6): δ 0.55 (q, $CH_2$$CH_3$, 2 H); 1.07 (t, $CH_2$$CH_3$, 3 H); 1.59 (s, *tert*-butyl, 18 H); 6.93 (t, *p*-H, 1 H); 7.34 (d, m-H, 2 H).

$[Zn(OAr)_2]_2$. To a 10-mL toluene solution of $Zn[N(SiMe_3)_2]_2$ (1.0 mL, 2.6 mmol) was added HOAr (1.07 g, 5.2 mmol). The solution was stirred for 1 h, yielding a pale yellow solution. The toluene was removed by evacuation and the resulting solid redissolved in a minimum of hexanes. Slow cooling to −20 °C overnight yielded colorless microcrystals, which were collected by *cold filtration* and dried to yield a colorless powder. An independent NMR-tube reaction showed the reaction to be quantitative, with liberation of $HN(SiMe_3)_2$. ^1H NMR (C_6D_6): δ 1.30 (s, *tert*-butyl, 18 H); 1.54 (s, *tert*-butyl, 18 H); 6.71 (overlapping triplets, *p*-H 2 H); 7.16 (overlapping doublets, *m*-H, 4 H).

$[Zn(OAr')_2]_2$. The synthesis and isolation are identical with those for the previous OAr analogue. An NMR-tube reaction shows this reaction also to be quantitative. ^1H NMR (C_6D_6): δ 1.29 (s, *tert*-butyl, 9 H); 1.35 (s, *tert*-butyl, 18 H); 1.36 (s, *tert*-butyl, 9 H); 1.59 (s, *tert*-butyl, 18 H); 7.33 (s, *m*-H, 2 H); 7.26 (s, *m*-H, 2 H). Cryoscopic molecular weight in C_6H_6, on material recrystallized from hexanes: 1100 ± 150 (calcd for a dimer, 1176), over the concentration range 1.80×10^{-3}–6.3×10^{-3} M.

$Zn(OAr)_2(THF)_2$. To a 10-mL THF solution of $Zn[N(SiMe_3)_2]_2$ (1.0 mL, 2.5 mmol) was added HOAr (1.07 g, 5.0 mmol). After the solution was stirred for 0.5 h, the volume of THF was reduced to 2 mL, and an equivalent amount of hexanes was added. Cooling to −20 °C overnight yielded colorless crystals, which were collected on a filter and dried at room temperature. ^1H NMR (C_6D_6): δ 1.08 (s, THF, 8 H); 1.58 (s, *tert*-butyl, 36 H); 3.36 (m, THF, 8 H); 6.86 (t, *p*-H, 2 H); 7.34 (d, *m*-H, 4 H).

$Zn(OAr')_2(THF)$. The reaction of $Zn[N(SiMe_3)_2]_2$ and 2 HOAr′ for 30 min in THF, followed by removal of THF with mild heating under vacuum, yields the monosolvate as a colorless powder. ^1H NMR (C_6D_6): δ 0.98 (m, THF, 4 H); 1.41 (s, *tert*-butyl, 18 H); 1.64 (s, *tert*-butyl, 36 H); 3.31 (m, THF, 4 H); 7.46 (s, *m*-H, 4 H).

$Zn(OAr')_2(THF)_2$. Recrystallization of $Zn(OAr')_2THF$ from THF/hexanes at −20 °C yields the bis solvate. ^1H NMR (C_6D_6): δ 1.20 (m, THF, 8 H); 1.39 (s, *tert*-butyl, 18 H); 1.61 (s, *tert*-butyl, 36 H); 3.45 (m, THF, 8 H); 7.43 (s, *m*-H, 14 H). Free THF in C_6D_6 shows resonances at δ 1.43 and 3.55.

Crystallography. In order to obtain a suitable crystal of $Zn(OAr')_2(THF)_2$, a larger sample was cleaved, under nitrogen, to yield a nearly equidimensional fragment of maximum dimension 0.14 mm. The sample was then affixed to a glass fiber on a goniometer head and transferred to the goniostat with use of standard inert-atmosphere handling techniques. The sample was then cooled to −161 °C for characterization and data collection, with use of graphite-monochromated radiation and a diffractometer of local construction.[5]

---

(1) Mehrotra, R. C. In *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.
(2) Kung, H. L. *Catal. Rev.* **1980**, *22*, 235.
(3) Moller, C. R. *Organic Syntheses*; Wiley: New York, 1943; Collect Vol. II, p 184.
(4) Burger, H.; Sawodny, W.; Wannaget, U. *J. Organomet. Chem.*, **1965**, *3*, 113.

0020-1669/86/1325-1803$01.50/0 © 1986 American Chemical Society

Table I. Crystal Data for $Zn(O\text{-}2,4,6\text{-}t\text{-}Bu_3H_2C_6)_2(THF)_2$

empirical formula	$C_{44}H_{74}O_4Zn$
color	colorless
cryst dimens, mm	0.12 × 0.13 × 0.14
space group	$P2_1/c$
cell dimens (at −161 °C, 34 reflecns)	
a, Å	17.604 (9)
b, Å	15.607 (8)
c, Å	17.679 (8)
β, deg	114.19 (2)
molecules/cell	4
vol, $Å^3$	4430.82
calcd density, g/cm^3	1.098
wavelength, Å	0.71069
mol wt	732.45
linear abs coeff, cm^{-1}	6.01
no. of unique intensities	5742
no. of intensities with $F > \sigma(F)$	2961
final residuals for $F > \sigma(F)$	
$R(F)$	0.0910
$R_w(F)$	0.0795
goodness of fit for last cycle	1.44
max Δ/σ for last cycle	0.05

A systematic search of a limited hemisphere of reciprocal space revealed a monoclinic lattice with extinctions that could be indexed as the unique centrosymmetric space group $P2_1/c$. Data were collected[5] to $2\theta = 45°$ $(+h,+k,\pm l)$, and processing revealed that only about half of the data were "observed" with use of a 2.33σ criterion. Examination of the intensities from 45 to 55° in 2θ indicated that no significant data were observed in this region (less than 5%), so no attempt was made to collect further data. The agreement factor calculated on redundant data was 0.043. Characteristics of the data collection and of the crystal appear in Table I.

The structure was solved by direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least-squares methods. Hydrogen atoms were clearly visible in a difference Fourier map phased on the non-hydrogen contributors and were included in the final cycles. Three different approaches were used in the final refinement: (1) all atoms were refined (anisotropic for Zn, O, and C and isotropic for H); (2) non-hydrogens were refined anisotropically and hydrogens were included only as fixed-atom contributors in idealized locations (C–H = 0.95 Å); (3) only the Zn atom was refined anisotropically, with fixed hydrogens and isotropic thermal parameters for O and C. There was a significant improvement in the residuals in each of the three cases in the order 1 < 2 < 3, as expected. Because the parameter to data ratio in the first procedure is much lower than desired (ca. 1:5), the results of the second refinement model are reported here with use of a 1σ criterion for "observed" data. In general, the distances were identical to within 1.5σ and only the estimated errors differed in the three refinements.

A final difference Fourier map was featureless, the largest peak being 0.18 e/$Å^3$. No attempt was made to correct the data for absorption, since ψ scans for several reflections were essentially flat.

The results of the structure determination are shown in Tables II and III and in Figure 1. Additional data are available as supplementary material.

Results and Discussion

Synthesis. The synthesis of monomeric $Zn(OAr)_2$, Ar = 2,6-di-*tert*-butylphenyl, has presented some special problems. Reaction of $ZnEt_2$ with excess HOAr even under vigorous conditions (18 h in refluxing toluene) has yielded only the product of a single ethyl replacement, $(EtZnOAr)_4$, analogous to compounds shown previously[6] to be cubanes with μ_3-OR groups and thus four-coordinate saturated zinc centers. Reaction of anhydrous zinc bromide with KOAr in THF yielded, upon recrystallization from toluene/hexane, solids that gave elemental analytical results consistent with the empirical formulation $KZn(OAr)_2Br$. This compound is slightly soluble in toluene and will not sublime but does dissolve sufficiently in CD_3CN to provide ^1H NMR spectra

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $Zn(O\text{-}2,4,6\text{-}t\text{-}Bu_3H_2C_6)_2(THF)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$
Zn(1)	7112 (1)	2034 (1)	8890 (1)	13
O(2)	6547 (4)	3072 (5)	8148 (4)	18
C(3)	6077 (7)	2974 (8)	7239 (6)	23
C(4)	5788 (7)	3862 (8)	6916 (7)	23
C(5)	6275 (7)	4457 (8)	7620 (7)	25
C(6)	6392 (7)	3932 (7)	8365 (7)	23
O(7)	7668 (4)	2271 (4)	10033 (4)	13
C(8)	8461 (5)	2150 (6)	10594 (5)	11
C(9)	9026 (6)	2817 (7)	10814 (6)	16
C(10)	9875 (6)	2648 (7)	11314 (6)	17
C(11)	10157 (6)	1838 (7)	11639 (6)	17
C(12)	9563 (6)	1210 (7)	11490 (6)	15
C(13)	8702 (6)	1333 (7)	10984 (6)	16
C(14)	8792 (6)	3770 (6)	10529 (6)	15
C(15)	9483 (7)	4403 (7)	10984 (7)	23
C(16)	8595 (7)	3844 (8)	9608 (7)	24
C(17)	8035 (7)	4019 (7)	10691 (7)	21
C(18)	11092 (7)	1653 (8)	12107 (7)	24
C(19)	11248 (7)	983 (8)	12770 (8)	31
C(20)	11573 (8)	2444 (10)	12508 (11)	68
C(21)	11385 (8)	1253 (14)	11471 (9)	67
C(22)	8093 (6)	610 (7)	10900 (6)	15
C(23)	8499 (7)	−119 (7)	11555 (7)	22
C(24)	7819 (7)	145 (8)	10056 (7)	25
C(25)	7333 (6)	897 (7)	11023 (6)	19
O(26)	6315 (4)	1148 (5)	8490 (4)	17
C(27)	5534 (5)	1216 (6)	7878 (5)	10
C(28)	4871 (6)	1573 (6)	8010 (6)	13
C(29)	4139 (6)	1776 (7)	7318 (6)	16
C(30)	4019 (6)	1537 (6)	6504 (6)	12
C(31)	4625 (6)	1064 (6)	6425 (6)	12
C(32)	5387 (6)	839 (7)	7079 (6)	16
C(33)	4894 (6)	1722 (6)	8888 (6)	13
C(34)	5179 (7)	857 (7)	9362 (6)	20
C(35)	4052 (7)	1902 (9)	8860 (7)	31
C(36)	5471 (7)	2454 (7)	9364 (6)	21
C(37)	3188 (6)	1781 (6)	5780 (6)	12
C(38)	3099 (7)	2763 (7)	5730 (7)	27
C(39)	2467 (7)	1372 (8)	5897 (7)	23
C(40)	3171 (6)	1458 (7)	4952 (6)	20
C(41)	6015 (6)	251 (7)	6956 (6)	16
C(42)	6215 (6)	−509 (7)	7578 (6)	16
C(43)	5662 (7)	−143 (7)	6080 (6)	21
C(44)	6808 (7)	702 (8)	7059 (7)	26
O(45)	8108 (4)	1982 (5)	8538 (4)	16
C(46)	8827 (7)	1403 (7)	8951 (7)	22
C(47)	9357 (8)	1548 (10)	8464 (9)	46
C(48)	9155 (8)	2386 (9)	8091 (8)	36
C(49)	8234 (7)	2480 (7)	7896 (7)	22

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

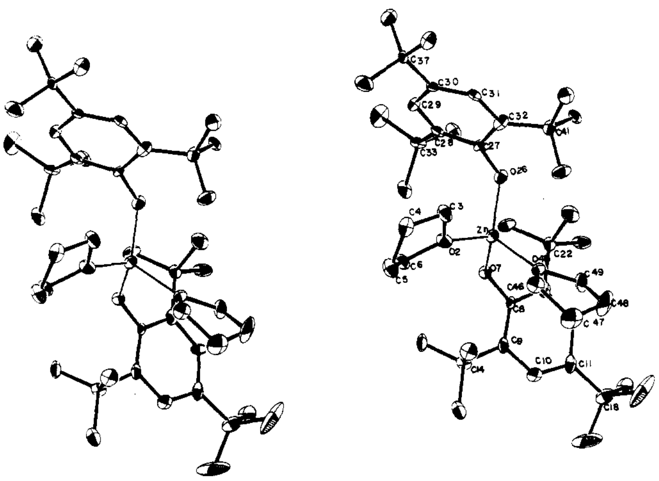


Figure 1. Stereoscopic ORTEP drawing of non-hydrogen atoms in $Zn(O\text{-}t\text{-}Bu_3H_2C_6)_2(THF)_2$.

---

(5) For general sample handling and data collection and processing methods, see: (a) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, D. C. *Inorg. Chem.* **1984**, *23*, 1021. The program library includes modifications of those of A. C. Larsen and J. A. Ibers.

(6) Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2046.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Zn(O\text{-}2,4,6\text{-}t\text{-}Bu_3H_2C_6)_2(THF)_2$

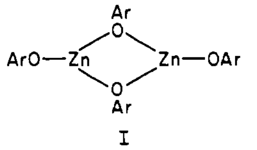
	Zn–O Distances		
Zn–O(2)	2.066 (7)	Zn–O(26)	1.889 (7)
Zn–O(7)	1.885 (6)	Zn–O(45)	2.088 (6)
	Distances within THF Ligands		
O(2)–C(3)	1.483 (12)	O(45)–C(46)	1.480 (12)
O(2)–C(6)	1.453 (13)	O(45)–C(49)	1.466 (12)
C(3)–C(4)	1.505 (16)	C(46)–C(47)	1.523 (17)
C(4)–C(5)	1.508 (16)	C(47)–C(48)	1.442 (20)
C(5)–C(6)	1.492 (16)	C(48)–C(49)	1.520 (16)
	Distances within Aryloxide Ligands		
O(7)–C(8)	1.354 (11)	O(26)–C(27)	1.361 (11)
C(8)–C(9)	1.382 (14)	C(27)–C(28)	1.396 (13)
C(8)–C(13)	1.428 (14)	C(27)–C(32)	1.452 (14)
C(9)–C(10)	1.415 (14)	C(28)–C(29)	1.402 (14)
C(9)–C(14)	1.570 (14)	C(28)–C(33)	1.555 (13)
C(10)–C(11)	1.393 (15)	C(29)–C(30)	1.416 (14)
C(11)–C(12)	1.378 (14)	C(30)–C(31)	1.351 (14)
C(11)–C(18)	1.537 (14)	C(30)–C(37)	1.546 (13)
C(12)–C(13)	1.422 (14)	C(31)–C(32)	1.410 (14)
C(13)–C(22)	1.522 (15)	C(32)–C(41)	1.519 (14)
C(14)–C(15)	1.516 (15)	C(33)–C(34)	1.559 (14)
C(14)–C(16)	1.524 (14)	C(33)–C(35)	1.488 (15)
C(14)–C(17)	1.525 (14)	C(33)–C(36)	1.531 (14)
C(18)–C(19)	1.510 (16)	C(37)–C(38)	1.540 (15)
C(18)–C(20)	1.501 (18)	C(37)–C(39)	1.509 (14)
C(18)–C(21)	1.548 (18)	C(37)–C(40)	1.537 (14)
C(22)–C(23)	1.571 (15)	C(41)–C(42)	1.557 (14)
C(22)–C(24)	1.547 (14)	C(41)–C(43)	1.540 (14)
C(22)–C(25)	1.509 (14)	C(41)–C(44)	1.506 (15)
	Angles		
O(2)–Zn(1)–O(7)	115.47 (28)	Zn(1)–O(2)–C(3)	121.2 (6)
O(2)–Zn(1)–O(26)	104.21 (28)	Zn(1)–O(2)–C(6)	130.6 (6)
O(2)–Zn(1)–O(45)	94.93 (27)	Zn(1)–O(7)–C(8)	133.3 (6)
O(7)–Zn(1)–O(26)	121.7 (3)	Zn(1)–O(26)–C(27)	126.4 (6)
O(7)–Zn(1)–O(45)	101.30 (27)	Zn(1)–O(45)–C(46)	122.0 (6)
O(26)–Zn(1)–O(45)	116.5 (3)	Zn(1)–O(45)–C(49)	128.5 (6)

indicative of one type of aryl group.

The above results speak for the high Lewis acidity of two-coordinate zinc, which in each case binds whatever basic center is available (Br or ZnOAr). We therefore attempted a halide-free route (eq 1), which simultaneously relies on the low basicity of

$$Zn[N(SiMe_3)_2]_2 + 2HOAr \xrightarrow[C_6H_6]{} Zn(OAr)_2 + HN(SiMe_3)_2 \qquad (1)$$

the eliminated amine. This reaction proceeds smoothly at 25 °C with no evidence of intermediates. The resulting $Zn(OAr)_2$ reveals, by ^1H NMR in C_6D_6, *two* types of aryl rings, for both the 2,6-di-*tert*-butylphenoxy and the 2,4,6-tri-*tert*-butylphenoxy (Ar′, synthesized as in eq 1) compounds. This we judge is due to aggregation to a stereochemically rigid dimer (I), driven again



I

by the demand of zinc to achieve coordination number 3 (or higher). This was confirmed for $[Zn(OAr')_2]_2$ by cryoscopic molecular weight determination in benzene. $[Zn(O\text{-}t\text{-}Bu_3H_2C_6)_2]_2$ is soluble in THF. Upon removal of THF with moderate heating, the resulting solid dissolves in C_6D_6 to give a ^1H NMR spectrum wholly consistent with the formulation $Zn(OAr')_2(THF)$; i.e., equivalent aryl rings and a single THF molecule per zinc. Of note is the fact that the THF β-CH_2 protons in this adduct experience a larger coordination chemical shift than do the α-CH_2 nuclei, due perhaps to aromatic ring currents.

Recrystallization of $Zn(OAr')_2(THF)$ by cooling a solution in hexane/THF yielded crystals shown by X-ray diffraction (see below) to be the bisadduct $Zn(OAr')_2(THF)_2$. This compound, when dissolved in C_6D_6, exhibits ^1H NMR chemical shifts for THF that lie exactly halfway between those of $Zn(OAr')_2(THF)$ and free THF. This evidence suggests that $Zn(OAr')_2(THF)_2$ has only a solid-state existence and that solutions in benzene furnish kinetically labile and coordinatively unsaturated $Zn(OAr')_2(THF)$, which accomplishes our goal of synthesizing a Lewis acidic, soluble, monomeric zinc bis(alkoxide).

Structure. $Zn(OAr')_2(THF)_2$ crystallizes as four-coordinate monomers of distorted-tetrahedral geometry. Angles between identical ligands are much larger for the aryl oxide (121.7 (3)°) than for the smaller THF (94.9 (3)°). The remaining four angles between OAr′ and THF are not equal (two at approximately 102°, two at 116°) but are complementary; they reveal some tendency for the planes Zn/O(7)/O(26) (aryloxide) and Zn/O(2)/O(45) (THF) to be skewed, not orthogonal. This distortion may be traced to repulsions between an *o*-*tert*-butyl group and a nearby THF. The Zn–O–C(aryl) angles (126–133°) are remarkably acute compared to those in early-transition-metal aryloxides,[7] suggesting reduced π donation from oxygen to zinc. The only smaller values (121–129°) are found in two-coordinate $M(OAr)_2$, M = Sn and Ge.[8] Bending at oxygen of course increases steric congestion between the aryl group and the THF ligands. Predictably, the rotational conformation about the Zn–O(aryl) bonds is such as to keep these groups far from each other.

The zinc–O(aryl) distances are equal within experimental error and are, to our knowledge, the shortest Zn–O bonds reported to date. The Zn–O(THF) distances are equal within experimental error and are a full 0.2 Å longer than those to aryloxide, consistent with the ready loss of THF in solution. The Zn–O(THF) distances (2.077 Å average) are quite comparable to those seen earlier[9] in $ZnCl_3(THF)^-$ (2.025 (3) and 2.121 (8) Å). Distances and angles within the aryl ring are unexceptional.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 83-05281). We thank Scott Horn for skilled technical assistance and Robert Tatz for a gift of chemicals.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom parameters, and intraligand angles (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, tables of calculated and observed structure factors (11 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

---

(7) Latesky, S. L.; McMuller, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, S. C. *Organometallics* **1985**, *1*, 902.

(8) Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

(9) Folting, K.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G.; Martin, J. L.; Smith, P. D. *Inorg. Chem.* **1984**, *23*, 4589 and references therein.