$\sum w(|F_0| - |F_c|)^2$) of the ruthenium atom in space group *Pnam* followed by a difference Fourier map revealed three peaks for the DMPE and PMe_3 phosphorus atoms. Isotropic refinement of these atoms followed by anisotropic refinement converged with $R_1 = 0.113$, $R_2 = 0.179$.[23] A difference Fourier map showed several peaks within bonding distance to phosphorus (1.7–1.9 Å), indicating disorder for the DMPE and PMe_3 carbons.

A group of six DMPE carbon atoms attached to P2 and P3 (three associated with each half of two separate DMPE ligands, conformation A) could be picked out as a contributor to one conformation from the difference Fourier map. Refinement of the six carbon atoms was carried out by first holding the position of each atom fixed with a population of 50% and varying only the isotropic thermal parameters. The positions were subsequently allowed to vary also. A difference Fourier map now showed a second conformation of the six DMPE carbons with the methylene bridges spanning P2 and P3 (conformation B). These six carbons were also introduced with populations of 50% and their thermal parameters refined. The positions were then also allowed to vary.

Next, the three carbon atoms attached to C1 were introduced and refined first isotropically and then anisotropically. The two independent DMPE conformations were refined anisotropically in separate groups, with the RuP_3 parameters varied as well. Alternate refinement of the P1 methyl group, DMPE conformation A, and DMPE conformation B ultimately gave $R_1 = 0.042$ and $R_2 = 0.066$. Distances and angles are given in Table I, positional parameters are in Table II, and an ORTEP drawing is shown in Figure 1.

X-ray Structural Determination of $Ru(DMPE)_2(CO)$ (2). Well-formed colorless crystals of **2** were prepared by slow diffusion of a layered hexane–ether solution of **2**. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 45°. Cell reduction with the program TRACER revealed only an orthorhombic crystal system. Data were collected on the crystal in accord with the parameters in Table VII. The Molecular Structure Corp. and Enraf-Nonius SDP programs were used for solution and refinement of the structure. The space group was determined to be *Pbca* on the basis of the systematic absences (0*kl*, *k* odd; *h*0*l*, *l* odd; *hk*0, *h* odd). Solution was accomplished with the direct-methods program MULTAN due to the large number of Ru–Ru vectors in the Patterson map. Least-squares refinement of one of the ruthenium atoms and three of the phosphorus atoms followed by a difference Fourier map revealed the remaining ruthenium and all phosphorus atoms. Subsequent difference Fourier maps and least-squares refinements showed all DMPE carbons and the CO ligand with no evidence for disorder. Anisotropic refinement of all non-hydrogen atoms with a non-Poisson weighting scheme ($p = 0.04$) coverged with $R_1 = 0.048$, $R_2 = 0.066$,[23] GOF = 2.15. Table IV contains relevant bond distances and angles for one of the two molecules, and Table V gives positional parameters.

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Registry No. **1**, 101519-28-2; **2**, 67409-67-0; $Ru(DMPE)_2(nap)H$, 24669-41-8; $Ru(DMPE)_2(CNCH_2CMe_3)$, 101519-29-3; PMe_3, 594-09-2; CO, 630-08-0.

Supplementary Material Available: A full ORTEP drawing of **1** and listings of anisotropic thermal parameters for **1** and **2** and bond distances and angles for **2** (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (52 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.

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(23) $R_1 = \{\sum||F_0| - |F_c||\}/\{\sum|F_0|\}$ and $R_2 = \{\sum w(|F_0| - |F_c|)^2\}^{1/2}/\{\sum wF_0^2\}$, where $w = \{\sigma^2(F_0) + [pF_0^2]^2\}^{1/2}$ for the non-Poisson-contribution weighting scheme or $w = 1$ for unit weights.

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A Binuclear Copper(II) Complex with a Bridging Thioether Ligand. Crystal and Molecular Structure of Dicopper Thiobis(ethylenenitrilo)tetraacetate Pentahydrate

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The copper(II) complex $Cu_2(TEDTA)\cdot 5H_2O$ (where TEDTA is the tetraanion of thiobis(ethylenenitrilo)tetraacetic acid) has been synthesized and its structure determined with use of X-ray diffraction methods. The crystals belong to the space group $P2_12_12_1$ with unit cell parameters $a = 9.646$ (4) Å, $b = 14.264$ (5) Å, $c = 14.724$ (5) Å, and $Z = 4$. The structure has been refined with use of full-matrix least squares to $R = 3.8\%$, $R_w = 4.7\%$. The crystal structure consists of binuclear units containing two independent Cu(II) ions, each in a tetragonally distorted octahedral environment. The thioether S atom bridges the Cu atoms. The crystal structure is held together by a combination of bridging carboxylate groups and an extended hydrogen-bond network.

Recent X-ray crystallographic studies of the blue copper proteins plastocyanin[1] and azurin[2] have revealed that the copper coordination sphere consists of a cysteinate sulfur, two nitrogens from histidine, and a thioether sulfur from methionine. Among the unanticipated features of this site is the strikingly long Cu–S(methionine) distance of 2.9 Å.[3] This Cu–S interaction is sufficiently long and weak that the sulfur atom makes a negligible contribution to the Cu extended X-ray absorption fine structure (EXAFS) even in single crystals of plastocyanin oriented so as to maximize its contribution.[4] These results have heightened the interest in Cu–thioether complexes as attempts to understand the electronic and reactivity properties of the blue copper site continue.

Recently, Peerce, Gray, and Anson reported on the coordination chemistry of the ligand thiobis(ethylenenitrilo)tetraacetic acid (TEDTA) with Cr(III).[5] They prepared two different isomers in aqueous solution and proposed mononuclear structures for them on the basis of their spectroscopic properties and reactivity. Here, we report the first structurally characterized complex of this ligand,

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0020-1669/86/1325-1800$01.50/0

Table I. Crystal Data and Structure Refinement

formula	$C_{12}H_{26}Cu_2N_2O_{13}S$ (M_r 565.49)
F_{000}	1160
a, Å	9.646 (4)
b, Å	14.264 (5)
c, Å	14.724 (5)
V, Å^3	2026 (2)
space group	$P2_12_12_1$
Z	4
abs coeff, cm^{-1}	23.5
transmission factors, %	39.6 (min), 55.5 (max)
scan range, deg	0.7 below Kα_1 to 0.7 above Kα_2
bkgd/scan time	0.25
data collected	$+h,\pm k,+l$, $3° < 2\theta < 40°$; $+h,+k,+l$, $40° < 2\theta < 60°$
unique data ($F_o^2 > 3\sigma(F_o^2)$)	2725
no. of variables	271
R, %	3.8
R_w, %	4.7
error in observn of unit wt, e	1.39

Cu_2(TEDTA)·$5H_2O$, a binuclear species with the thioether S atom bridging two Cu(II) ions.

Experimental Section

Thiobis(ethylenenitrilo)tetraacetic acid was a generous gift from R. Baar and Dr. F. Anson. All other chemicals were commercially available. Electronic spectra were recorded on a Cary 14 spectrophotometer. Microchemical analysis was performed at the microchemical laboratory of Stanford University.

Preparation of Cu_2(TEDTA)·$5H_2O$. TEDTA (176 mg, 0.5 mmol as the free acid) was added to 80 mL of deionized water. This mixture was heated to boiling, during which time the ligand completely dissolved. Cupric hydroxide (98 mg, 1.0 mmol) was added and the solution was gently boiled until the volume reached 8 mL. The solution was allowed to cool and evaporate until 2 mL remained and blue prismatic crystals had appeared. The crystals were collected by filtration to yield 267 mg of product (94%). The compound may be recrystallized from hot water. Anal. Calcd for $C_{12}H_{26}Cu_2N_2O_{13}S$: C, 25.49; H, 4.63; Cu, 22.5; N, 4.95; S, 5.67. Found: C, 25.20; H, 4.52; Cu, 22.0; N, 4.94; S, 5.60. The electronic spectrum in H_2O shows two bands at 242 nm (ϵ = 5800) and 741 nm (ϵ = 130). Extinction coefficients are in units of cm^{-1} M^{-1} per binuclear complex. Attempts to prepare mononuclear species by using a 1:1 stoichiometry led to the isolation of the above complex and unreacted ligand.

Collection and Reduction of X-ray Data. A crystal suitable for X-ray studies was selected from the reaction product. X-ray diffraction measurements were performed on a Syntex P2$_1$ four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation at 22–24 °C. Machine and crystal parameters are summarized in Table I. Fifteen machine-centered reflections with $15° < 2\theta < 20°$ were used in a least-squares refinement of the unit cell parameters and orientation matrix. Partial rotation photographs were taken to confirm the *mmm* diffraction symmetry. Several ω scans were recorded, and these had full widths at half-height of <0.25°, indicating suitable crystal mosaicity. The systematic absences $h00$ ($h \neq 2n$), $0k0$ ($k \neq 2n$), and $00l$ ($l \neq 2n$) are consistent only with the space group $P2_12_12_1$. Since this is a noncentric space group and Cu and S show significant anomalous scattering effects with Mo K$\bar{\alpha}$ radiation, reflections of the form $+h,\pm k,+l$ were collected for $3° < 2\theta < 40°$. For $40° < 2\theta < 60°$, only $+h,+k,+l$ reflections were collected. Three standard reflections, monitored every 60 reflections, showed no significant fluctuations.

All calculations were performed on a PDP 11/55 computer using the Enraf-Nonius structure determination package. The data were processed as described previously.[6] An analytical absorption correction was applied to the data. No extinction correction was applied. A total of 2725 reflections, including the Friedel pairs collected, with $F_o > 3\sigma(F_o)$ were used in the full-matrix least-squares refinement on F.

Table II. Positional Parameters for Non-Hydrogen Atoms

atom	x	y	z
Cu1	0.55442 (6)	0.75572 (4)	0.58131 (4)
Cu2	0.47493 (7)	0.47701 (4)	0.36185 (4)
S1	0.5224 (2)	0.57236 (9)	0.52743 (9)
O1	0.7321 (3)	0.7474 (3)	0.5125 (2)
O2	0.9559 (4)	0.7085 (2)	0.5302 (2)
O3	0.4141 (4)	0.7690 (2)	0.6741 (2)
O4	0.4006 (4)	0.8008 (3)	0.8223 (3)
O5	0.3217 (4)	0.5658 (2)	0.3590 (3)
O6	0.0949 (4)	0.5715 (3)	0.3795 (3)
O7	0.6040 (4)	0.3736 (2)	0.3756 (3)
O8	0.6008 (4)	0.2188 (3)	0.3949 (3)
OW1	0.6052 (4)	0.5500 (2)	0.2865 (3)
OW2	0.3748 (5)	0.4183 (3)	0.2225 (3)
OW3	0.6413 (4)	0.7286 (2)	0.3269 (3)
OW4	−0.1380 (5)	0.4741 (5)	0.4469 (3)
OW5	0.4874 (5)	0.0488 (3)	0.3870 (3)
N1	0.6659 (4)	0.7005 (3)	0.6839 (3)
N2	0.3480 (4)	0.3979 (3)	0.4369 (3)
C1	0.8151 (5)	0.7127 (4)	0.6614 (3)
C2	0.8346 (5)	0.7222 (3)	0.5589 (3)
C3	0.6202 (5)	0.7566 (4)	0.7639 (3)
C4	0.4661 (5)	0.7781 (4)	0.7557 (4)
C5	0.6323 (6)	0.6005 (4)	0.6999 (4)
C6	0.6451 (6)	0.5404 (4)	0.6152 (4)
C7	0.3668 (6)	0.4113 (4)	0.5367 (4)
C8	0.3688 (6)	0.5111 (4)	0.5675 (4)
C9	0.2070 (6)	0.4255 (4)	0.4078 (4)
C10	0.2058 (6)	0.5295 (4)	0.3805 (4)
C11	0.3873 (6)	0.3003 (4)	0.4125 (4)
C12	0.5447 (6)	0.2950 (4)	0.3936 (4)

Table III. Selected Bond Distances (Å) and Angles (deg)

Cu1–S1	2.750 (1)	Cu2–S1	2.829 (1)
Cu1–N1	2.015 (4)	Cu2–N2	1.998 (4)
Cu1–O1	1.994 (5)	Cu2–O5	1.948 (3)
Cu1–O3	1.932 (3)	Cu2–O7	1.941 (3)
Cu1–O2′	1.965 (3)	Cu2–OW1	1.973 (3)
Cu1–O6′	2.561 (4)	Cu2–OW2	2.418 (4)
S1–C6	1.810 (5)	S1–C8	1.819 (5)
S1–Cu1–N1	84.51 (11)	S1–Cu2–N2	83.94 (12)
S1–Cu1–O1	83.89 (11)	S1–Cu2–O5	80.13 (12)
S1–Cu1–O3	102.62 (11)	S1–Cu2–O7	99.86 (11)
S1–Cu1–O2′	87.23 (10)	S1–Cu2–OW1	97.35 (11)
S1–Cu1–O6′	175.68 (10)	S1–Cu2–OW2	164.29 (11)
N1–Cu1–O1	84.21 (14)	N2–Cu2–O5	85.09 (15)
N1–Cu1–O3	83.22 (15)	N2–Cu2–O7	84.59 (14)
N1–Cu1–O2′	170.56 (15)	N2–Cu2–OW1	177.40 (15)
N1–Cu1–O6′	97.23 (14)	N2–Cu2–OW2	91.65 (15)
O1–Cu1–O3	165.20 (13)	O5–Cu2–O7	169.62 (14)
O1–Cu1–O2′	90.38 (13)	O5–Cu2–OW1	97.35 (15)
O1–Cu1–O6′	92.33 (14)	O5–Cu2–OW2	84.49 (15)
O3–Cu1–O2′	103.09 (14)	O7–Cu2–OW1	92.95 (14)
O3–Cu1–O6′	81.54 (14)	O7–Cu2–OW2	94.70 (15)
O2′–Cu1–O6′	90.70 (13)	OW1–Cu2–OW2	87.69 (14)
Cu1–S1–Cu2	136.38 (5)	C6–S1–C8	100.37 (25)

Structure Solution and Refinement. The coordinates of the two Cu atoms were determined from a three-dimensional Patterson map. All remaining non-hydrogen atoms were located from difference Fourier maps. At this point, the structure was refined isotropically to convergence. Because of the noncentric nature of the space group, these coordinates were inverted and the structure was again refined. A comparison of the agreement factors combined with inspection of the individual Friedel pairs indicated that the second choice of coordinates corresponded to the proper enantiomorph. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions for the ligand were calculated by assuming tetrahedral geometries and C–H distances of 0.98 Å. Hydrogen atoms on the water molecules were located from a difference Fourier map. For two of the water molecules (OW1 and OW3) two sets of hydrogens were located and the multiplicity factors for these atoms were set to 0.5. The hydrogen atoms were included as fixed contributors in the final least-squares refinement cycles with temperature factors set to 5 and 6 Å^2 for the ligand and water hydrogens, respectively. A final difference Fourier map showed no peak larger than 15% of the height of a carbon atom peak. The final agreement factors are given in Table I. Other results tabulated are positional parameters for non-hydrogen atoms (Table II), selected bond distances and angles (Table III), anisotropic thermal parameters (Table IV), positional parameters for hydrogen atoms (Table V), additional bond distances and angles (Table VI), and values of F_o and F_c (Table VII). The last four tables are

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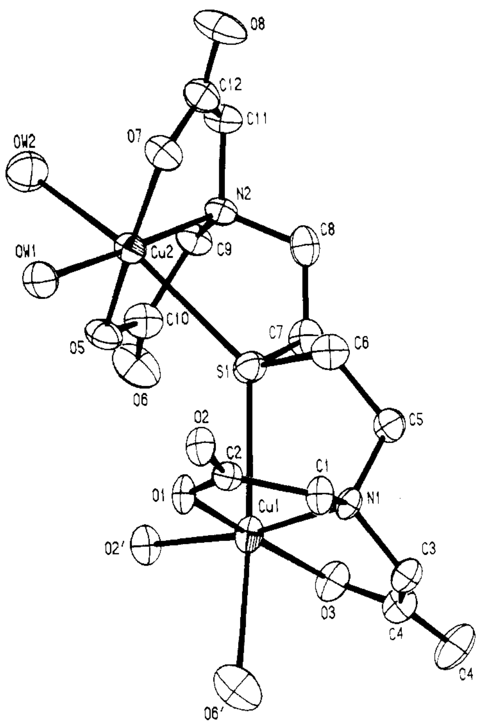

Figure 1. One binuclear unit from the crystal structure of Cu_2(TEDTA)·$5H_2O$ showing the atomic numbering scheme. The ORTEP drawing shows 50% probability ellipsoids.

available as supplementary material.

Results and Discussion

The asymmetric unit consists of one TEDTA ligand, two Cu atoms, and five water molecules. The structure of one dimeric unit is shown in Figure 1. The two Cu atoms are in slightly different tetragonally distorted octahedral environments. In each case, three of the equatorial donor atoms are the nitrogen and two carboxylate oxygens from one arm of the TEDTA ligand. For Cu1, the remaining equatorial site is occupied by a carboxylate oxygen bridging from a neighboring molecule, whereas for Cu2 this position is filled by a water molecule. For each Cu, the bridging thioether S atom lies in one axial site. The remaining axial ligand is a bridging carboxylate and a water for Cu1 and Cu2, respectively. Bond distances and angles around the Cu(II) ions are given in Table III.

The most interesting structural feature of the complex is the bridging thioether group. A number of thioether complexes of Cu(II)[7-30] and Cu(I)[12,19,23,24,26,28,30-40] have now been structurally characterized, although this appears to be the first example of a thioether group bridging between two Cu(II) ions. The Cu(II) complexes generally exhibit distorted-octahedral or five-coordinate structures with Cu–S distances for equatorial thioether ligands ranging from 2.297 to 2.488 Å and those for axial thioethers ranging from 2.560 to 2.919 Å. The Cu(I) complexes favor lower coordination numbers with a range of Cu–thioether distances of 2.230–2.469 Å. Thus, the Cu–S distances in the present structure of 2.750 (1) and 2.829 (1) Å are fairly typical of thioether coordinated axially to Cu(II). The Cu–O[29,41] and Cu–N[15,25] distances are quite typical of similar structures and will not be discussed further. The Cu1–S–Cu2 angle of 136.38 (5)° is somewhat larger than the Cu–S–Cu angle of 118.6° in $[(C_2H_5)_2S]_3[Cu_4I_4]$,[34] in which a diethyl sulfide molecule bridges two Cu_4I_4 cubane clusters. Such angles vary quite widely and are easily affected by other structural influences. One additional structural comparison deserves comment. A binuclear complex of Cu(II) and oxidized glutathione has recently been characterized.[41] Each Cu atom shows distorted-square-pyramidal coordination with the apical position occupied by one S from a bridging disulfide group. The Cu–S distances of 3.16 (1) and 3.28 (1) Å are significantly longer than in the TEDTA complex.

The crystal structure is held together by two types of interactions. First, there are two bridging carboxylate groups per asymmetric unit. The Cu–Cu distances across these bridges are 5.387 (1) and 5.629 (1) Å compared to 5.180 (1) Å across the thioether bridge. Second, there is an extended hydrogen bond network involving the water molecules and the carboxylate oxygens. The O···O distances across these hydrogen bonds range from 2.633 to 2.945 Å. The apparent O–H···O angles range from 139 to 175°.

The synthesis and characterization of Cu_2(TEDTA)·$5H_2O$ provides the first complex of this potentially useful ligand with unambigously known structure. Moreover, the structure determination demonstrates the binucleating capability of this ligand, which must be considered in the assignment of structure to other TEDTA complexes. Finally, an example of a new type of Cu-

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

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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.

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Soluble Zinc Bis(aryloxides)

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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_2CH$_3$, 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]

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