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A Trimeric, Chair-Shaped Zinc Dialkylphosphine Complex: Synthesis and Structure of $\{[Zn(Et)(\mu\text{-}PCy_2)]_3{\cdot}THF\}{\cdot}2THF$ [Cy = Cyclohexyl (C_6H_{11})]

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Summary: Metalation of dicyclohexylphosphine (Cy_2PH) with $ZnEt_2$ (1:1 equiv) in THF gives a trimeric zinc dialkylphosphine complex $\{[Zn(Et)(\mu\text{-}PCy_2)]_3{\cdot}THF\}{\cdot}2THF$ (1), which has been characterized by elemental analyses, ^1H NMR, ^{31}P NMR, and IR spectroscopic data and by a low temperature X-ray structural study. The complex crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with cell dimensions $a = 13.059(3)$ Å, $b = 13.889(3)$ Å, $c = 18.635(3)$ Å, $\alpha = 75.98(3)°$, $\beta = 85.45(3)°$, $\gamma = 64.37(3)°$, $V = 2955.4(11)$ Å^3, and $Z = 2$. The complex has a chair-shaped Zn_3P_3 core in which only one tetrahedral Zn center is coordinated by THF and the other two planar Zn centers are three coordinate. Two uncoordinated THF molecules reside in the lattice of 1. The title compound is a rare example of a zinc dialkyl- or diarylphosphine complex and the first such trimeric complex.

Introduction

We have recently become interested in the syntheses and structures of compounds at the boundary between transition metals (group 12; Zn–Hg) and the p block metals (group 13, Al–Tl). The $[Zn(Et)(\mu\text{-}N(H)(naphthyl)){\cdot}THF]_3$ (naphthyl = $C_{10}H_7$) complex, which was the first structurally characterized trimeric amido Zn compound, was shown by us to have a chair-shaped Zn_3N_3 core in which the acidic H atoms adopt an all cis conformation.[1] This orientation contrasts with that in the analogous dimeric Al complex $[Me_2AlN(H)(naphthyl)]_2$ where trans H atoms are found in the Al_2N_2 ring.[1]

Our interest in group 12 phosphide complexes has been stimulated both by the absence of much structural work in this area[2,3] and by the possible applications of some of these complexes as precursors for 2/5 semiconductors.[4] The scarcity of structurally characterized group 12 phosphide complexes, especially the dialkyl- and diarylphosphide derivatives, has been due to the general difficulty in obtaining crystalline materials suitable for X-ray analysis. In this context, in an early detailed study of the metalation reactions of R_2PH (R = Ph and Bu^t) in benzene by Noltes only polymeric powders identified as "$Zn[PR_2]_2$" could be obtained.[5] To date there have only been two Zn–phosphide complexes characterized in the solid state; the dimeric $\{Zn[P(SiMe_3)_2][\mu\text{-}P(SiMe_3)_2]\}_2$,[3] in which bulky disilylphosphide ligands are present, and the tetrameric Zn dialkylphosphide–hydroxide complex $[Zn_2(PBu^t_2)_2(OH)(\mu\text{-}OH)]_2$,[2] which was crystallized only by virtue of adventitious hydrolysis from the reaction of $LiP(Bu^t)_2$ with $ZnCl_2$ in toluene. Recently, Cowley and Jones have synthesized the trimeric $[MeCd(\mu\text{-}PBu^t_2)]_3$ complex from the exchange reaction of $Ga(PBu^t_2)_3$ with Me_2Cd.[6] This was the first Cd–diorganophosphide complex to be structurally characterized and has a twist-boat-shaped Cd_3P_3 core geometry. We report the synthesis and structure of $[Zn(Et)(\mu\text{-}PCy_2]_3{\cdot}THF]{\cdot}2THF$ [Cy = cyclohexyl (C_6H_{11})] (1), the first trimeric zinc phosphide and the first mixed organometallic Zn phosphide complex to be structurally characterized. The complex contains a chair-shaped Zn_3P_3 core in which only one pseudotetrahedral Zn center is coordinated by THF and the other two centers are trigonal planar.

Results and Discussion

Complex 1 is synthesized by the metalation reaction of Cy_2PH with $ZnEt_2$ (1:1 or 2:1 equiv, respectively) in THF.[7] Cooling of the resulting solution to −35 °C gives crystals of 1. It is isolated in ca. 50% yield as a colorless viscous oil at +25 °C. The complex is extremely air- and moisture-sensitive, and the THF solvation is highly labile. Placing 1 under prolonged vacuum (0.1 atm, 10–20 min) liberates almost all the THF of solvation and converts the initial oil into a white powder. However, careful isolation of 1, which was transferred for immediate investigations to the glovebox without evacuation of the sample, allowed reproducible analytical and NMR work to be obtained which is in accord with the X-ray data for the complex.

The ^1H NMR spectrum of 1 (benzene-d_6, 250 MHz) is dominated by cyclohexyl groups which appear as a collection of overlapping multiplets (66H, δ 2.1–1.1). The Zn-attached and lattice-bound THF molecules are not separated at +25 °C presumably because they are rapidly exchanging at this temperature. One THF resonance is distinct from the cyclohexyl region (12H, δ 3.54), and the other similarly sharp resonance can be picked out among

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(7) **Health and Safety Warning**: $ZnEt_2$ is a pyrophoric material and ignites violently in air if used neat. This material should be handled under nitrogen or argon using a vacuum line and a glovebox. Cy_2PH is highly toxic and should always be used in a fume cupboard under nitrogen or Ar, as exposure even to vapor can cause nauseous headaches.

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Table I. Crystal Data and Details of Measurements for {[Zn(Et)(μ-PCy$_2$)]$_3$·THF}·2THF (1)[a]

empirical formula	$C_{54}H_{105}O_3P_3Zn_3$
M	1091.27
cryst size (mm)	0.41 × 0.38 × 0.32
system	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	13.059(3)
b (Å)	13.889(3)
c (Å)	18.635(4)
α (deg)	75.98(3)
β (deg)	85.45(3)
γ (deg)	64.37(3)
V (Å^3)	2955.4(11)
Z	2
F(000)	1144
λ(Mo Kα) (Å)	0.710 73
μ(Mo Kα) (mm^{-1})	1.325
θ range (deg)	3.53–22.50
index range	$-14 \le h \le 14$, $-14 \le k \le 14$, $0 \le l \le 20$
no. of reflns collcd	7964
no. of ind reflns	7682 (R_{int} = 0.012)
abs corr	ψ-scans
refinement method	full-matrix least squares on F^2
GOF on F^2	0.879
R values [$I > 2\sigma(I)$][b]	R_1 = 0.050, R_{w2} = 0.152
R values (all data)[b]	R_1 = 0.061, R_{w1} = 0.185
largest diff peak and hole (e Å^{-3})	1.816 to –0.907

[a] Data collection at 153(2) K. [b] $R_1 = \sum|F_o - F_c|/\sum F_o$ and $R_{w2} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$, G. M. Sheldrick, SHELXL-92, Göttingen, 1992.

the cyclohexyl multiplets whose signals are significantly broader (12H, δ 1.37). The Zn-attached Et groups of 1 are observed only as a poorly resolved triplet (9H, δ 2.26, $-CH_3$) and quartet (6H, δ 0.93, $-CH_2-$). The methylene proton resonance is particularly broad. Overall, the appearance of the ^{1}H NMR spectrum of the complex, particularly the broadness of the cyclohexyl and Et resonances and the fact that the separate environments present in the solid-state structure of 1 could not be separated, implies that a large amount of molecular motion is present in such solutions of 1 at ambient temperature. The same conclusion can be reached from the ^{31}P NMR spectrum of 1 (benzene-d_6, 100.3 MHz) in which only a singlet is observed at room temperature.

The X-ray structure of the complex was determined at low temperature (153 K). When the crystals were mounted at –40 °C directly from solution using perfluorcarbon oil,[8] solvent loss was prevented and the crystallinity of the complex was sustained during data collection. Details of the X-ray structural refinement are given in Table I, and Table II lists the atomic coordinates and isotropic and thermal parameters. Selected bond lengths and angles for 1 are shown in Table III.

The X-ray crystallographic study of 1 shows it to be a trimeric complex in the solid state, {[Zn(Et)(μ-PCy$_2$)]$_3$·THF}·2THF (Figure 1). The complex has a chair-shaped Zn_3P_3 core in which there is a symmetrical pattern of long and short Zn–P bonds [Zn(1)–P(1,2), Zn(2,3)–P(3) (long) average 2.407(2) Å, and Zn(3)–P(1), Zn(2)–P(2) (short) average 2.373(2) Å] (Figure 2). These Zn–P distances are similar to those observed for the μ_2-P phosphide ligands in the solid-state structures of {Zn[P(SiMe$_3$)$_2$][μ-P(SiMe$_3$)$_2$]}$_2$ [2.419(1)–2.421(1) Å][3] and [Zn$_2$(PBu$^t_2$)(OH)(μ-OH)$_2$]$_2$ (2.368(4)–2.428(2) Å).[2] Interestingly, in 1 only one Zn is solvated by THF and has a pseudotetrahedral geometry [average angles around Zn(1) 102.6°]. The remaining two (unsolvated) Zn centers have almost identical trigonal planar geometries [sum of the three angles about Zn(2) and Zn(3) average 359.8°]. Although the core geometry of 1 is similar to that observed in [Zn(Et)(μ-N(H)(naphthyl))·THF]$_3$,[1] the ring angles at Zn and P are both greater than the corresponding angles in the latter [average P–Zn–P 108.2(1)°, average Zn–P–Zn 118.6(1)° in 1; cf. N–Zn–N 99.7(3)°, Zn–N–Zn 103.7(3)° in [Zn-

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å × 10^3) for {[Zn(Et)(μ-PCy$_2$)]$_3$·THF}·2THF (1)[a]

	x	y	z	U(eq)
Zn(1)	2012(1)	6308(1)	8808(1)	29(1)
Zn(2)	390(1)	7981(1)	6821(1)	25(1)
Zn(3)	1563(1)	9524(1)	7991(1)	26(1)
P(1)	2620(1)	7738(1)	8735(1)	24(1)
P(2)	1639(1)	6280(1)	7567(1)	23(1)
P(3)	1079(1)	9325(1)	6836(1)	24(1)
O(1)	177(4)	7361(4)	9041(2)	44(1)
C(1)	3168(9)	3957(7)	9542(5)	101(4)
C(2)	2389(9)	4979(6)	9652(4)	70(3)
C(3)	–2037(6)	8320(8)	6710(5)	78(3)
C(4)	–1051(5)	8418(5)	6271(4)	44(2)
C(5)	1607(7)	11038(6)	8904(4)	57(2)
C(6)	1256(6)	10976(5)	8178(3)	41(2)
C(7)	–460(8)	7018(7)	9640(4)	67(2)
C(8)	–1656(9)	7635(13)	9404(7)	118(5)
C(9)	–1713(7)	8660(9)	8892(8)	102(4)
C(10)	–563(6)	8397(6)	8589(4)	57(2)
C(11)	2751(5)	7914(5)	9683(3)	28(1)
C(12)	3537(5)	6871(5)	10231(3)	36(1)
C(13)	3587(6)	7089(6)	10991(3)	43(2)
C(14)	2404(6)	7575(6)	11297(4)	51(2)
C(15)	1613(6)	8610(6)	10758(4)	48(2)
C(16)	1558(5)	8386(5)	10001(3)	38(1)
C(21)	4056(5)	7378(4)	8317(3)	27(1)
C(22)	4622(5)	8092(5)	8452(3)	32(1)
C(23)	5720(5)	7890(5)	8028(3)	37(1)
C(24)	6546(5)	6675(5)	8214(4)	39(2)
C(25)	5984(5)	5968(5)	8074(4)	40(2)
C(26)	4895(5)	6154(4)	8513(3)	31(1)
C(31)	1139(5)	5180(4)	7655(3)	27(1)
C(32)	110(5)	5416(5)	8167(3)	32(1)
C(33)	–302(6)	4522(5)	8300(3)	41(2)
C(34)	–605(6)	4370(6)	7575(4)	46(2)
C(35)	400(6)	4134(6)	7068(4)	48(2)
C(36)	827(5)	5027(5)	6930(3)	37(1)
C(41)	3018(4)	5832(4)	7078(3)	25(1)
C(42)	2916(5)	6076(5)	6234(3)	31(1)
C(43)	4079(5)	5756(5)	5886(3)	42(2)
C(44)	4859(5)	4560(6)	6197(4)	45(2)
C(45)	4981(5)	4315(5)	7031(3)	37(1)
C(46)	3822(5)	4627(5)	7386(3)	33(1)
C(51)	–28(5)	10678(4)	6321(3)	29(1)
C(52)	323(5)	11623(5)	6119(4)	37(1)
C(53)	–662(5)	12688(5)	5746(4)	46(2)
C(54)	–1679(6)	12966(5)	6219(5)	57(2)
C(55)	–2062(5)	12045(5)	6423(4)	49(2)
C(56)	–1094(5)	10967(5)	6798(4)	38(1)
C(61)	2405(5)	8991(4)	6282(3)	27(1)
C(62)	3162(5)	9531(5)	6426(3)	31(1)
C(63)	4252(5)	9151(6)	5995(3)	41(2)
C(64)	3996(6)	9398(6)	5169(3)	44(2)
C(65)	3255(5)	8872(5)	5020(3)	38(1)
C(66)	2155(5)	9212(5)	5451(3)	32(1)
O(2)	–3476(14)	6313(13)	5159(9)	216(6)
C(70)	–2784(15)	6170(14)	4535(10)	143(5)
C(71)	–1840(25)	6401(23)	4732(17)	247(12)
C(72)	–1753(21)	6385(20)	5473(15)	217(10)
C(73)	–2901(14)	6325(13)	5822(9)	138(5)
O(3)	5044(21)	1323(18)	6809(13)	289(9)
C(80)	3862(24)	1678(21)	7007(16)	222(10)
C(81)	4018(22)	1587(20)	7810(15)	210(9)
C(82)	5086(27)	1290(22)	8094(16)	231(11)
C(83)	5792(25)	1074(23)	7487(18)	239(11)

[a] *U(eq) is defined as one-third of the trace of the orthogonalized* $\mathbf{U}_{ij}$ tensor.

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(Et)(μ-N(H)(naphthyl)).·THF]$_3$]. Additionally, all the Zn-attached ethyl groups of 1 assume an equatorial conformation with respect to the core. This can be compared with an all axial conformation for these groups in [Zn(Et)(μ-N(H)(naphthyl))·THF]$_3$].[1] This conformational difference and the aforementioned angular expansions in the core of 1 can be attributed largely to the differences in the conformational and steric requirements of the ligands as well as to the different heteroatoms (N and P) involved.[1]

Table III. Selected Bond Lengths and Angles for {[Zn(Et)(μ-PCy$_2$)]$_3$·THF}·2THF (1)

	Distances, Å		
Zn(1)–P(1)	2.410(2)	Zn(1)–C(2)	2.013(7)
Zn(1)–P(2)	2.414(2)	Zn(2)–C(4)	1.995(6)
Zn(2)–P(2)	2.368(2)	Zn(3)–C(6)	1.992(6)
Zn(3)–P(1)	2.378(2)	Zn(1)–O(1)	2.275(4)
Zn(2)–P(3)	2.404(2)	P–C(Cy)	1.872(5)–1.882(5)
Zn(3)–P(3)	2.401(2)		
	Angles, deg		
P(1)–Zn(1)–P(2)	108.34(6)	C(2)–Zn(1)–O(1)	101.2(3)
P(1)–Zn(3)–P(3)	107.95(6)	C(2)–Zn(1)–P(1)	125.1(2)
P(2)–Zn(2)–P(3)	108.33(6)	C(2)–Zn(1)–P(2)	121.7(2)
Zn(1)–P(1)–Zn(3)	119.97(6)	C(4)–Zn(2)–P(2)	131.4(2)
Zn(1)–P(2)–Zn(2)	115.81(6)	C(4)–Zn(2)–P(3)	120.2(2)
Zn(2)–P(3)–Zn(3)	120.09(6)	C(6)–Zn(3)–P(1)	128.9(2)
O(1)–Zn(1)–P(1)	94.2(1)	C(6)–Zn(3)–P(3)	122.7(2)
O(1)–Zn(1)–P(2)	95.9(1)	av about P(1,2,3)	107.5

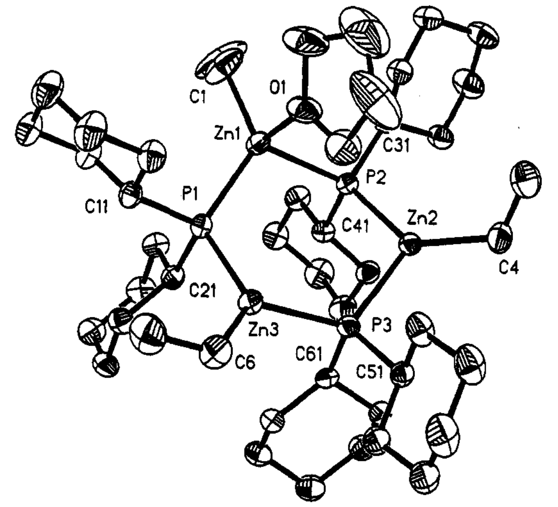

Figure 1. ORTEP drawing of 1 in the asymmetric unit. Thermal ellipsoids at the 50% level are shown. All hydrogen atoms are omitted for clarity.

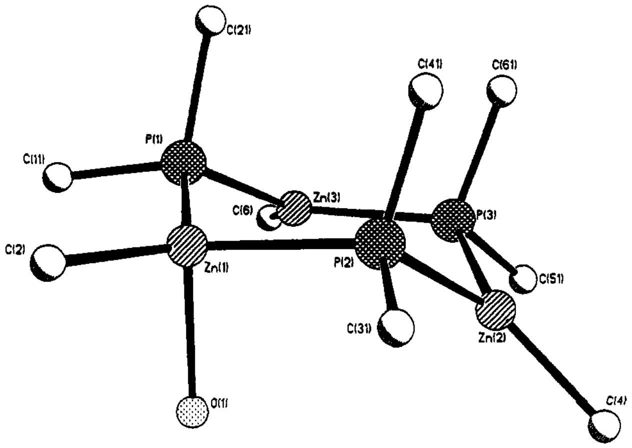

Figure 2. Core Zn_3P_3 ring structure of 1.

Presumably, steric factors are responsible for the unusual molecular stoichiometry of 1, the steric bulk of the cyclohexyl groups precluding solvation of two of the Zn ions. In this context it is interesting to note that there are two lattice-bound THF molecules per formula unit of 1 so that overall, by relation to [Zn(Et)(μ-N(H)(naphthyl))·THF]$_3$],[1] the complex has the anticipated (THF:Zn) stoichiometry. The steric crowding in the core of 1 further manifests itself both in the way in which the lone axial Zn-attached THF ligand is distorted toward the center of the Zn_3P_3 ring, away from the neighboring equatorial cyclohexyl groups attached to P(1) and P(2), and in the relatively long Zn(1)–O(1) THF bond [2.275(4) Å: cf. 2.195(8) Å in [Zn(Et)(μ-N(H)(naphthyl))·THF]$_3$[1]].

As mentioned previously, only two other structurally characterized Zn phosphide complexes have been reported.[2,3] The only other complex containing dialkylphosphide ligands is that of the tetrameric Zn phosphide–hydroxide complex $[Zn_2(PBu^t{}_2)_2(OH)(\mu\text{-}OH)]_2$.[2] In this complex, which was prepared by the reaction of $ZnCl_2$ and $LiP(Bu^t)_2$ in which adventitious entry of water allows crystallization of the product, as in 1 both planar and tetrahedral Zn geometries are observed. In this previous work it was noted that the parent Zn phosphide complex (without hydroxide inclusion) could not be isolated. It appears in general that the difficulty in obtaining crystalline materials, at least where simple dialkyl- and diarylphosphines are concerned, has been a significant factor limiting progress in the area of Zn–phosphides. In this context, the facile synthesis of crystalline 1 is worthy of note. Complex 1 is the first trimeric dialkyl- or diarylphosphide complex and the first mixed organometallic Zn phosphide to be characterized in the solid state.

Tetranuclear clusters and cages are by far the most commonly occurring structural types for Zn complexes in general.[9] In the few structurally characterized trimeric complexes, planar Zn_3X_3 rings (X = O, S) are most common where bulky organic groups restrict the core geometry and prevent Lewis base solvation.[10] As can be concluded from the structure of [Zn(Et)(μ-N(H)(naphthyl))·THF]$_3$[1] and now from that of 1, where less bulky groups are present and where Lewis base solvation can consequently occur, this planar core geometry is disrupted by solvation and nonplanar rings result.

Experimental Section

All the starting materials ($ZnEt_2$, Cy_2PH) and the product (1) are air- and moisture-sensitive. They were handled on a vacuum line using standard inert atmosphere techniques and under dry/O_2 free Ar.[11] The THF solvent was dried using Na/benzophenone, and hexane was dried by prolonged distillation over Na wire. Both solvents were degassed with Ar prior to their use in reactions. Complex 1 was isolated and characterized with the aid of an argon filled glovebox (Faircrest Mark 4A) fitted with an O_2 and

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H_2O recirculation system (Type B) and equipped with an O_2 and a moisture meter (reading ca. 5–10 vppm for both when in use). IR spectra were recorded as Nujol mulls using NaCl windows and were run on a Perkin-Elmer FT2400 spectrophotometer which allowed fast collection. Elemental analyses were performed by first sealing samples in preweighed airtight aluminum boats (1–2 mg). C, H, and N analyses were performed using a Perkin-Elmer 240 elemental analyzer, and P was analyzed by spectrophotometric means. Samples for P analysis were boiled in phosphoric acid prior to the formation of the blue phosphomolybdate complex. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC 250-MHz spectrometer. For ^1H samples, benzene-d_6 was used as the internal standard (C_6D_5H, δ 7.16). For ^{31}P NMR spectra, an external standard of P in Me_3P (TMP) in benzene was employed. Thin walled Wilmad 528PP NMR tubes with airtight Teflon screw-cap septa were used throughout.

Synthesis of {[Zn(Et)(μ-PCy$_2$)]$_3$·THF}·2THF (1). $ZnEt_2$ (2.0 mL, 1.0 mol L^{-1} in hexanes solution, 2.0 mmol) was added to a stirred solution of Cy_2PH (0.22 mL, 2.0 mmol) in 10 mL of THF.[7] No apparent reaction occurred, but removal of the volatiles *in vacuo*, followed by the addition of 6 mL of hexane, resulted in a white solid precipitate. This redissolved with the addition of 2 mL of THF. Cooling the colorless solution to −35 °C gave highly air-sensitive crystals of 1 in ca. 50% yield (1.0–1.1 g). A 2:1 reaction of Cy_2PH to $ZnEt_2$ also produced 1, as proved unequivocally by the determination of the cell dimensions of the crystalline product of this reaction at low temperature. Mp: the complex is a viscous oil at +25 °C. Anal. Calc: C, 59.5; H, 9.6; P, 8.5. Found: C, 58.9; H, 9.5; P, 9.5. ^1H NMR (benzene-d_6, +25 °C, 250 MHz): δ 3.54 (m, 12H, THF), 2.26 (t, 9H, CH_3– of Et–Zn), 1.37 (m, 12H, THF), 2.1–1.1 (collection of overlapping mult, 66H, Cy), 0.93 (q, 6H, $-CH_2-$ of Et–Zn). ^{31}P NMR (benzene-d_6, +25 °C, 100.3 MHz): δ 176.4 (s).

X-ray Structure Determinations of 1. Crystals of 1 were mounted directly from solution at −40 °C under Ar using a perfluorocarbon oil which protects them from atmospheric O_2 and moisture. The oil "freezes" at reduced temperatures and holds the crystals static in the X-ray beam.[8] Data were collected on a Siemans-Stoe AED diffractometer, and a semiempirical absorption correction based on ψ-scans was employed. Details of the structure solution and refinement of 1 are shown in Table I. Atomic coordinates and isotropic thermal perameters are shown in Table II, and Table III gives selected bond lengths and angles for 1. The structure was solved by direct methods (SHELX Tl PLUS) and refined by full-matrix least squares on F^2 (SHELXL-92). Atomic coordinates, bond lengths and angles, and thermal parameters for 1 have been deposited with the Cambridge Crystallographic Data Centre.

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Supplementary Material Available: Tables of structure determination data, atomic coordinates, bond lengths, bond angles, and displacement parameters for 1 (9 pages). Ordering information is given on any current masthead page.

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