7.01–6.75 (m, 20 H, phenyl), 1.60–1.45 (m, 6 H, $CH_2CH_2CH_2$). ^{13}C NMR (CD_2Cl_2): δ 136.1 (C_{ipso}), 130.7 (C_{ortho}), 127.8 (C_{meta}), 127.0 (C_{para}), 114.5 (m, PhC:), 103.8 (m, P_2C), 35.9 (m, $CH_2\mathit{C}H_2CH_2$), 25.7 (m, $\mathit{C}H_2CH_2\mathit{C}H_2$).

X-ray Structure Determination for 9. Crystals of **9**, $C_{33}H_{26}FeP_4\cdot{}^1/_2C_6H_6$, were grown at room temperature from a benzene/methanol solution of the compound. Data were collected at 20 ± 1 °C on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf-Nonius supplied SDP package. The compound crystallizes in space group $P2_1/c$, with $a = 18.913$ (1) Å, $b = 11.362$ (1) Å, $c = 29.621$ (3) Å, $\beta = 106.49$ (1)°, $V = 6103.55$ (1.8) Å^3, $Z = 8$, $d_{calc} = 1.396$ g/cm^3, $\lambda = 0.71073$ Å (Mo Kα radiation with a graphite monochromator), $\mu = 7.2$ cm^{-1}, and $F(000)$ 2648. A total of 10728 unique reflections were recorded in the range $2° \leq 2\theta \leq 50.0°$ of which 8287 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 2441 for the solution and refinement (due to the small size of the crystal, a large number of reflections were unobservable; hence, there is a poor ratio of observed reflections to refined parameters). The structure was solved by direct methods, yielding a solution for the iron and phosphorus atoms. The hydrogen atoms were included as a fixed contribution in the final stages of least-squares refinement while anisotropic temperature factors were used for all other atoms except C7, corresponding to C44 in the second molecule. This atom is librating between the two possible conformations of the aliphatic chain and can only be refined at the average position listed in the tables of supplementary material. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.045$, $R_w = 0.056$, and GOF = 1.13.

Registry No. **1**, 136911-21-2; **2a**, 136911-22-3; *trans*-**2a**, 136983-85-2; *trans*-**2b**, 136911-23-4; **3a**, 136911-24-5; *trans*-**3a**, 136983-86-3; *trans*-**3b**, 136911-25-6; **4a**, 136911-26-7; *trans*-**4a**, 136983-87-4; *trans*-**4b**, 136911-27-8; **5a**, 136911-28-9; *trans*-**5a**, 136983-88-5; *trans*-**5b**, 136911-29-0; **6b**, 136911-30-3; *trans*-**6b**, 136983-89-6; **6c**, 136911-31-4; *trans*-**6c**, 136983-90-9; **7b**, 136911-32-5; **8**, 136911-36-9; **9**, 136946-97-9; **9**$\cdot{}^1/_2C_6H_6$, 136946-98-0; Me_2SiCl_2, 75-78-5; PhCOCl, 98-88-4; $PhCH_2COCl$, 103-80-0; PhCH=CHCOCl, 102-92-1; $ClCOCO_2Et$, 4755-77-5; $ClCOC_6H_4$-*o*-COCl, 88-95-9; $ClCO(CH_2)_3COCl$, 2873-74-7; $[(p\text{-xylene})_2Fe][PF_6]_2$, 103123-09-7; *trans*-1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphete, 96693-28-6; lithium 2,4,5-triphenyl-1*H*-1,3-diphosphole, 136911-33-6; lithium 2-benzyl-4,5-diphenyl-1*H*-1,3-diphosphole, 136911-34-7; lithium 2-styryl-4,5-diphenyl-1*H*-1,3-diphosphole, 136911-35-8.

Supplementary Material Available: Tables of crystallographic details, least-squares planes and dihedral angles, positional and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (19 pages); a table of structure factors (13 pages). Ordering information is given on any current masthead page.

Transition-Metal-Containing Inorganic Ring Systems: Synthesis and X-ray Crystal Structure of the First Cyclozincadisilatriazane

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Summary: Reaction of $ZnCl_2$ with $MeN(Me_2SiNEtLi)_2$ results in the formation of the first stable six-membered Si_2N_3Zn metallacycle. Spectral and X-ray crystal structure studies of this compound, crystallized from toluene–pyridine mixtures, indicate the molecule to be dimeric in nature with the formula $[MeN(Me_2SiNEt)_2Zn\cdot py]_2$ (py = pyridine). The Zn atom is tetrahedrally coordinated, and pyridine and three of the nitrogens bonded to ethyl groups are involved in the coordination.

Recent developments in inorganic heterocyclic chemistry include syntheses of novel Zn–O and Zn–S heterocycles.[1] In contrast, studies on cyclic metal amides of Zn have been quite limited.[2] In their contributions to the silazane chemistry, Bürger and co-workers have also reported on the synthesis of a few group 4 and 5 transition-metal-containing cyclic silylamides. These include six-membered Si–N rings of Ti,[3] Zr,[4] and V,[5] which have been characterized by various spectral techniques. X-ray crystal structure studies on four-membered Ti, Zr,[6] Hf, V, and Nb[7] cyclic silylamides and for the five-membered $TiSi_2N_2$[8] ring system have also been reported, many of them being spirocyclic in nature. In continuation of our contributions in syntheses of novel transition-metal-containing inorganic ring systems,[9] we report herein the synthesis and X-ray structure of the first example of a six-membered Si_2N_3Zn ring system.

Experimental Section

All manipulations were performed under an atmosphere of dry oxygen-free nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and distilled in an inert atmosphere prior to use.

Infrared spectra were obtained with Bio-Rad FTS 7 spectrophotometer as Nujol mulls. Proton, carbon-13, and silicon-29 NMR spectra were recorded on Bruker WP80SY and 250M spectrometers. Chemical shifts are reported in δ units downfield from tetramethylsilane with the solvent as the reference signal. C_6D_6 was used for room-temperature measurements, while toluene-d_8 was used at low temperatures. Mass spectra were recorded on Finnigan MAT system 8230, and microanalysis was carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry of the University of Göttingen.

Preparation of 4. A 0.88-g (3.8 mmol) sample of $MeN(Me_2SiNEtH)_2$ prepared by the literature method,[10] taken in 10 mL of hexane was treated with 3.2 mL of of an *n*-butyllithium solution (2.36 M in hexane). After warming for a short period,

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(1) Power, P. P. *J. Organomet. Chem.* **1990**, *400*, 49.

(2) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid amides*; Ellis Horwood Limited: Chichester, U.K., 1980; p 545.

(3) (a) Bürger, H.; Wiegel, K. *J. Organomet. Chem.* **1977**, *124*, 279. (b) Brauer, D. J.; Bürger, H.; Wiegel, K. *J. Organomet. Chem.* **1978**, *150*, 215.

(4) Bürger, H.; Wiegel, K. *Z. Anorg. Allg. Chem.* **1976**, *426*, 301.

(5) Wiegel, K.; Bürger, H. *J. Organomet. Chem.* **1977**, *129*, 309.

(6) (a) Brauer, D. J.; Bürger, H.; Essig, E.; Geschwandtner, W. *J. Organomet. Chem.* **1980**, *190*, 343. (b) Beiersdorf, W. D.; Brauer, D. J.; Bürger, H. *Z. Anorg. Allg. Chem.* **1981**, *475*, 56.

(7) Brauer, D. J.; Bürger, H.; Liewald, G. R.; Wilke, J. *J. Organomet. Chem.* **1986**, *310*, 317.

(8) Bürger, H.; Wiegel, K.; Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1975**, *87*, 301.

(9) (a) Roesky, H. W. *Synlett* **1990**, *11*, 651. (b) Roesky, H. W. In *Rings, Clusters and Polymers of Main Group and Transition Elements*; Roesky, H. W., Ed.; Elsevier: Amsterdam, 1989; p 369.

(10) Wannagat, U.; Braun, R. *Monatsh. Chem.* **1969**, *100*, 1910.

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Table I. Crystal Data for $[MeN(Me_2SiNEt)_2Zn\bullet py]_2$

formula	$C_{28}H_{60}N_8Si_4Zn_2$
mol wt	751.9
cryst syst	monoclinic
space group	$P2_1/n$
cell constants	
a, Å	9.646 (1)
b, Å	10.540 (2)
c, Å	19.471 (4)
β, deg	99.16 (1)
vol, Å^3	1954.3 (6)
formula/cell Z	2
calc dens ρ, Mg m^{-3}	1.28
abs coeff $\mu_{Mo\ K\alpha}$, mm^{-1}	1.406
STOE four-circle diffractometer (AED2 Rev. 6.2), Mo Kα	
T, K	293
profile	fitted $2\theta,\omega$ scans
cryst size, mm^3	$0.4 \times 0.8 \times 0.8$
abs corr by azimuthal scans	
transm$_{min-max}$	0.24–0.31
$2\theta_{max}$, deg	45
no. of measured reflns	3563
no. of unique reflns	2558
R_{int}	0.018
with $\vert F_0\vert > 3\sigma(\vert F_0\vert)$	
no. of obsd refls m	2299
no. of refined params n	210
goodness of fit	
$[\sum w(\vert F_0\vert - \vert F_c\vert)^2/(m-n)]^{1/2}$	1.95
$R = \sum\Vert F_0\vert - \vert F_c\Vert/\sum\vert F_0\vert$	0.039
$R_wR_g = [\sum w(\vert F_0\vert - \vert F_c\vert)^2/\sum w\vert F_0\vert^2]^{1/2}$	0.054
weighting scheme	
$w^{-1} = [\sigma^2(\vert F_0\vert) + 0.0004\vert F_0\vert^2]$	
largest diff peak, e Å^{-3}	0.3
largest diff hole, e Å^{-3}	-0.3

it was brought to room temperature and transferred to a dropping funnel. This solution was added dropwise to an ice-cooled solution of $ZnCl_2$, 0.52 g (3.8 mmol), in 10 mL of THF. After stirring for 6 h at room temperature, all solvents were removed in vacuo, the residue was extracted in 20 mL of toluene, and the solution was filtered over a thin Celite column. The solution was treated with 2.5 mL of pyridine, upon which it turned bright yellow. The mixture was then cooled at 4 °C for 48 h, and with slight disturbance to induce crystallization, pale yellow octahedral-shaped crystals were obtained, 0.91 g (64%). Mp: 89 °C. Anal. Calcd for $C_{28}H_{60}N_8Si_4Zn_2$: C, 44.7; H, 8.0; N, 14.9. Found: C, 44.2; H, 8.3; N, 14.5. IR (KBr/Nujol; ν, cm^{-1}): 1606 (m), 1243 (s), 1152 (m), 1104 (m), 1039 (vs), 933 (m), 908 (s), 875 (vs), 818 (s), 792 (s), 764 (s), 703 (m). EI-MS: m/z 79 (100%), 189 (20%), 295 (1.5%), 590 (0.5%). FI-MS: m/z 79 (100%), 189, 295, 590. ^{1}H NMR (C_6D_6, room temperature, 80 MHz): δ 0.40 (s, Me_2Si), 1.23 (t, C–CH_3), 2.70 (s, N–CH_3), 3.17 (q, N–CH_2), 6.6–8.6 (m, C_5H_5N). ^{13}C NMR (C_6D_6, room temperature, 62.90 MHz): δ 2.26 (s, Me_2Si), 23.80 (s, C–CH_3), 32.04 (s, N–CH_3), 42.25 (s, N–CH_2), 137.40 (s, py C), 124.49 (s, py C), 150.05 (s, py C). ^{29}Si NMR (C_6D_6, room temperature, 49.69 MHz): δ 0.60 (s, Me_2Si).

Crystallography. An octahedral-shaped pale yellow crystal of 4 obtained as described above, was sealed in a nitrogen-filled capillary with fluorinated grease and mounted on a Stoe AED 2 four-circle diffractometer. Crystallographic programs used for structure solution and refinement were of SHELXTL PLUS.[11] The structure was solved using heavy atoms and was refined by full-matrix least-squares method. A riding model was used for the hydrogen atoms with fixed isotropic U. Crystallographic data for compound 4 are given in Table I. Table II lists the positional parameters, and Table III, selected bond distances and bond angles for compound 4.

Results and Discussion

Slow addition of $MeN(Me_2SiNEtLi)_2$ to a solution of $ZnCl_2$ in tetrahydrofuran followed by removal of LiCl by filtration and recrystallization of the residue from toluene–pyridine solutions produces pale yellow crystals of $[MeN(Me_2SiNEt)_2Zn{\cdot}py]_2$ (4) (Scheme I).

The compound which melts to dark brown at 89 °C is moderately stable in hydrocarbon solvents at room temperature but decomposes immediately in halogenated solvents, turning dark brown. The electron impact and field ionization mass spectra for compound 4 gave peaks for the monomeric six-membered Si–N–Zn ring system at m/z 295. Also interesting is the peak at m/z 590, which can be attributed to the dimeric species without the pyr-

Table II. Positional Parameters ($\times10^4$, Esd's in Parentheses) for $[MeN(Me_2SiNEt)_2Zn\bullet py]_2$

	x	y	z	U(eq)[a]
Zn(1)	-16 (1)	1110 (1)	4606 (1)	51 (1)
N(1)	761 (4)	1604 (3)	3785 (2)	65 (1)
Si(1)	1250 (1)	479 (1)	3259 (1)	68 (1)
N(2)	496 (4)	-969 (3)	3426 (2)	66 (1)
Si(2)	-1140 (1)	-1233 (1)	3669 (1)	63 (1)
N(3)	-1196 (3)	-567 (3)	4478 (2)	50 (1)
C(3)	3212 (5)	263 (7)	3374 (3)	107 (3)
C(4)	733 (5)	891 (5)	2312 (2)	87 (2)
C(5)	998 (7)	-2017 (5)	3010 (3)	105 (3)
C(7)	-1441 (6)	-2986 (5)	3671 (3)	104 (2)
C(8)	-2548 (5)	-540 (7)	3004 (2)	102 (2)
C(9)	-2639 (4)	-315 (4)	4638 (2)	64 (1)
C(10)	-3588 (5)	-1449 (5)	4659 (3)	90 (2)
N(11)	-1620 (3)	2471 (3)	4640 (2)	64 (1)
C(12)	-2267 (5)	2874 (5)	4023 (3)	88 (2)
C(13)	-3464 (7)	3564 (6)	3943 (3)	124 (3)
C(14)	-4065 (8)	3840 (7)	4500 (4)	143 (4)
C(15)	-3419 (7)	3468 (6)	5143 (3)	124 (3)
C(16)	-2195 (5)	2758 (5)	5197 (3)	83 (2)
C(1)	1166 (27)	2859 (9)	3567 (9)	143 (9)
C(1′)	1461 (25)	2835 (12)	3890 (9)	122 (11)[b]
C(2)	1316 (17)	3847 (13)	4101 (7)	150 (9)
C(2′)	979 (23)	3792 (25)	3363 (10)	146 (11)[b]

[a] Equivalent isotropic U (Å$^2 \times 10^3$) are defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Disordered positions with occupancy 0.56.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[MeN(Me_2SiNEt)_2Zn\bullet py]_2$

Zn(1)–N(1)	1.940 (4)	Zn(1)–N(3)	2.095 (3)
Zn(1)–N(11)	2.119 (3)	Zn(1)–Zn(1A)	2.796 (1)
Zn(1)–N(3A)	2.053 (3)	N(1)–Si(1)	1.684 (4)
N(1)–C(1)	1.462 (13)	N(1)–C(1′)	1.462 (16)
Si(1)–N(2)	1.744 (4)	Si(1)–C(3)	1.884 (5)
Si(1)–C(4)	1.881 (5)	N(2)–Si(2)	1.740 (4)
N(2)–C(5)	1.495 (7)	Si(2)–N(3)	1.733 (3)
Si(2)–C(7)	1.871 (5)	Si(2)–C(8)	1.869 (5)
N(3)–C(9)	1.497 (5)	N(3)–Zn(1A)	2.053 (3)
C(9)–C(10)	1.510 (6)	N(11)–C(12)	1.333 (6)
N(11)–C(16)	1.329 (6)	C(12)–C(13)	1.352 (8)
C(13)–C(14)	1.342 (12)	C(14)–C(15)	1.364 (10)
C(15)–C(16)	1.388 (8)	C(1)–C(2)	1.461 (19)

N(1)–Zn(1)–N(3)	113.8 (1)	N(1)–Zn(1)–N(11)	102.9 (1)
N(3)–Zn(1)–N(11)	100.9 (1)	N(1)–Zn(1)–N(3A)	123.3 (1)
N(3)–Zn(1)–N(3A)	95.2 (1)	N(11)–Zn(1)–N(3A)	118.6 (1)
Zn(1)–N(1)–Si(1)	119.6 (2)	Zn(1)–N(1)–C(1)	129.7 (8)
Si(1)–N(1)–C(1)	110.3 (8)	N(1)–Si(1)–N(2)	109.7 (2)
N(1)–Si(1)–C(3)	112.7 (2)	N(2)–Si(1)–C(3)	108.3 (2)
N(1)–Si(1)–C(4)	112.2 (2)	N(2)–Si(1)–C(4)	109.4 (2)
C(3)–Si(1)–C(4)	104.5 (2)	Si(1)–N(2)–Si(2)	127.9 (2)
Si(1)–N(2)–C(5)	111.4 (3)	Si(2)–N(2)–C(5)	114.5 (3)
N(2)–Si(2)–N(3)	110.1 (2)	N(2)–Si(2)–C(7)	107.8 (2)
N(3)–Si(2)–C(7)	111.7 (2)	N(2)–Si(2)–C(8)	109.8 (2)
N(3)–Si(2)–C(8)	110.3 (2)	C(7)–Si(2)–C(8)	107.0 (3)
Zn(1)–N(3)–Si(2)	110.7 (2)	Zn(1)–N(3)–C(9)	109.4 (2)
Si(2)–N(3)–C(9)	115.2 (2)	Zn(1)–N(3)–Zn(1A)	84.8 (1)
Si(2)–N(3)–Zn(1A)	125.5 (2)	C(9)–N(3)–Zn(1A)	106.8 (2)
N(3)–C(9)–C(10)	116.9 (4)	Zn(1)–N(11)–C(12)	115.2 (3)
Zn(1)–N(11)–C(16)	125.6 (3)	C(12)–N(11)–C(16)	117.9 (4)
N(11)–C(12)–C(13)	122.9 (5)	C(12)–C(13)–C(14)	119.6 (6)
C(13)–C(14)–C(15)	119.1 (7)	C(14)–C(15)–C(16)	118.9 (6)
N(11)–C(16)–C(15)	121.5 (5)	N(1)–C(1)–C(2)	116.0 (13)

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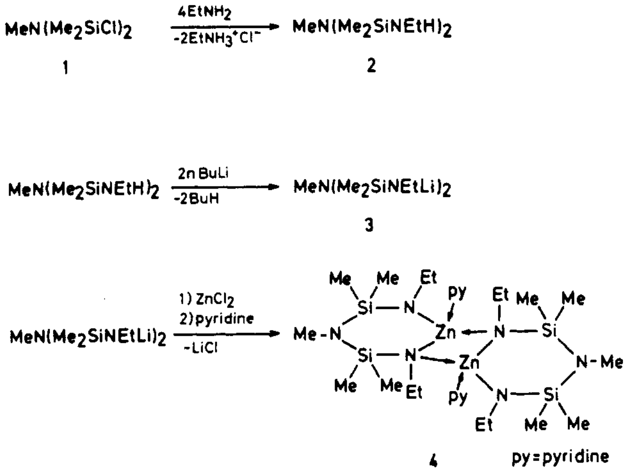
(11) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

Scheme I



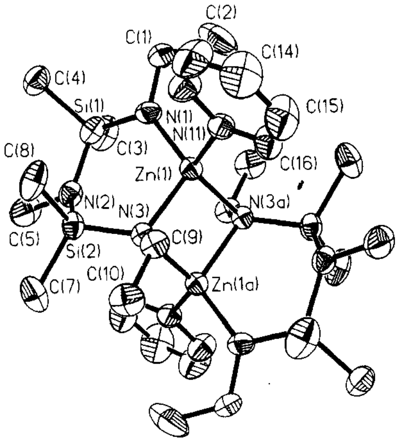


Figure 1. Thermal ellipsoid diagram of $[MeN(Me_2SiNEt)_2Zn{\cdot}py]_2$ (50% probability).

idine molecules. The base peaks in both cases corresponded to pyridine.

The X-ray crystal structure (Figure 1) as well as the spectral studies on compound 4 indicate similarities as well as interesting differences with alumadisilatriazane $[MeN(Me_2SiNMe)_2AlCl]_2$[12] and the diazadisilaberyllacyclohexane $[CH_2(Me_2SiNMe)_2Be]_2$,[13] both being dimers with one ring nitrogen involved in coordination with the main-group metal atom of the other ring system. Also similar is the unusual shortening of the Zn–N bond distance involving the noncoordinating ethyl-substituted nitrogen compared to the Zn–N bond involving the coordinating nitrogen atom (Δ = 0.155 Å) (Table III). As in the Be compound the latter is even longer than the bond distance between the zinc and the coordinating nitrogen atom from the other heterocycle [Zn(1)–N(3a)].

The NMR spectral studies on $[MeN(Me_2SiNEt]_2Zn{\cdot}py]_2$ at different temperatures showed interesting variations. Spectral studies reported on alumadisilatriazane[12] and diazadisilaberyllacyclohexane[13] provides evidence for the existence of the rigid dimeric species in solution at room temperature. In contrast, room-temperature spectral studies on 4 tend to indicate that the compound exists more or less as a monomeric species in solution. This is evidenced by the observation of a broad singlet at δ 0.60 ppm in the ^{29}Si NMR spectrum of 4, while for the alumadisilatriazane two separate peaks at δ 4.0 and 11.6 ppm have been reported. This is also supported by the room-temperature ^{13}C and ^{1}H NMR data (see Experimental Section). On cooling of the solutions to subzero temperatures, separate peaks identifiable for the dimeric species were observed.

Similar to alumadisilatriazane,[12] four sharp singlets at δ 0.34, 0.46, 0.55, and 0.60 ppm for the Me_2Si group were observed in the proton NMR spectra at −30 °C for 4. These were found to coalesce to a broad singlet above 0 °C. The triplet due to the methyl groups on the $N{-}CH_2CH_3$ moiety as well as the multiplet due to the $N{-}CH_2$ groups were also found to separate out to two different groups at −30 °C. ^{13}C NMR spectra, which showed broad singlets for Me_2Si group and methyl group of the $N{-}CH_2CH_3$ moiety at room temperature, were found to show four separate singlets at δ 0.52, 1.20, 1.99, and 4.86 (Me_2Si) and two sharp singlets (Me) at δ 21.68 and 23.79 ppm, respectively, at −30 °C. The sharp singlet for the NCH_2 carbon observed at δ 42.25 ppm at room temperature separated out to two peaks at δ 42.74 and 43.30 ppm at −30 °C.

These low-temperature observations are in good agreement with the room-temperature spectral data reported for the alumadisilatriazane dimer.[12] Similarly, −30 °C ^{29}Si NMR spectra of 4 also showed two separate peaks at δ −1.43 and 3.60 ppm for the dimeric species in solution. All these data indicate that at subzero temperatures formation of a rigid dimeric species in solution is favored for 4, which tends to become monomeric at room temperature. An attempt to obtain a solution-phase molecular weight of the compound was however unsuccessful due to the very high air and moisture sensitivity of the compound.

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Registry No. 2, 25206-33-1; 4, 137203-37-3; $ZnCl_2$, 7646-85-7.

Supplementary Material Available: Tables of crystal structure data, atomic coordinates, thermal parameters, and bond lengths and angles (5 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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[12] Wannagat, U.; Blumenthal, T.; Brauer, D. J.; Bürger, H. *J. Organomet. Chem.* **1983**, *249*, 33.

[13] Brauer, D. J.; Bürger, H. *J. Organomet. Chem.* **1979**, *170*, 161.