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Polyhedral Members of the $Mg_{2n}P_{2m}$ Family Derived from Dimeric Magnesium Trialkylsilylphosphandiide

Matthias Westerhausen,* Mathias Krofta, Peter Mayer, Marcus Warchhold, and Heinrich Nöth

Department Chemie, Ludwig-Maximilians-Universität, Butenandtstrasse 9 (Haus D),
D-81377 München, Germany

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The magnesiation of tri(*tert*-butyl)silylphosphane in THF yields tetrameric (tetrahydrofuran-*O*)magnesium tri(*tert*-butyl)silylphosphandiide **1**. The central moiety is a slightly distorted Mg_4P_4 cube with tetracoordinate magnesium and phosphorus atoms. The reaction of dibutylmagnesium with $H_2PSi^tBu_3$ in toluene gives tetramagnesium tetrakis[μ-tri(*tert*-butyl)silylphosphanide] bis[μ_4-tri(*tert*-butyl)silylphosphandiide] **2**. The central fragment is a Mg_4P_2 octahedron with the phosphorus atoms in a trans position. The $Mg\cdots Mg$ edges are bridged by the phosphanide substituents. Crystallographic data of **1**: $C_{68}H_{148}Mg_4O_5P_4Si_4$, monoclinic, $P2_1/c$, $a = 13.454(1)$ Å, $b = 26.123(1)$ Å, $c = 24.539(2)$ Å, $\beta = 96.53(1)°$, $Z = 4$; crystallographic data of **2**: $C_{72}H_{166}Mg_4P_6Si_6$, monoclinic, $P2_1/n$, $a = 13.951(1)$ Å, $b = 14.269(1)$ Å, $c = 24.209(2)$ Å, $\beta = 102.415(1)°$, $Z = 2$.

Introduction

Geminal dianions of the alkali and alkaline earth metals are widely used within organic synthetic chemistry;[1] however, the isolation of these metalorganic compounds is usually avoided due to their sensitivity to moisture and air. In this context, the structural characterization of the geminal bis-Grignard reagent $(Me_3Si)_2C[Mg(THF)_2Br]_2$ earns special attention in the field of carbodianions.[2] The synthesis of twice-metalated amines leads very often to insoluble and badly characterized substances. The breakthrough occurred in 1994 by Power and co-workers,[3] who prepared hexameric and solvent-free magnesium phenylimide. The wide variety of reactions was shown thereafter.[4] A heteroleptic bromide containing magnesium imide with a Mg_6N_4 adamantane-like structure was isolated by the same research group.[5] Due to the diagonal relationship and similar electronegativities, the CH fragment and a phosphorus atom are interchangeable. Therefore, the phosphandiides gained the interest of several research groups. Very often the trialkylsilyl substituted lithium phosphandiides and arsandiides are oxygen centered due to the inclusion of Li_2O.[6,7] Driess and co-workers[8] also observed during the formation of $(^iPr_3Si-E)_{10}Li_{16}$ ($E = P$, As) that the lithiation of $H_2E-Si^iPr_3$ can be accompanied by a reduction and the evolution of hydrogen gas. Homoleptic phosphandiides are structurally well-known for magnesium tri(*tert*-butyl)silylphosphandiide, which precipitated as a hexameric molecule with a central slightly distorted hexagonal Mg_6P_6 prism.[9] The magnesiation of triisopropylsilylphosphane in THF yielded tetrameric (tetrahydrofuran)magnesium triisopropylsilylphosphandiide with a Mg_4P_4 cube as the central structural motif.[10] To the phosphandiides of the heavier alkaline earth metals additional molecules of metal bis(phosphanides) are coordinated.[11,12] Similar reactions were observed if the trialkylsilyl substituent was less demanding.[10] Phosphandiides of less positive metals such as tin(II)[13,14] and the mixed-valent indium(II)/indium(lI) complex[15] were published recently.

Results and Discussion

Preparation. To ensure solubility of the phosphandiides in common organic solvents, sterically demanding trialkylsilyl substituents are necessary to shield the $Mg_{2n}P_{2m}$ core. Therefore, we magnesiated tri(*tert*-butyl)silylphosphane[16] with commercially available dibutylmagnesium in toluene and THF. As mentioned above, the 1:1 stoichiometry yields hexameric

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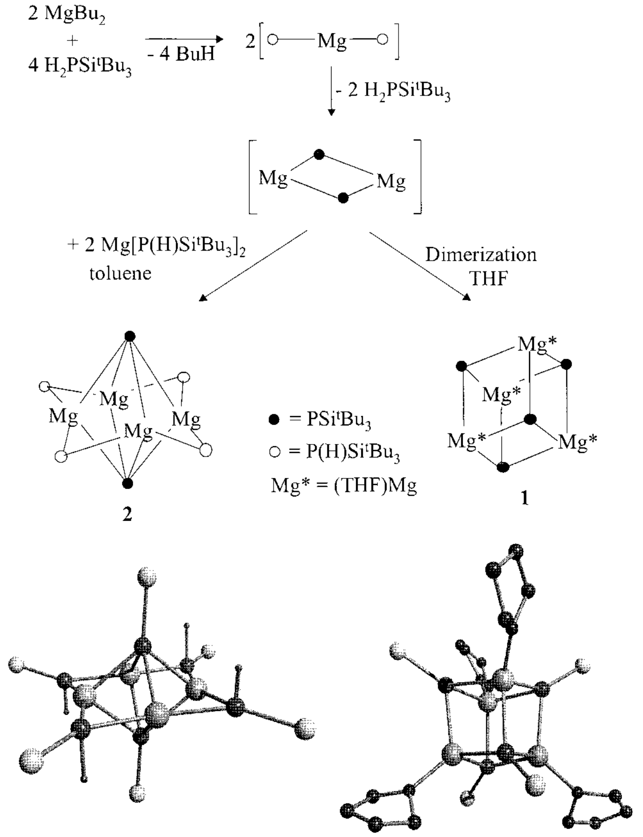
10.1021/ic000038c CCC: $19.00

Scheme 1. Synthesis of **1** and **2** by Magnesiation of Tri(*tert*-butyl)silylphosphane in THF and Toluene, Respectively[a]



[a] The bottom row shows the $Mg_{2n}P_{2m}$ polyhedra under neglect of the *tert*-butyl groups at the silicon atoms.

magnesium tri(*tert*-butyl)silylphosphandiide in the absence of coordinating coligands.[9] However, if this reaction is performed in a THF solution, tetrameric (tetrahydrofuran-*O*)magnesium tri(*tert*-butyl)silylphosphandiide **1** with a slightly distorted cubelike Mg_4P_4 unit is isolated. In this molecule the magnesium as well as the phosphorus atoms are four-coordinate.

The synthesis of the dimer $[MgPSiR_3]_2$ has not been successful yet, because the sterically most demanding tri(*tert*-butyl)silyl substituent leads to a hexamer. The enhancement of the intramolecular strain by binding of neutral coligands such as THF to the metal centers leads to a tetramerization of (THF)-$MgPSiR_3$ (R = ^iPr,[10] ^tBu) instead of the formation of a hexamer as described for solvent-free $[MgPSi^tBu_3]_6$.[9] The variation of the stoichiometric ratio of dibutylmagnesium and trialkylsilylphosphane between 1:2 (magnesium bis(phosphanides)) and 2:2 (magnesium phosphandiides) gives different oligomeric molecules with a $Mg_{2n}P_{2m}$ backbone of both phosphanide and phosphandiide ligands. The central $Mg_{2n}P_{2m}$ polyhedra known thus far can be derived from dimeric (cube) or trimeric Mg_2P_2 cycles (hexagonal prism) where opposite four-membered Mg_2P_2 planes can be capped by $Mg[P(H)SiR_3]_2$ molecules thus forming polyhedra with the general formula of $Mg_{2n}P_{2n+2}$. However, a capped monocyclic Mg_2P_2 unit is unknown so far. According to Scheme 1, the magnesiation of $H_2PSi^tBu_3$ in toluene leads to a quantitative formation of tetrakismagnesium tetrakis[μ-tri(*tert*-butyl)silylphosphanide] bis[μ_4-tri(*tert*-butyl)silylphosphandiide] **2**. When the toluene solution of **2** is heated under reflux the elimination of tri(*tert*-butyl)silylphosphane and the precipitation of the well-known[9] hexameric $MgPSi^tBu_3$ are observed. The inner core of **2** can be regarded as a Mg_4P_2 octahedron with the P atoms in a trans position. The Mg···Mg edges are bridged by phosphanide ligands. The ^2J(p,p) coupling constant amounts 70 Hz, whereas the ^1J(P,H) coupling constant amounts 220 Hz. The ^2J(p,p) coupling is in the expected order of magnitude[17] whereas the ^1J(P,H) value seems to be rather high.

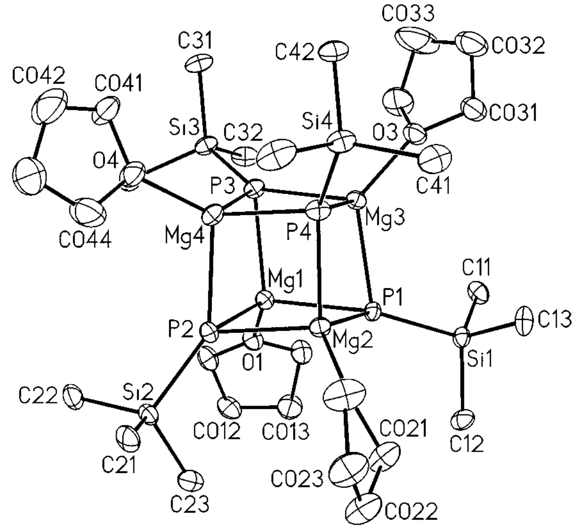


Figure 1. Molecular structure and numbering scheme of **1**. The hydrogen atoms and the methyl groups are omitted for clarity. The ellipsoids represent a 40% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **1**

	n = 1	*n* = 2	*n* = 3	*n* = 4
Mg(*n*)−P1	2.591(1)	2.570(2)	2.586(2)	
Mg(*n*)−P2	2.552(2)	2.578(2)		2.582(2)
Mg(*n*)−P3	2.583(2)		2.583(2)	2.559(2)
Mg(*n*)−P4		2.564(2)	2.550(2)	2.562(2)
P(*n*)−Si(*n*)	2.223(1)	2.221(1)	2.215(1)	2.211(1)
Mg(*n*)−O(*n*)	2.095(3)	2.078(3)	2.088(3)	2.075(3)
Mg(*n*)−P1−Sil	144.48(6)	129.75(5)	117.28(5)	
Mg(*n*)−P2−Si2	125.26(6)	123.30(6)		142.96(6)
Mg(*n*)−P3−Si3	118.41(5)		146.87(6)	125.38(6)
Mg(*n*)−P4−Si4		141.02(6)	125.81(6)	123.91(6)
P(*n*)−Mg1−O1	111.93(9)	123.12(9)	122.10(9)	
P(*n*)−Mg2−O2	122.1(1),	118.2(1)		118.23(9)
P(*n*)−Mg3−O3	123.17(9)		111.92(9)	122.65(9)
P(*n*)−Mg4−O4		115.6(1)	124.9(1)	118.4(1)

Molecular Structures

Molecular Structure of 1. Figure 1 shows the molecular structure and the numbering scheme of **1**. The methyl groups are neglected for clarity. The central moiety is a slightly distorted Mg_4P_4 cube with distorted tetrahedrally coordinated magnesium and phosphorus atoms. In Table 1 the structural data is summarized. The Mg−P bond lengths vary between 2.55 and 2.59 Å. The rhomboid distortion of the Mg_2P_2 planes of the Mg_4P_4 heterocubane structure leads to PMgP as well as MgPMg bond angles of approximately 98° and 82°, respectively. The intramolecular strain between the THF ligands and the tri(*tert*-butyl)silyl substituents enforces strongly different MgPSi angles (Table 1). A similar observation was reported for the tetrameric $[(THF)MgPSi^iPr_3]_4$. The Mg−O distances lie in the same range as in the sterically loaded bis(tetrahydrofuran-*O*)magnesium bis[bis(trimethylsilyl)amide].[18]

Molecular Structure of 2. The molecular structure as well as the numbering scheme of **4** is presented in Figure 2. For

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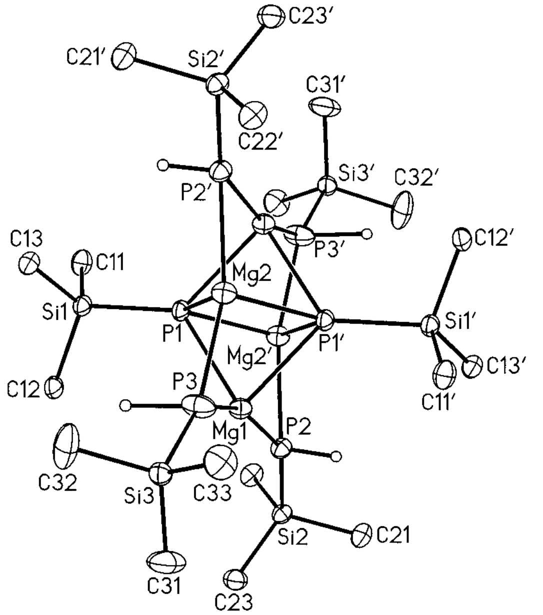

Figure 2. Molecular structure and numbering scheme of **2**. The methyl groups are omitted for clarity. The P-bonded hydrogen atoms are drawn with arbitrary radii; all other H atoms are omitted for clarity. The ellipsoids represent a 40% probability. The atoms of the symmetry-related half of the molecule are marked with primes.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **2**[a]

	$n = 1$	$n = 2$	$n = 3$	$n = 1'$	$n = 2'$
Mg1−P(n)	2.637(1)	2.612(1)	2.573(1)	2.642(1)	
Mg2−P(n)	2.652(1)		2.530(1)	2.663(1)	2.556(1)
P(n)−Si(n)	2.2777(9)	2.284(1)	2.261(1)		
P(n)−H(n)		1.30(3)	1.61(6)		
Mg1−P(n)−Mg2	68.04(3)		70.91(3)		
Mg1−P(n)−Mg1′	103.16(3)				
Mg1−P(n)−Mg2′	66.92(3)	68.86(3)			
Mg1′−P(n)−Mg2	67.02(3)				
Mg1′−P(n)−Mg2′	67.82(3)				
Mg2−P(n)−Mg2′	103.78(3)				
Mg1−P(n)−Si(n)	126.97(4)	151.00(4)	142.44(4)		
Mg2−P(n)−Si(n)	125.23(4)		146.65(5)		
Mg1′−P(n)−Si(n)	129.76(4)				
Mg2′−P(n)−Si(n)	130.96(4)	134.05(4)			

[a] The atoms generated by an inversion center ($-x$, $-y + 1$, $-z$) are marked with primes.

reasons of clarity the methyl groups are not drawn. Symmetry-equivalent atoms are marked by primes. Table 2 contains selected bond lengths and angles. The magnesium atoms are tetracoordinate by two phosphanide and two phosphandiide ligands. The P1 atom of the phosphandiide substituent with a coordination number of five exhibits a quite unusual square pyramidal environment. The atoms P2 and P3 of the phosphanide groups show a coordination number of four with the isotropically free refined hydrogen atoms H2 and H3, respectively.

The central moiety is a Mg_4P_2 octahedron with the phosphorus atoms P1 and P1′ in trans positions. The Mg···Mg edges (Mg1···Mg2 2.960(1) Å, Mg1···Mg2′ 2.922(1) Å) are bridged by phosphanide ligands (P2−Mg1−P3 160.67(4)°, P2′−Mg2−P3 157.84(5)°). Another point of view is to take a dimeric magnesium tri(*tert*-butyl)silylphosphandiide with a central Mg1−P1−Mg1′−P1′ (or alternatively Mg2−P1−Mg2′−P1′) cycle as the basic fragment, which is capped on each side with a $Mg[P(H)Si^tBu_3]_2$ molecule. Due to the rather high coordination number of five at P1, elongated Mg(n)−P1 bonds of 2.64 Å are observed. The P(n)−Si(n) bond lengths which are approximately 5 pm longer than in **1** are also a consequence of the high coordination number and of intramolecular strain. Furthermore, the flatening of the Mg_2PSi moieties which display angle sums ∑M−P2−M of 354° and ∑M−P3−M of 360° is in agreement with this finding. Due to the crystallographically enforced symmetry a cis/trans/cis/trans conformation of the PH functions is realized; however, the broadness of the ^{31}P resonances shows that other isomers are also present in solution.

Summary and Conclusion

The structure of **2** shows a Mg_4P_2 octahedron with the phosphorus atoms in trans positions. This is a very rare example of this kind of a phosphandiide because the intramolecular electrostatic repulsion between the dianions as well as between the cations is expected to be rather high. This forces are overcome by the steric pressure of the tri(*tert*-butyl)silyl substituents favoring small aggregation grades and, furthermore, the bridging phosphanide ligands stabilizing this cation arrangement. In principle, the formal substitution of a $^tBu_3SiP(H)Mg^+$ moiety by a monovalent cation such as Na^+, K^+, or Cu^+ seems to be possible; however, due to the loss of shielding groups a higher aggregation grade is realized in the solid state.[19]

Thus far, there are only a few examples of phosphandiides of the electropositive alkali and alkaline earth metals; however, homoleptic derivatives are described solely for magnesium as mentioned in the Introduction.[9,10] The lithium phosphandiides either are oxygen centered[7] or contain additional phosphinidene units.[8] Little is known about the reactivity of these homoleptic phosphandiides, namely, the tetrameric THF solvates $[(THF)MgPSiR_3]_4$ (R = ^iPr,[10] ^tBu) as well as hexameric $[MgPSi^tBu_3]_6$.[9] Further investigations concerning this question are in progress.

Experimental Section

General Methods. All experiments and manipulations were carried out under an atmosphere of argon or nitrogen. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting $H_2PSi^tBu_3$ was prepared by a literature procedure.[16] NMR spectra were recorded on JEOL spectrometers GSX270 and EX400. A Nicolet 520 FT-IR spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between KBr plates (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The low carbon values at the elemental analysis result from carbide and carbonate formation as well as loss of neutral coligands during handling and combustion of the compounds.

Tetrakis[(tetrahydrofuran-*O*)magnesium μ_3-tri(*tert*-butyl)silylphosphandiide] 1. A 1 M heptane solution of dibutylmagnesium (0.20 mL, 0.20 mmol) was added slowly to a solution of 46 mg of tri(*tert*-butyl)silylphosphane (0.20 mmol) in 0.5 mL of toluene and 16 μL of THF (0.20 mmol). After heating in an ampule (120 °C, 15 h) a clear yellow solution had formed. At room temperature **1** crystallized as moisture- and air-sensitive yellow prisms: yield, 105 mg (80 μmol), 45%; dec above 300 °C. ^1H NMR ([D_6]benzene): δ 1.45 [Si^tBu_3], 1.43 and 4.13 [m, THF]. $^{13}C\{^1H\}$ NMR ([D_6]benzene): δ 24.67 [PSi*C*], 32.55 [PSiC*Me*$_3$], 24.41 and 70.53 [THF]. $^{31}P\{^1H\}$ NMR (toluene): δ −305.9 [PSi^tBu_3]. IR (cm^{-1}): ν = 1498 w, 1479 s, 1444 w, 1393 w, 1381 m,

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1368 w, 1352 w, 1262 m, 1181 w, 1097 s, 1077 s, 1024 vs, 1014 vs, 934 w, 912 w, 892 m, 875 m, 817 vs, 729 w, 697 w, 674 w, 661 w, 631 w, 614 w, 594 m, 563 s, 511 vs, 462 m, 430 w, 403 m, 357 w, 320 m. Anal. Calcd for $Mg_4P_4Si_4C_{48}H_{108}$: C, 56.59; H, 10.68. Found: C, 56.57; H, 10.87.

Tetramagnesium Tetrakis[tri(*tert*-butyl)silylphosphanide] Bis[tri(*tert*-butyl)silylphosphandiide] 2. A 1 M solution of dibutylmagnesium in *n*-heptane (1.0 mL; 1.0 mmol) was added to a solution of 0.349 g of tri(*tert*-butyl)silylphosphane (1.5 mmol) in 15 mL of toluene. After approximately 5 min at room temperature the solution turned cloudy; after an additional 2 h a clear yellow solution had formed. From this reaction mixture colorless and crystalline tetramagnesium tetrakis[tri(*tert*-butyl)silylphosphanide] bis[tri(*tert*-butyl)silylphosphandiide] **2** precipitated. This compound was extremly moisture- and air-sensitive; yield, 119 mg (80 μmol), 31%; dec at 324 °C. ^{1}H NMR ([D$_6$]benzene): δ 1.30 [PHSi^t*Bu*$_3$], 1.50 [PSi^t*Bu*$_3$], PH group not found. ^{31}P NMR (toluene): δ −256.0 [bm, PSi^{t}Bu$_3$], −262.9 [mt, ^1J(P,H) = 220 Hz, ^2J(P,P) = 70 Hz, PHSi^{t}Bu$_3$]. IR (cm^{-1}): ν = 2345 vw, 2177 vw, 1478 s, 1443 m, 1398 m, 1388 s, 1365 m, 1359 m, 1260 w, 1180 m, 1098 w, 1064 w, 1013 s, 933 m, 884 w, 816 vs, 727 w, 691 w, 649 w, 604 s, 564 s, 506 vs, 499 vs, 458 m, 421 m, 398 m, 363 m, 348 m, 330 w. Anal. Calcd for $Mg_4P_6Si_6C_{72}H_{166}$: C, 58.29; H, 11.28. Found: C, 56.34; H, 11.22.

Crystal Structure Determinations. Data was collected on a STOE-IPDS (**1**) or on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector (**2**) with graphite-monochromated Mo Kα radiation (λ = 71.073 pm) using oil-coated rapidly cooled single crystals.[20,21] Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 3.

All structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[23] Neutral scattering factors were taken from Cromer and Mann[24] and for the hydrogen atoms from Stewart et al.[25] The non-hydrogen atoms were refined anisotropically. The H atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms. The P-bonded hydrogen atoms of **2** were refined isotropically without any restrictions. Compound **1** crystallizes with an additional THF between the tetrameric magnesium tri(*tert*-butyl)silylphosphandiide molecules.

Table 3. Crystallographic Data of **1** and **2**

	1·THF	**2**
empirical formula	$C_{68}H_{148}Mg_4O_5P_4Si_4$	$C_{72}H_{166}Mg_4P_6Si_6$
fw (g·mol^{-1})	1379.34	1483.64
temp T (K)	200(2)	183(2)
space group[22]	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	13.454(1)	13.951(1)
b (Å)	26.123(1)	14.269(1)
c (Å)	24.539(2)	24.209(2)
β (deg)	96.53(1)	102.415(1)
V (Å^3)	8569(1)	4706.6(6)
Z	4	2
ρ_{calcd} (g·cm^3)	1.069	1.047
λ (Å)	0.71073	0.71073
μ (cm^{-1})	0.214	0.251
wR2[a] (on F^2)	0.1516	0.1750
R1[a] ($I > 2\sigma(I)$)	0.0542	0.0611
goodness-of-fit s^b on F^2	1.062	1.026

[a] Definition of the R indices: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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