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A Unique Barium−Carbon Bond: Mechanism of Formation and Crystallographic Characterization

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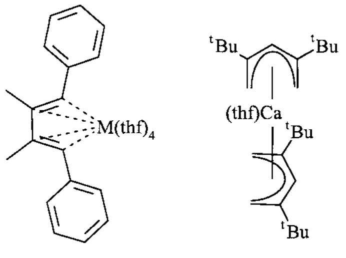
Abstract: The reaction of tetrakis(tetrahydrofuran-*O*)barium bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne yields dimeric (tetrahydrofuran-*O*)barium 2,5-diphenyl-3-(1,4-diphenylbutene-3-yne-2-ide-1-yl)-4-trimethylsilyl-1-phosphacyclopentadienide **1**. The alkenide moiety bridges two barium atoms, with Ba−C bond lengths of 2.881 and 3.071 Å, thus forming a unique three-center two-electron Ba−C−Ba bond. Furthermore, the coordination sphere of the alkaline earth metal atom contains the phosphacyclopentadienide moiety as well as one tetrahydrofuran molecule. A loose side-on coordination of the alkyne moiety completes the coordination sphere of the barium center. A similar reaction with magnesium bis[bis(trimethylsilyl)-phosphanide] gives the dimeric addition product magnesium bis(trimethylsilyl)phosphanide 1,4-diphenyl-1-bis(trimethylsilyl)phosphanyl-but-1-ene-3-yne-2-ide **2**. A reaction mechanism for the formation of the barium derivative is suggested.

Thus far, crystallographically characterized molecules with barium−carbon bonds have been limited to barocenes[1] or side-on coordinated aromatic systems.[2] Up to now, *σ* bonds between the heavier alkaline earth metals and carbon atoms have only been structurally characterized for calcium. Lappert and co-workers[3] inserted a calcium atom into a C−Br bond by co-condensation of the alkaline earth metal and bromobis(trimethylsilyl)methane; the addition of 1,4-dioxane led to the crystallization of $(\text{diox})_2\text{Ca}[\text{CH}(\text{SiMe}_3)_2]_2$ with Ca−C distances of 2.48 Å. Smith, Eaborn and co-workers[4] prepared bis[tris(trimethylsilyl)methyl]calcium with a bent C−Ca−C fragment of 150° and Ca−C bond lengths of 2.46 Å via the metathesis reaction. The bridging phenylacetylide[5] between two calcium atoms in $[(\text{C}_5{}^i\text{Pr}_4\text{H})\text{Ca-C}{\equiv}\text{C-Ph}]_2$ shows Ca−C bond lengths of 2.52 and 2.55 Å. Similar calcium−carbon distances were found in the tetrakis(tetrahydrofuran-*O*)calcium and -strontium 2,3-dimethyl-1,4-diphenylbutadiene complex **A** with a η^4-bonded ligand.[6] 2,4-Di(*tert*-butyl)pentadienide coordinates in a η^5-fashion to calcium (**B**, Scheme 1).[7] Here we report for the first time a crystallographically characterized alkenyl−barium bond.

Scheme 1



M = Ca, Sr (**A**) **B**

Results and Discussion

Synthesis. The reaction of (tetrahydrofuran-*O*)barium bis[bis(trimethylsilyl)phosphanide][8] with diphenylbutadiyne in toluene at room temperature yields dimeric (tetrahydrofuran-*O*)barium 2,5-diphenyl-3-(1,4-diphenylbutene-3-yne-2-ide-1-yl)-4-trimethylsilyl-1-phosphacyclopentadienide **1**. The proposed reaction mechanism is presented in eq 1. The first reaction step is the addition of a Ba−P bond to the C≡C bond. If magnesium bis[bis(trimethylsilyl)phosphanide][9] is used instead of the barium derivative, the product **2**, which represents the first step of the reaction sequence, precipitates from a toluene solution. The subsequent 1,3-trimethylsilyl shift is well-known for the addition reaction of barium bis[bis(trimethylsilyl)phosphanide] with benzonitrile[10] where barium bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide] is isolable. The addition of the thus formed Ba−P bond to the remaining C≡C triple bond (eq 1)

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[‡] Crystal structure analysis.

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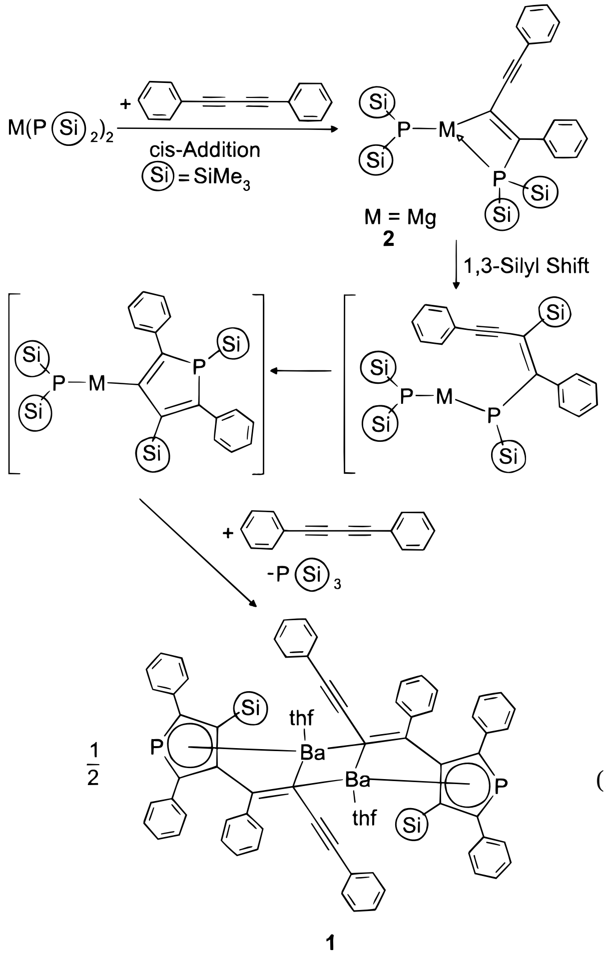

(1)

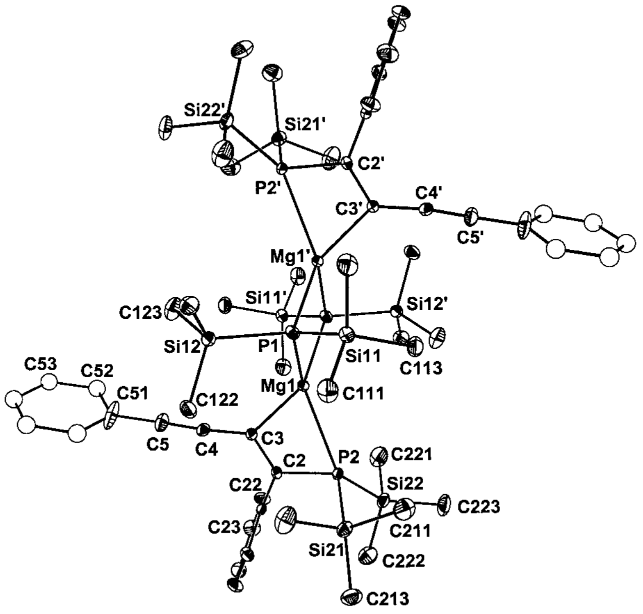

Figure 1. Molecular structure and numbering scheme of dimeric **2**. Symmetry-related atoms are marked with an apostrophe. The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity. The thermal motion of the phenyl substituents with C(5m) is not shown. Selected bond lengths [Å]: Mg1−P1 2.559(2), Mg1−P1′ 2.569(2), Mg1−C3 2.157(3), Mg1−P2 2.708(3), P1−Si11 2.236(2), P1−Si12 2.237(2), P2−Si21 2.275(2), P2−Si22 2.268(1), P2−C2 1.850(3), C2−C3 1.365(3), C2−C21 1.495(4), C3−C4 1.424(4), C4−C5 1.209(4), C5−C51 1.448(4). Angles [deg]: P1−Mg1−P1′ 93.40(7), Mg1−P1−Mg1′ 86.60(7), P2−C2−C3 113.4(2), C21−C2−C3 126.7(2), P2−C2−C21 119.8(2), C2−C3−C4 122.6(2), C3−C4−C5 169.7(3), C4−C5−C51 176.1(3).

leads to cyclization and the formation of a phosphacyclopentadienyl moiety, a new ligand within the alkaline earth metal chemistry. The elimination of $P(SiMe_3)_3$ which was detected by NMR spectroscopy, and the addition of another equivalent of diphenylbutadiyne explains the formation of **1**. Compound **1** is far more moisture- and air-sensitive than **2**.

If the reaction according to eq 1 is performed in toluene containing additional THF, dimeric **1** also crystallizes. However, if the coordinated neutral coligand THF is removed in a vacuum, thus leaving a coordination gap at the barium atom, decomposition of **1** is observed.

Spectroscopic Characterization. The $^{31}P\{^{1}H\}$ NMR shift of δ 122.7 for a toluene solution of **1** is comparable to the chemical shifts of known alkali phosphacyclopentadienides.[11] The $^{31}P\{^{1}H\}$ NMR spectrum of **2** shows two resonances at δ −98.4 and −262.3 for the phosphanyl groups and the bridging phosphanide ligands, respectively, with a $^{2}J(^{31}P,^{31}P)$ coupling constant of 5 Hz. The stretching frequencies of the carbon−carbon triple and double bonds at 2131 and 1596 cm^{-1} indicate a weak conjugation. For **1**, a stronger shift to lower wavenumbers is observed for the stretching vibrations of the C≡C moiety at 1949 cm^{-1}, whereas the C═C double bond vibration with a value of 1594 cm^{-1} lies in the same region as that found for **2**. This finding results from a side-on coordination of the triple bond to the barium center as also shown by the crystal structure determination.

Molecular Structures. Compound **2** crystallizes from a toluene solution as a dimer with a central centrosymmetric Mg_2P_2 cycle. The molecular structure and the numbering scheme are shown in Figure 1. The Mg−C bond length of 2.157(3) Å resembles a characteristic value for a terminal Mg−C bond.[12] The bis(trimethylsilyl)phosphanyl fragment shows a coordination to the magnesium center (Mg1−P2 2.708(3) Å), and therefore this molecule is one of the rare examples[13] of an alkaline earth metal−phosphane complex. The P2−C2 bond length of 1.850(3) Å is characteristic for a single bond. The endocyclic Mg1−P1 distances of 2.559(2) and 2.569(2) Å are in the same range as that reported for the bridging phosphanide substituents in trimeric magnesium bis[bis(trimethylsilyl)phosphanide].[9] A slight delocalization of the anionic charge within the carbanionic ligand as found by IR spectroscopy leads to a marginal lengthening of the C═C (C2−C3 1.365(3) Å) and C≡C bonds (C4−C5 1.209(4) Å), whereas the C3−C4 distance of 1.424(4) Å between these fragments displays a characteristic value[14] for a single bond between sp- and sp^2-hybridized carbon atoms.

Compound **1** crystallizes as a centrosymmetric dimer with a planar Ba_2C_2 cycle. The space between the molecules contains

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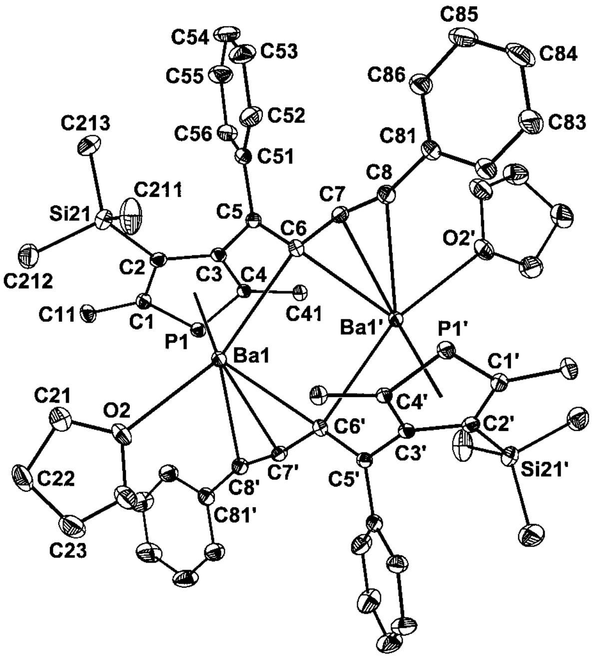

Figure 2. Molecular structure and numbering scheme of dimeric **1**. Symmetry-related atoms are marked with an apostrophe. The ellipsoids represent a probability of 40%. The phenyl substituents at the phosphacyclopentadienide fragments as well as the hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: P1−C1 1.752(6), P1−C4 1.768(5), C1−C2 1.425(8), C1−C11 1.487(7), C2−C3 1.443(7), C2−Si21 1.880(6), C3−C4 1.408(8), C3−C5 1.492(7), C4−C41 1.477(7), C5−C6 1.358(7), C5−C51 1.494(7), C6−C7 1.416(7), C7−C8 1.211(7), C8−C81 1.445(8). Angles [deg]: C1−P1−C4 90.1(3), C3−C5−C6 118.1(5), C5−C6−C7 120.2(5), C6−C7−C8 167.6(6), C7−C8−C81 160.4(6).

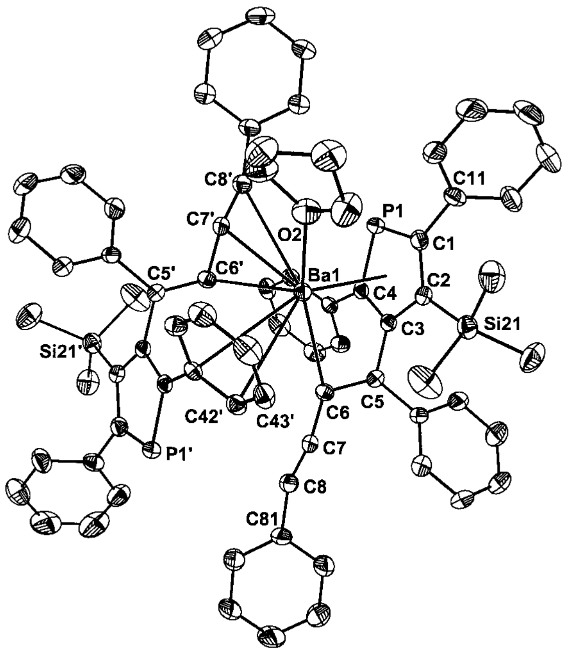

Figure 3. Representation of the coordination sphere of Ba1 in **1**. The hydrogen atoms and Ba1′ are omitted for clarity. The ellipsoids represent a probability of 40%. Selected bond lengths [Å]: Ba1−O2 2.758(4), Ba1−P1 3.487(2), Ba1−C1 3.368(5), Ba1−C2 3.125(5), Ba1−C3 2.899(5), Ba1−C4 3.033(5), Ba1−C6 3.071(5), Ba1−C6′ 2.881(5), Ba1−C7′ 3.003(6), Ba1−C8′ 3.363(6), Ba1−C41′ 3.358(5), Ba1−C42′ 3.356(5). Angle [deg]: Ba1−C6−Ba1′ 89.7(1).

two toluene molecules per asymmetric unit. The molecular structure as well as the numbering scheme of **1** is represented in Figure 2. The P1−C bond lengths (av 1.76 Å) within the phosphacyclopentadienide ligand as well as the endocyclic C−C distances between 1.41 and 1.44 Å clearly show the delocalization of the anionic charge. The C1−P1−C4 angle of 90.1(3)° is very narrow and excludes significant contributions of the s orbital of the phosphorus atom to the P−C bonds. The P−C bond lengths (av 1.73 Å) within unsubstituted[15] and substituted phosphabenzenes[16] are slightly shorter than those in **1**. Due to a rather stiff backbone of the carbdianionic ligand, the Ba−C distances range from 2.90 to 3.37 Å with the shortest bond length Ba1−C3. The Ba1−P1 distance of 3.487(2) Å is drastically longer than that observed for the barium phosphanides.[8,17] The exocyclic C−C multiple bonds (C5−C6 1.358(7) Å, C7−C8 1.211(7) Å) as well as the value for the C6−C7 bond of 1.416(7) Å indicates a better conjugation than in **2**, which is also confirmed by IR spectroscopy.

The central fragment is the four-membered ring which consists of Ba1, Ba1′, C6, and C6′. The Ba1−C6′ bond length of 2.881(5) Å is only slightly smaller than the Ba1−C3 distance of 2.899(5) Å. As is already well-known for the organo alkali metal chemistry, this bond can be described as a three-center two-electron Ba1−C6−Ba1′ bond. Furthermore, the coordination sphere of the barium atom is enhanced by a side-on coordination of the C7′−C8′ alkyne unit, which also explains the stronger lowering of the C≡C stretching vibration and the deviation from linearity (C6−C7−C8 167.6(6)°, C7−C8−C81 160.4(6)°). Thus far, the side-on coordinated bis(trimethylsilyl)-butadiyne to calcium in $Cp^*_2Ca(Me_3SiC{\equiv}C\text{-}C{\equiv}CSiMe_3)$ has been the only structurally characterized example of an alkaline earth metal−alkyne complex.[18]

The THF molecule bonded to barium in the starting material, $(THF)Ba[P(SiMe_3)_2]_2$, remains at the alkaline earth metal atom during the reaction with diphenylbutadiyne. The Ba1−O2 bond length of 2.758(4) Å lies in the characteristic region as found, for example, for $(THF)_2Ba[N(SiMe_3)_2]_2$.[19] A further shielding of Ba1 is achieved by close contacts to the ipso and ortho carbon atoms, C41′ and C42′, of a phenyl group at the phosphacyclopentadienide ligand. The complete coordination sphere of the barium atom and relevant bond distances are given in Figure 3.

In addition to these new compounds with alkaline earth metal−carbon bonds, it has been demonstrated that the magnesium bis(phosphanide) certainly reacts differently than the heavier homologous derivatives. Even heating of **2** under reflux in toluene in the presence of an equimolar amount of diphenylbutadiyne does not lead to a molecule similar to that observed for **1**.

Concluding Remarks

Barium compounds prefer high coordination numbers for the soft alkaline earth metal in contrast to the hard magnesium atom which forms Mg−C σ bonds with rather low coordination numbers at the metal center. Due to the high reactivity of the Ba−C bonds, it reacts immediately with still-present butadiyne

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to form softer phosphacyclopentadienides. The high reactivity of **1** leads to decomposition when the coordinated THF molecule is removed in a vacuum thus leaving a coordination gap. Investigations concerning the reaction of calcium and strontium bis[bis(trimethylsilyl)phosphanides] with diphenylbutadiyne are in progress.

Experimental Section

General Methods. All experiments and manipulations were carried out under argon purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting $Mg[P(SiMe_3)_2]_2$[20] and $(THF)_4Ba[P(SiMe_3)_2]_2$[8] were prepared by literature procedures. NMR spectra were recorded on JEOL GSX270 and EX400 spectrometers. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between CsBr windows (vs, very strong; s, strong; m, medium strong; w, weak; vw, very weak; sh, shoulder). The frequencies in the region of the Nujol vibrations were not listed.

Synthesis of 1. A V-shaped reaction tube with a diaphragm separating the sides was filled with 17 mL of toluene. To one side 0.26 g of $(THF)Ba[P(SiMe_3)_2]_2$ (0.46 mmol) was added, and 0.18 g of diphenylbutadiyne was dissolved in the toluene in the other side. After 12 days without stirring, the NMR spectroscopic control measurements showed the absence of the starting materials. Reduction to approximately 8 mL in vacuo and cooling to −30 °C afforded the precipitation of 0.29 g of crystalline **1** (yield: 87%). Mp: 99−102 °C (under argon, dec). IR (CsBr, selected values): 1949 w, 1883 w, 1803 w, 1594 m, 1248 s, 1176 m, 1156 m, 1068 m, 1057 m, 1031 m, 942 m, 915 m, 840 vs, 755 vs, 697 sh, 689 vs, 526 m. ^1H NMR (toluene-d_8): δ −0.07 (s, $SiMe_3$), 6.9−7.2 (m, phenyl). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 122.69 (s). Anal. Calcd for $Ba_2P_2Si_2C_{106}H_{106}O_2$: C, 70.54; H, 5.92. Found: C, 70.61; H, 5.96.

Synthesis of 2. A solution of dibutylmagnesium in heptane (1.2 mL of a 1 M solution) was added slowly to 0.52 mL of bis(trimethylsilyl)phosphane (2.4 mmol) in 20 mL of toluene. The precipitated magnesium bis[bis(trimethylsilyl)phosphanide] redissolved within 6 h. The addition of 0.49 g of diphenylbutadiyne (2.4 mmol) led to a slightly reddish solution which turned yellow within 30 min. Refrigeration to 5 °C gave 0.46 g of yellow crystalline **2** (yield: 66%). A workup of the mother liquor was not considered. Mp: 180−183 °C (under argon, dec). IR (CsBr, selected values): 1934 w, 1874 vw, 1808 vw, 1596 m, 1260 sh, 1249 vs, 1005 m, 987 m, 845 sh, 837 vs, 752 vs, 739 m, 704 m, 689 s, 625 s, 474 m, 432 m, 390 m, 342 m. ^1H NMR (toluene-d_8): δ 0.35 (d, $^3J(P,H) = 5.6$ Hz, phosphanyl), 0.68 (pseudo-t, $^3J(P,H) \approx 5.6$ Hz,), 6.8−7.8 (m, phenyl). $^{29}Si\{^1H\}$ NMR (toluene-d_8): δ 3.63 (d, $^1J(P,Si) = 6.3$ Hz, phosphanyl), 4.56 (s, $^1J(P,Si) < 2$ Hz, $Mg_2P\mathit{Si}Me_3$). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ −98.40 (t, phosphanyl), −262.29 (t, $Mg_2\mathit{P}SiMe_3$), $^2J(P,P) = 5$ Hz. Anal. Calcd for $Mg_2P_4Si_8C_{56}H_{92}$ (1162.52): C, 57.85; H 7.98. Found: C, 57.86; H, 7.76. MS (70 eV), *m/z*: 379 (100, $(Me_3Si)_2PC_4Ph_2$), 306 (80, $Me_3SiPC_4Ph_2$), 291 (99, $Me_2SiPC_4Ph_2$), 177 (19, PSi_2Me_6), 73 (82, $SiMe_3$).

X-ray Structure Determination of 1 and 2. A suitable single crystal of the derivative **1** was covered with Nujol and mounted on a glass fiber. The crystal structure analysis was performed on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation and a SMART-CCD area detector. A suitable single crystal of **2** was covered with Nujol and sealed in a thin-walled glass capillary. The data collection was performed on a diffractometer equipped with an area detector of the type STOE-IPDS. The crystallographic data as well as details of the structure solution and refinement procedures are summarized in Table 1.

Table 1. Summary of Crystallographic Data of **1** and **2** with Details of the Structure Solution and Refinement Procedures

	1	**2**
empirical formula	$C_{53}H_{37}BaOPSi$	$C_{28}H_{46}MgP_2Si_4$
fw (g mol^{-1})	886.23	581.26
temp T (°C)	−80	−80
space group[21]	$P2_1/n$	$P\bar{1}$
unit cell dimens		
a (Å)	16.429(3)	11.607(2)
b (Å)	16.175(3)	11.981(2)
c (Å)	18.248(4)	13.650(2)
α (deg)	90	75.54(2)
β (deg)	112.697(7)	72.63(2)
γ (deg)	90	77.88(2)
V (Å^3)	4473(1)	1742(1)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.316	1.108
λ (Å)	0.71073	0.71073
μ (cm^{-1}, Mo Kα)	0.987	0.296
no. of data collcd	26131	30071
no. of indep data (R_{int})	7950 (0.0439)	7729 (0.0550)
no. of params	456	350
no. of restraints	45	0
goodness-of-fits on F^2 [a]	1.066	1.048
R, indices [all data][b]		
R_1	0.0780	0.0739
wR$_2$	0.1333	0.1462
R indices[b] [data with $I > 2\sigma(I)$]	4949	5632
R_1	0.0452	0.0506
wR$_2$	0.1062	0.1344
residual dens (e Å^{-3})	1.58; −0.56	1.27; −1.40

[a] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$. [b] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.[22]

The crystal structures were solved by direct methods with the program SHELXTL Plus.[23] The refinement of the structures succeeded with the program packages SHELXL-93[22] and SHELXTL PC, version 5.03,[23] where the function $\sum[w(F_o2-F_c2)^2]$ was minimized. The displacement parameters of all non-hydrogen atoms were treated anisotropically. For all calculations the atom form factors of the neutral atoms Ba, Mg, P, Si, O, and C[24] as well as hydrogen[25] were used. The H atoms were taken into account in idealized positions with fixed U values and C−H distances of 96 pm. The crystal of **1** contains two toluene molecules in the asymmetric unit. One of these solvent molecules is disordered, and the geometry had to be fixed by restraints to maintain reasonable bond lengths and angles.

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Supporting Information Available: For compounds **1** and **2**, tables of positional coordinates, bond distances, bond angles, fractional parameters of all H atoms, and thermal parameters of the non-H atoms and stereoscopic views of the molecular structures and unit cells (17 pages, print/PDF). An X-ray crystallographic file in CIF format is available on the Internet. See any current masthead page for ordering information and Web access instructions.

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