Triphenylphosphonioacetylide: A Species Isoelectronic with Isocyanides

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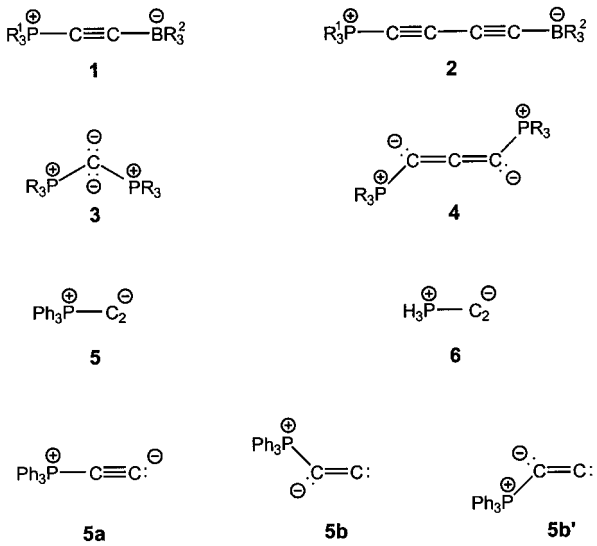
In memory of Gerrit L'abbé

We have for some time been interested in "naked" carbon chains such as **1**–**4**, which are stabilized by donor and acceptor groups.[1, 2] Carbon chains stabilized by donors and acceptors have an even number of carbon atoms with betaine-like character (**1**, **2**), whereas the corresponding compounds



stabilized with two donors have an odd number of carbons and belong to the heterocumulene ylides (**3**, **4**).[3] In the course of this work, questions arose regarding the structure, stability, and reactivity of **5**, in which the C_2 unit is only stabilized by a single donor without an acceptor. This compound can be described by structures **5a** and **5b**/**5b′**. The former can be viewed as a triphenylphosphonioacetylide, whereas **5b**/**5b′** would be regarded as (methylenecarbenylidene)triphenylphosphoranes. Compound **5** is thus isoelectronic with isocyanides.

We utilized several computational techniques to determine the bond lengths, angles, and charge distribution in **5**: the semiempirical MO packages VAMP 6.1[4] and SPARTAN 4.1.1[5] with the PM3 Hamiltonian operator,[6] as well as ab initio [7, 8] and density functional theory (DFT)[9] techniques within Gaussian94.[10] Ab initio and DFT calculations relied on the following methods and basis sets:[8] HF/6-31G(d),[11] MP2/6-31G(d),[12, 13] MP2/6-311+G(d,p), and Becke3LYP/6-311+G(d).[9] Stationary points were characterized as minima or transition states at the appropriate level of calculation. NMR chemical shifts and coupling constants were calculated by the IGLO method[14] with DeMon 1.0.[15] In this case, PW91/IGLO-II//Becke3LYP/6-31G(d) was used for **5**, and PW91/IGLO-III//Becke3LYP/6-311+G(d) for the unsubstituted model compound **6**.

According to semiempirical calculations (Table 1), **5** is linear (P-C_α-C_β 179.98°). The most important bond lengths are

Table 1. Calculated geometries and energies for **5**.

Quantity	PM3	Becke3LYP/6-31G(d)
C–C [pm]	124.1	126.1
C–P [pm]	154.8	167.6
P–C(Ph) [pm]	180.4	183.8
C-P-C(Ph) [°]	112.3	110.2
E_{total}	180.471[a]	−1112.37540[b]
NIMAG[c]	0	1
ZPE[d]	175.424[a]	0.28353[b]

[a] In kcal mol^{-1}. [b] In Hartree. [c] NIMAG: Number of imaginary frequencies. [d] ZPE: Zero-point energy.

154.8 pm (P–C_α) and 124.1 pm (C_α–C_β); the latter is slightly longer than a C–C triple bond.[16] The PPh_3 group bears a net positive charge of +1.14 centered on the phosphorus atom (+2.14 on the P atom, −1.00 on all the phenyl rings combined). The most negative site is at C_α with a charge of −1.18, whereas C_β is practically neutral with a charge of +0.04 (Table 2).

Dipole moments for the individual atoms were derived with the help of the natural atomic orbital point charge (NAO-PC) method.[17] These experimentally nonobservable variables are a measure of the anisotropy of the atomic polarizability. The β-carbon atom in **5** has a dipole moment of 2.00 D, one of the largest yet ascertained with this technique. The molecule has essentially C_{3v} symmetry (the planes of the three phenyl rings intersect at angles of 120° at the P-C-C axis).

DFT Becke3LYP/6-31G(d) optimization (with the symmetry constrained to C_{3v}) gives slightly different values (Table 1). The C_α–C_β and P–C_α distances are 126.1 and 167.6 pm, respectively, and these bonds are expected to become somewhat longer upon inclusion of electron correlation. Atomic charges derived from an natural bond orbital (NBO) population analysis (C_α: −1.01, C_β: +0.02, P: +1.70, PPh_3: +0.99) agree well with those obtained by the NAO-PC method, which can be seen as a confirmation of the effectiveness of semiempirical techniques. Calculation of the normal vibrations for **5** at the Becke3LYP/6-31G(d) level results in one imaginary vibration with a frequency of −53 cm^{-1}. This vibration, which may be a result of numerical errors in the DFT integration, corresponds to a slight bending of the P-C-C unit.

To obtain more information about whether **5** is linear or not, we performed calculations at higher levels on the model compound **6**. H_3P–C_2 was therefore first optimized with C_{3v} symmetry (Table 3). At the RHF/6-31G(d), MP2/6-31G(d), and Becke3LYP/6-311+G(d) levels, this structure proved to be a minimum on the energy hypersurface. Only the structure optimized at the MP2/6-311+G(d,p) level proved to be a second-order saddle point with two imaginary vibrations. Structure **6** was therefore optimized without symmetry constraints (C_1, Table 3). The resulting geometry deviates

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Table 2. Atomic charges for **5** and **6** determined at different levels of theory.

Atom	**5**[a]	**5**[b]	**6**[c]	**6**[d]	**6**[e]	**6**[f]
C_β	+0.04	+0.02	−0.04 to +0.03	−0.11	−0.34	−0.42
C_α	−1.18	−1.01	−0.58 to −0.60	−0.38	−0.16	+0.06
P	+2.14	+1.70	+0.58 to +0.62	+0.40	+0.47	+0.08
H/Ph[g]	−1.00	−0.71	−0.06 to +0.06	+0.09	+0.03	+0.28

[a] PM3. [b] Becke3LYP/6-31G(d). [c] HF/6-31G(d), HF/6-31+G(d), HF/6-311+G(d,p). [d] MP2/6-31G(d). [e] MP2/6-311+G(d,p). [f] Becke3LYP/6-311+G(d). [g] Sum of all residuals on P.

Table 3. Calculated geometries and energies for **6** with various symmetries.

Symmetry	Quantity	RHF/6-31G(d)	MP2/6-31G(d)	MP2/6-311+G(d, p)	Becke3LYP/6-311+G(d)
C_{3v}	C−C [pm]	124.3	127.3	126.9	125.6
	C−P [pm]	164.4	165.3	165.6	165.2
	P−H [pm]	138.8	140.5	140.0	141.1
	C-C-P [°]	180.0	180.0	180.0	180.0
	C-P-H [°]	116.0	116.3	115.6	116.3
	E_{total} [Hartree]	−418.02689	−418.36887	−418.46541	−419.23912
	NIMAG[a]	0	0	2	0
	ZPE[b]	0.03856	0.03601	0.03541	0.03461
C_1	C−C [pm]	124.3	127.3	127.0	125.7
	C−P [pm]	164.4	165.3	165.7	165.3
	P−H [pm]	138.8	140.5	140.0	141.1
	C-C-P [°]	179.9	179.9	172.1	179.9
	C-P-H [°]	116.0	116.9/116.3	115.5/115.6	116.2
	E_{total} [Hartree]	−418.02885	−418.36887	−418.46543	−419.23912
	NIMAG[a]	0	0	0	0
	ZPE[b]	0.03856	0.03601	0.03569	0.03467

[a] NIMAG: Number of imaginary frequencies. [b] ZPE: Zero-point energy.

slightly from C_s symmetry, and **6** is nonlinear with a P-C-C angle of 172°. We assume that the corresponding angle is similar in **5**.

Calculations at all levels agree that the P-C-C unit can be bent very easily (frequencies 0–100 cm^{-1}). The difference in energy between **6** with C_{3v} symmetry and **6** with C_1 symmetry is only 0.00002 Hartree (0.01 kcal mol^{-1}) at the MP2/6-311+G(d,p) level; the nonlinearity should have no experimentally observable consequences. The calculated geometries show short C−C distances (124.3–127.3 pm) that suggest a C−C triple bond, as for the triphenyl compound. The P−C bond lengths (164.4–165.6 pm) are also short and lie in the range of formal P−C double bonds (cf. CH_2=PH 167.5 pm at the MP2/6-31G(d) level). The C-P-C(Ph) angle in the phenyl-substituted compound **5** is, as expected, somewhat smaller than the analogous C-P-H angle in **6**.

Coulson and Mulliken charges are very similar for semiempirical (PM3) and ab initio Hartree–Fock calculations. The phosphorus atom carries less charge in **6** because charge delocalization to the phenyl rings is not possible. Atom C_β is essentially neutral, C_α negatively charged, and P positive (+0.6 e). Methods that take electron correlation into account (MP2 and DFT) give results with the opposite trends, dependent on the basis set. The changes are most extreme for Becke3LYP/6-311+G(d) calculations: C_β now has a partial negative charge (−0.42e), whereas the other atoms are all slightly positive.

The three highest occupied molecular orbitals of **6** (Figure 1) are two almost degenerate orthogonal π orbitals (HOMO and HOMO − 1) with C−C bonding character and

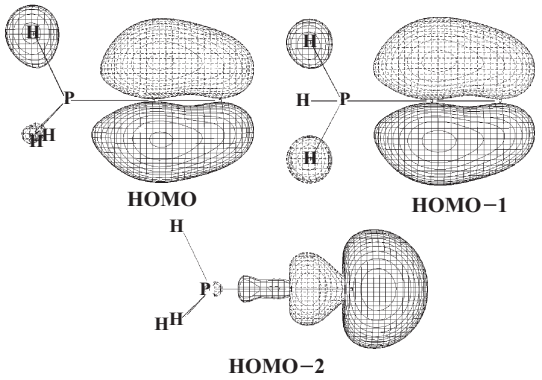


Figure 1. The orbitals HOMO, HOMO − 1, and HOMO − 2 for **6** (HF/6-31G(d)//Becke3LYP/6-311+G(d), PSI88[18]).

a σ orbital (HOMO − 2) with a large orbital lobe beyond C_β (lone pair) and significant C−C bonding character. Strong polarization of all three MOs leads to an accumulation of electron density at the lone pair and on C_α this is not fully reflected in the calculated net atomic charges. In **5**, only the ordering of these three MOs is changed (Figure 2). In this case, the lone pair is the HOMO (σ orbital). All these calculations point to the fact that it is not possible to formulate a single Lewis structure for **5** that correctly reproduces the geometry and charge distribution.

To synthesize **5** a solution of the known (silylethinyl)phosphonium salt **7**[19] in dichloromethane was added dropwise to benzyltrimethylammonium fluoride (**8**) in the same solvent at

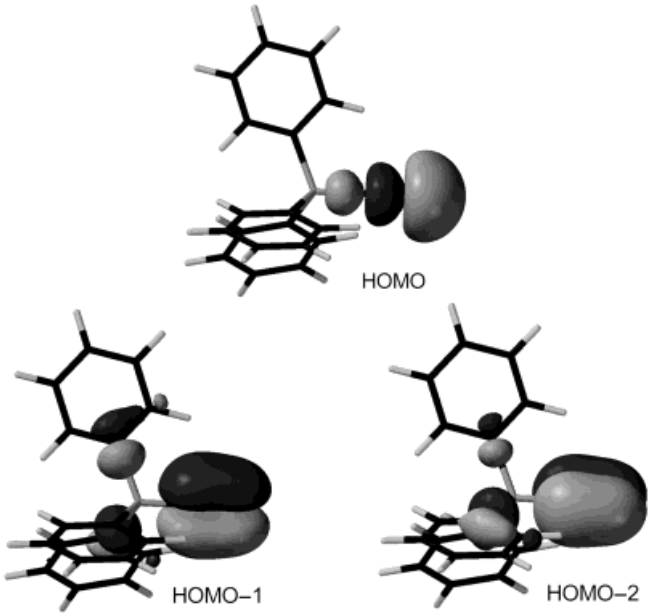
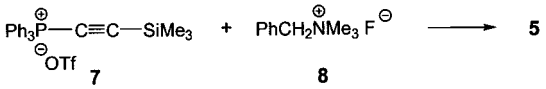


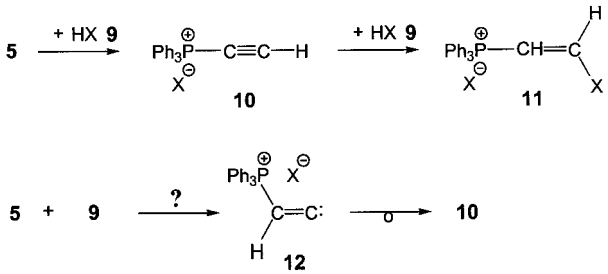
Figure 2. The orbitals HOMO, HOMO – 1, and HOMO – 2 for **5** (PM3/Spartan 4.1.1).

– 90 °C. The low-temperature (– 78 °C) ^{31}P NMR spectrum of the product showed (apart from small amounts of by-products) only one signal at $\delta = -13.85$. The signals of starting material **7** at ($\delta(^{31}P) = 5.22$, $\delta(^{29}Si) = -9.78$) had disappeared. Since **5** is stable only at low temperature and



decomposes upon warming to room temperature, all spectra were recorded at – 78 °C. Because the ^{13}C NMR data were not completely clear, we prepared ^{13}C-enriched **7**.[20] The corresponding ^{13}C NMR spectrum showed doublets for C_α and C_β (C_α: $\delta = 83.87$, $^1J(P,C) = 161.7$ Hz; C_β: $\delta = 133.03$, $^2J(P,C) = 18.4$ Hz). After desilylation of **7** to **5** the signals for C_α and C_β appeared at $\delta = 83.15$ (d, $^1J(P,C) = 132.4$ Hz) and 228.90 (d, $^2J(P,C) = 12.8$ Hz). These data support the results of the calculations extremely well (Table 4). The large downfield shift in the signal for C_β in **5** with respect to that for **7** (over 95 ppm) shows that this atom is electron deficient. The observed P–C_α coupling constant lies between the usual values for alkenyl- (ca. 90 Hz)[21] and alkinylphosphonium salts (ca. 180 Hz),[22] indicating some nonlinearity of the molecule in solution.[23] The ^{31}P NMR spectrum of ^{13}C-labeled **5** shows (apart from a singlet at – 13.687 ppm for the ^{12}C isotopomer) two doublets at $\delta = -13.693$ and – 13.710, which result from coupling of C_α or C_β of the two ^{13}C isotopomers with the phosphorus atom. The ^{31}P NMR signal of **5** is shifted upfield, as are those for **4** ($R^2 = C_6H_5$)[2] and other phosphaallene ylides.[24] The IR spectrum of **5** shows a sharp peak at 1957 cm^{-1} (**7**: 2135 cm^{-1}); cumulated ylides also absorb in this range.[23]

Compound **5** reacts with acids HX (**9**) initially to form ethinylphosphonium salts **10**, which could be characterized by ^{31}P NMR spectroscopy as intermediates between – 78 and – 30 °C (Scheme 1). A possible insertion into the H–X bond,



Scheme 1. Reaction of **5** with **9** (X = OMe, Cl, OCOMe) and possible reaction pathways that proceed directly via **10** or via carbene intermediate **12**.

which might be expected on the basis of the carbene structure **5b**/**5b**′, is not observed. At about 0 °C a further reaction with **9** takes place to give the vinylphosphonium salts **11**, which are formed as mixtures with widely differing *Z*:*E* isomeric ratios.[25] We assume that electrophilic attack at the β-carbon atom of **5** occurs to lead to a dynamic back-polarization of electron density from C_α to C_β. In principle, nucleophilic attack on the negatively charged α-carbon atom might be possible to form the vinylidenecarbenephosphonium salt **12**, which would be expected to undergo rapid rearrangement to the ethinylphosphonium salt **10** (Scheme 1).[26] However, in a series of experiments (e.g., reaction with electrophiles in the presence of alkenes) we found no evidence for the formation of carbene **12** or similar intermediates substituted at the α-carbon atom. Reaction of **5** with trifluoromethanesulfonic acid methyl ester (**13**) gives the propinylphosphonium salt **14**.

We further investigated whether **5**, which is isoelectronic with isocyanides, undergoes reactions analogous to the Passerini reaction.[27] We therefore treated solutions of **5** at – 78 °C with a ketone (**15**) and then at – 40 °C with carboxylic acid **17** (Scheme 2), and isolated the corresponding (3-acyloxy-2-oxo-alkylidene)triphenylphosphorane **21** about five hours later (Table 5). We assume that betaine **16** is initially formed and then is protonated by **17** to give alkynylphospho-

Table 4. Structurally relevant spectroscopic data for **5** and **7**.

	$\delta(^{31}P)/J(P,C)$ [Hz]	$\delta(^{29}Si)/J(Si,P)$ [Hz]	$\delta(^{13}C)/J(P,C)$ [Hz]	IR [cm^{-1}]
7[a]	5.22 (s)/ –	– 9.78 (d)/3.5 (^3J)	83.87 (d, C_α)/161.7 (^1J) 133.03 (d, C_β)/18.4 (^2J)	2135
5[b]	– 13.710 (d)/132.1 (^1J) – – 13.693 (d)/12.3 (^2J) – 13.687 (s)/ –		83.15 (d, C_α)/132.4 (^1J) 228.90 (d, C_β)/12.8 (^2J)	1957
5[c]	– 45.8	–	61.6 (C_α)/108.9 (^1J) 285.8 (C_β)/ – 57.0 (^2J)	–

[a] Determined in $CDCl_3$ at room temperature, IR as KBr pellet. [b] Determined in CH_2Cl_2 or CD_2Cl_2 at – 78 °C. [c] Calculated at the PW91/IGLO-II//Becke3LYP/6-31G(d) level.

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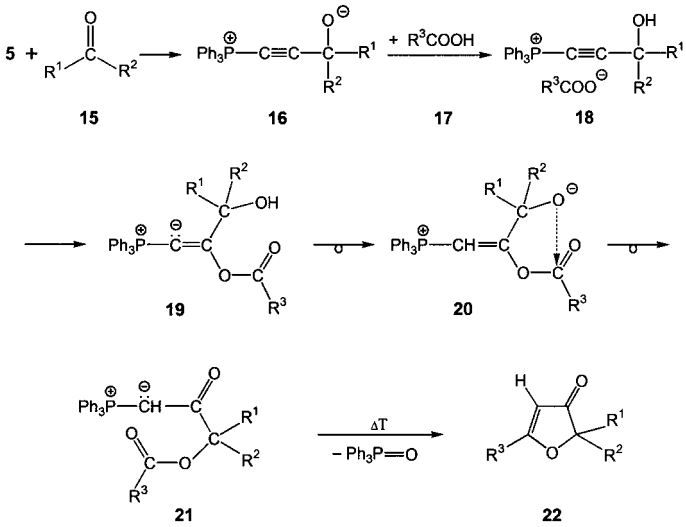


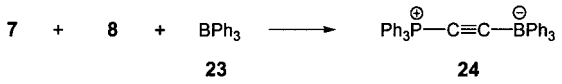
Scheme 2. Reaction of **5** that resembles the Passerini reaction.

Table 5. Acyl ylides **21** and furanones **22** prepared from **5**, ketones, and carboxylic acids.

	R^1	R^2	R^3	**21** [%]	M.p. [°C]	**22** [%]	M.p. [°C]
a	Me	*t*Bu	*p*-$MeOC_6H_4$	40	–	76	89
b	Et	Ph	*p*-$MeOC_6H_4$	42	170	82	97
c	Me	Me	*p*-$MeOC_6H_4$	45	172	83	93
d	Me	Me	Me	54	146	–	–

nium salt **18**. The carboxylate anion then adds at the position β to phosphorus in a slow reaction at room temperature. The resulting phosphaallene ylide **19** in turn undergoes a proton shift to provide **20**. The reaction sequence is terminated by an acyl shift to give **21**. The similarity between this sequence and the Passerini reaction is clear. Upon heating in benzene or toluene at reflux, acyl ylides **21** undergo an intramolecular Wittig reaction[28] to yield 2,2,5-trisubstituted 3(2*H*)-furanones **22** (cf. Table 5).

If **7** is desilylated in the presence of triphenylborane (**23**) at $-78\,^{\circ}C$, (triphenylphosphonioethinyl)triphenylborate (**24**),[29] which belongs to the phosphonioboratoacetylenes **1**, is formed in 84% yield. A comparison of the X-ray crystal structure of **24**[29] with that of **1**,[1] in which one phenyl is replaced by a



methyl group, shows no significant differences. The C_α–C_β distance in **24** (124.3 pm) is slightly greater than that in the analogue (121.6 pm), [1] and both molecules are slightly bent (**24**: P-C_α-C_β 177°, B-C_β-C_α 171.3°).

Experimental Section

All operations were carried out under a nitrogen atmosphere and in absolute solvents.

5 (in solution): **8** (169 mg, 1.0 mmol) was dissolved/suspended in CH_2Cl_2 (2 mL) and cooled to $-90\,^{\circ}C$. A solution of **7** (509 mg, 1.0 mmol) in CH_2Cl_2 (3.5 mL) was added dropwise over a period of 10 min. A deep red solution was obtained, which appeared yellow when viewed as a thin layer. To complete the reaction, the mixture was stirred for about 10 min and allowed to warm to $-78\,^{\circ}C$. Smaller batches (0.6 mmol) in absolute CD_2Cl_2 were prepared to obtain low-temperature spectra.

21: To a solution of **5** at $-78\,^{\circ}C$ was added an aromatic or aliphatic ketone (**16**, 5.0 mmol). The mixture was first allowed to react for 10 min at $-78\,^{\circ}C$, and then maintained for 30 min at $-40\,^{\circ}C$ before an aromatic or aliphatic carboxylic acid (**17**, 0.8 mmol) was added. The mixture was allowed to warm to room temperature and then stirred for 5 h. From this point on, a nitrogen atmosphere was no longer necessary. The solution was evaporated to 2 mL and washed with Et_2O (10 mL), and the residue was twice precipitated from CH_2Cl_2/Et_2O (little CH_2Cl_2). The oily red residue was discarded. The combined ether phases were evaporated, and the crude acyl ylides **21** chromatographed over silica gel with ethyl acetate as eluent.

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[29] **24**: colorless crystals, m.p. 203–205 °C (decomp); IR: $\tilde{\nu} = 2090$ cm^{-1} (C≡C); ^{1}H NMR (60 MHz, [D$_5$]pyridine): $\delta = 7.1$–8.0 (m, 30H, aromatic H); ^{13}C NMR (100.4 MHz, [D$_5$]pyridine): $\delta = 71.3$ (d, ^1J(P,C) = 186.2 Hz, C_α), 122.3 (d, ^1J(P,C) = 99.2 Hz, *ipso*-C, P-phenyl), 124.4 (s, *para*-C, B-phenyl), 127.3 (s, *ortho*-C, B-phenyl), 130.3 (d, ^3J(P,C) = 13.7 Hz, *meta*-C, P-phenyl), 133.3 (d, ^2J(P,C) = 12.2 Hz, *ortho*-C, P-phenyl), 134.8 (d, ^4J(P,C) = 3.0 Hz, *para*-C, P-phenyl), 135.5 (s, *meta*-C, B-phenyl), 157.6 (s, *ipso*-C, B-Phenyl); ^{31}P NMR (161.7 MHz, [D$_5$]pyridine): $\delta = 0.04$; ^{11}B NMR (128 MHz, C_6D_6): $\delta = -11.2$.

A Three-Dimensional Framework with Accessible Nanopores: $RbCuSb_2Se_4 \cdot H_2O$**

Jason A. Hanko and Mercouri G. Kanatzidis*

The synthesis of nonoxidic chalcogen-based open frameworks is motivated by the prospect of obtaining interesting semiconducting analogues of zeolites.[1] Planned syntheses of open-framework structures based on germanium and tin sulfides were reported in 1989.[2] This discovery led to a rapid expansion in this area, and compounds such as $[Et_4N]_2Cu_2Ge_4S_{10}$,[3] $[Me_4N]_2MGe_4S_{10}$ (M = Mn,[4, 5] Fe,[5, 6] Co,[5] Zn[5]), and $[Me_4N]_6(Cu_{0.44}Ge_{0.56}S_{0.73})Ge_4S_{10}$[7] were prepared. Hydrothermal synthesis is a common route to these materials. Solid-state lattices can be generated by the self-assembly of the appropriate molecular building blocks in the presence of organic template ions. Using this approach, we have demonstrated that $[EQ_3]^{3-}$ (E = As, Sb; Q = S, Se) units are versatile building blocks from which interesting compounds such as KBi_3S_5,[8] $[Ph_4P]InSe_{12}$,[9] $[Me_4N]HgAs_3S_6$,[10] $[Me_4N]RbBiAs_6S_{12}$,[11] and $[Co(en)_3]CoSb_4S_8$[12] can be made. A transition metal is not necessary for the formation of extended structures. Several of these germanium,[13] tin,[14–22] and antimony sulfide[23, 24] frameworks are also accessible by condensation of molecular building blocks.

Here we report on the new three-dimensional material $RbCuSb_2Se_4 \cdot H_2O$ (**1**), which was prepared by heating CuCl with Rb_3SbSe_3[25] and Ph_4PBr in H_2O at 130 °C. The black needlelike crystals are insoluble in common organic solvents. Compound **1** has a three-dimensional framework in which tetrahedral Cu centers are connected to both pyramidal $SbSe_3$ and square-pyramidal $SbSe_5$ units.[26] The novel feature of this framework is the presence of large channels running along the [010] direction (Figure 1). The channels have an irregular

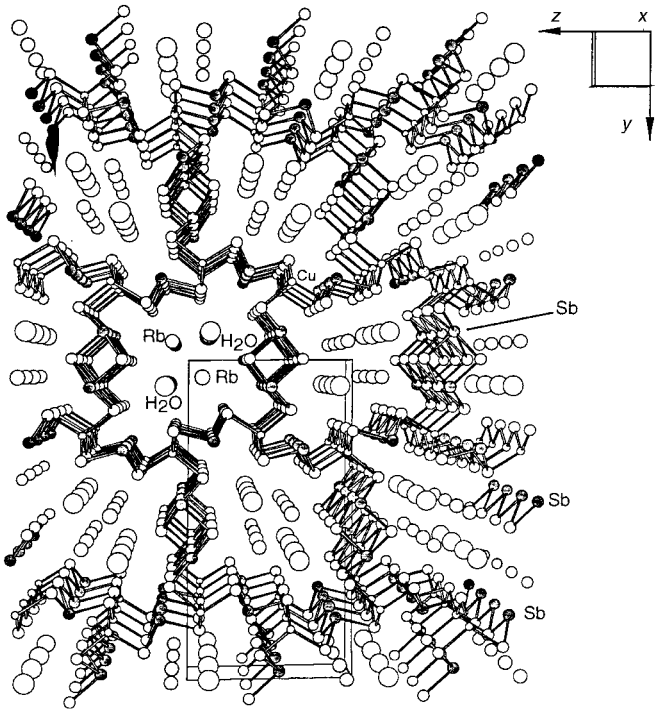

Figure 1. View of the structure of **1** along the *b* axis showing the channels occupied by the rubidium centers and water molecules.

cross section with dimensions of 11.29 × 10.52 × 8.16 Å (Figure 2). Another unique feature is the presence of two kinds of $[SbSe_2]_n^{n-}$ chains which run parallel to the channels. One is a single $[SbSe_2]_n^{n-}$ chain of corner-sharing pyramids in which all of the terminal Se centers on the same side; the Sb–Se bond lengths range from 2.556(4) to 2.726(3) Å (av 2.66(5) Å), and the Se-Sb-Se angles from 95.5(1) to 99.1(1)°. The other contains associated double $\{[SbSe_2]_2\}_n^{2n-}$ chains with Sb–Se bond lengths in the range 2.585(4)–2.972(3) Å (av 2.83(8) Å) and Se-Sb-Se angles between 84.8(1) and 173.9(1)°. Such double chains are also found in Sb_2Se_3.[27] Figure 2 highlights the two different $[SbSe_2]_n^{n-}$ chains. The $[SbSe_2]_n^{n-}$ single chains are connected to the Cu atoms to give corrugated $CuSbSe_2$ sheets composed of alternating rows of tetrahedrally coordinated Cu and pyramidally coordinated Sb units. These sheets are held together by the $\{[SbSe_2]_2\}_n^{2n-}$ double chains, which complete the tetrahedral coordination sphere of the Cu atoms

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