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Synthesis and Crystal Structures of $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-}\mathrm{ESiMe}_3)(\mathrm{InMe}_3)]$ (E = S, Se): Lewis Acid–Base Adducts with Chalcogen Atoms in Planar Coordination

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The structures of $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-}\mathrm{SSiMe}_3)(\mathrm{InMe}_3)]$ and $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-}\mathrm{SeSiMe}_3)(\mathrm{InMe}_3)]$ were determined by single-crystal X-ray diffraction. Both complexes are Lewis acid–base adducts of the InMe_3 acceptor and the chalcogen donor atom linking a $\mathrm{Me}_3\mathrm{Si}$ group and a $(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}$ moiety. They are very unstable under atmospheric conditions and decompose at ambient temperatures. Results of DFT calculations for these complexes and the related hypothetical $[(\mathrm{Me}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-}\mathrm{SSiMe}_3)(\mathrm{InMe}_3)]$ compound show that the unusual planar coordination of the chalcogen atoms is due to steric crowding.

Introduction

The donor–acceptor bond in Lewis acid–base adducts of group 13 organometallic compounds and the chalcogen atoms S and Se is relatively weak, as these chalcogen atoms are only moderate donors and the organic groups at the metal atom diminish their acceptor ability.[1] Consequently, structural reports of such adducts are very scarce. The solid-state structures of thioether adducts with AlMe_3 and InMe_3,[2] organometallic complexes with two Al or Ga atoms coordinating a SMe^- or SPh^- moiety,[3] and some corresponding intramolecular stabilized adducts with S donor atoms[4] have been reported. The first adduct between TlMe_3 and a S donor atom was presented recently,[5a] and so far, the only structurally elucidated example for an Se atom coordinating a group 13 purely organometallic unit is the anion $[\mathrm{MeSe}(\mathrm{AlMe}_3)_3]^-$.[6]

In our investigations concerning organometallic single-source precursors for the deposition of ternary semiconductors used for thin-film solar cells,[7] we follow the concept of the reaction of $\mathrm{E}(\mathrm{SiMe}_3)_2$ (E = S, Se) with phosphane-coordinated copper(I) acetate under cleavage of E–SiMe_3 bonds and the formation of the volatile $\mathrm{Me}_3\mathrm{SiOAc}$ side product. Applying this method, Fenske, Corrigan et al. synthesized a broad variety of metal chalcogenide clusters.[8] It was also possible to incorporate group 13 metal atoms into the clusters through the use of GaCl_3 and InCl_3 as additional reagents.[9] Corrigan et al. isolated mononuclear complexes of the general formula $[(R_3\mathrm{P})_3\mathrm{CuESiMe}_3]$ (R = alkyl, phenyl; E = S, Se, Te) that carry an ESiMe_3 group that coordinates terminally to the copper atom.[10] These complexes are intermediates in the formation of copper–chalcogenide clusters and are powerful starting materials for further reactions with other metal compounds. They are stable only at low temperatures; at room temperature they react under cleavage of the second E–SiMe_3 bond. Herein, we present the crystal structures of such mononuclear complexes as adducts with InMe_3, which may represent the first intermediates in the formation of organometallic copper–indium–chalcogenide clusters.

Results and Discussion

In reactions of InMe_3 with in situ generated silylchalcogenolate complexes of the type $[(i\mathrm{Pr}_3\mathrm{P})_n\mathrm{CuESiMe}_3]$ (E = S, Se), we expected cleavage of the E–SiMe_3 bond with elimination of tetramethylsilane (TMS) as a side product[5] and the formation of a molecule with a $[(i\mathrm{Pr}_3\mathrm{P})_n\mathrm{Cu–E–InMe}_2]$ motif, which should oligomerize to rings or clusters to achieve tetrahedral coordination of the indium atom. As it turned out, TMS was not formed in this reaction, as shown by NMR spectroscopy after the addition of InMe_3 to a chilled solution containing $[(i\mathrm{Pr}_3\mathrm{P})_n\mathrm{CuESiMe}_3]$. Instead, we obtained simple adducts, in which InMe_3 is coordinated by the chalcogen atom. After evaporation of the solvent and volatile side products at low temperature, we were able to grow colorless crystals of $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-}\mathrm{ESiMe}_3)(\mathrm{InMe}_3)]$ (**1**: E = S, **2**: E = Se), which are very sensitive towards air and moisture and decompose at temperatures above –15 °C. Complex **1** crystallizes in the $Pna2_1$ space group with three molecules in the asymmetric unit. Selenium analogue **2** crystallizes in the acentric Cc space group with one mo-

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lecule per asymmetric unit.[11] Figure 1 shows the molecular structure of one of the three crystallographically independent molecules of **1**, as determined by single-crystal X-ray diffraction. The two other independent molecules of **1** differ in the angles between the (P1, P2, Cu) and (Si, S, In) planes, which are arranged approximately perpendicular to each other (76–89°). The structural motif of selenium compound **2** is almost identical. Table 1 presents structural details of the molecules of **1** and **2**. The trigonal planar coordination of the copper atom is in accordance with the steric demand of the bulky $i\mathrm{Pr}_3\mathrm{P}$ ligands. Unusual is the planar environment of the chalcogen atom, which connects the copper atom with the indium and silicon atoms. Typically, bridging chalcogenolate ligands have a pyramidal coordination,[12] although some exceptions are known. A detailed investigation of such an exception in the case of phosphane-stabilized copper(I) phenylchalcogenolate complexes was recently reported.[13]

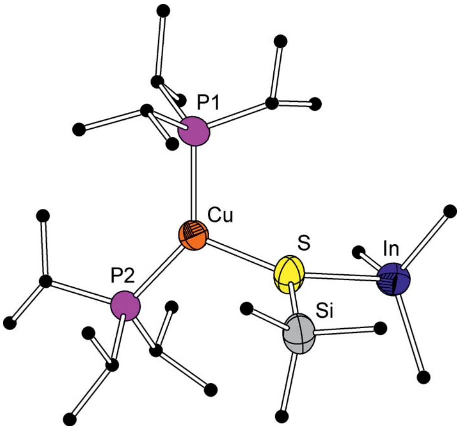

Figure 1. Molecular structure of **1**. H atoms are omitted for clarity; P, Cu, S, In, and Si atoms are drawn as 50% ellipsoids. A unit cell plot of **1** as well as a depiction of the molecular structure of **2** are available in the Supporting Information.

If bond lengths and angles of **1** and **2** are compared with those of the copper trimethylsilylchalcogenolates $[(\mathrm{R}_3\mathrm{P})_3\mathrm{CuESiMe}_3]$,[10] we note that the E–Si bonds do not show significant deviation. The Cu–P and Cu–E bonds are slightly shorter in **1** and **2** (3–4 and 6–7 pm, respectively), as in **1** and **2** the Cu atoms have a lower coordination number than the tetrahedrally coordinated copper atoms in $[(R_3\mathrm{P})_3\mathrm{CuESiMe}_3]$. The Cu–E–Si angles are almost the same as those in Corrigan's complexes (123°).

One of the free electron pairs of the chalcogen atom is used in the formation of a Lewis acid–base adduct with the electron-deficient InMe_3 moiety. In a comparable way, SO_2 adducts have been observed in $[(\mathrm{Ph}_2\mathrm{MeP})_3\mathrm{Cu}(\mu\text{-SPh})(\mathrm{SO}_2)]$ and related selenium complexes.[14] Given the absence of reports on the structures of adducts between indium triorganyls and a single S or Se donor atom, the In–E bond lengths lack a direct comparison. As can be expected from inductive effects,[1c] the In–E bond lengths in the indium dimethyl $[(\mathrm{Me}_2\mathrm{InEPh})_n]$ compounds (≈260 pm reported for E = S and 272 pm for E = Se)[5] are slightly shorter than those in **1** and **2**. Much longer In–S distances (297 and 313 pm) were observed in the polymeric $[\mathrm{Me}_3\mathrm{In}(1,4\text{-}\mathrm{C}_4\mathrm{H}_8\mathrm{S}_2)]$ adduct, in which planar $\mathrm{Me}_3\mathrm{In}$ groups are bridged by the cyclic 1,4-$\mathrm{C}_4\mathrm{H}_8\mathrm{S}_2$ thioether.[2c] In **1** and **2**, the In atoms deviate by 45–48 pm from the C_3 planes because of interaction with only one chalcogen atom. The Cu–E–In angles are around 127° in **1** and 124° in **2**, whereas the In–E–Si angles are compressed to approximately 108°. Notably, a large M–E–M angle (in the present case M = Cu, In) is necessary to provide sufficient overlap between the lone pairs of electrons of the chalcogenolate ligand and the empty metal atomic orbitals, if the chalcogen atom has a nearly planar environment.[13]

To examine the assumption that the high steric demand of the phosphane ligands causes the planarity of the chalcogen atoms, we performed DFT structure optimizations for **1**, **2**, and the hypothetical, less-crowded $[(\mathrm{Me}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-SSi-}$

Table 1. Structural details of $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-SSiMe}_3)(\mathrm{InMe}_3)]$ (**1**), $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-SeSiMe}_3)(\mathrm{InMe}_3)]$ (**2**) (from crystal-structure determination as well as DFT calculations), and the hypothetical $[(\mathrm{Me}_3\mathrm{P})_2\mathrm{Cu}(\mu\text{-SSiMe}_3)(\mathrm{InMe}_3)]$ (**3**) complex (DFT calculations).

Distances and angles [pm and °]	**1** (E = S) molecule 1	molecule 2	molecule 3	DFT calcd.	**3** (E = S) DFT calcd.	**2** (E = Se)[a]	**2** (E = Se) DFT calcd.
Cu–E	233.8(3)	232.9(3)	231.0(3)	235.98	232.06	247.7/242.9(2)	244.85
In–E	263.8(3)	263.2(3)	262.3(3)	273.45	271.59	276.4/273.4(2)	288.11
Si–E	210.9(4)	211.5(4)	212.7(5)	214.66	214.60	233.3/231.4(3)	229.80
In–C (avg.)	220.1 ± 0.8	218 ± 1	218 ± 3	219.3 ± 0.4	219 ± 1	220 ± 4	219.3 ± 0.5
Cu–P (avg.)	226.5 ± 0.8	226 ± 1	227.3 ± 0.8	232.2 ± 0.2	225 ± 2	226.3 ± 0.3	233.0 ± 0.3
P1–Cu–P2	136.6(1)	136.5(1)	136.5(1)	133.17	131.02	137.87(9)	131.93
P1–Cu–E	107.5(1)	108.0(1)	109.1(1)	113.31	107.44	118.4/103.1(1)	116.83
P2–Cu–E	115.8(1)	115.4(1)	114.4(1)	113.41	121.50	103.6/119.0(1)	111.18
In–E–Si	108.2(2)	108.2(1)	109.3(2)	112.75	115.23	107.23(8)/108.8(1)	109.71
Cu–E–In	126.5(1)	127.2(1)	128.6(1)	122.35	103.31	122.17(6)/125.41(9)	120.44
Cu–E–Si	123.5(2)	123.6(2)	122.0(2)	123.53	120.06	120.82(9)/123.8(1)	121.66
C–In–C (avg.)	115 ± 4	116 ± 4	116 ± 4	116.5 ± 0.5	114 ± 2	115 ± 2	116.8 ± 0.5
(P1, P2, Cu)/(Si, E, In)	76.04(7)	75.98(8)	89.20(8)	80.4	82.0	83.40/84.01(6)	77.57
In out of (C,C,C) plane	47.40(7)	46.63(7)	45.0(1)	41.1	42.0	47.6(7)	39.7
Cu out of (P,P,E) plane	2.8(1)	3.4(1)	1.1(1)	4.0	2.7	4.5(2)/3.0(2)	3.2
E out of (In,Si,Cu) plane	18.5(4)	14.2(4)	3.8(4)	16.2	63.1	45.6(2)/20.5(4)	41.8

[a] Se atom disordered with SOF = 0.6 and 0.4.

Me_3)($InMe_3$)] (**3**) complex. The results of these calculations are presented in Table 1 together with the data from the experimental crystal structure determinations. Most calculated values are in quite good agreement with the experimental results.[15] Even the calculated out-of-plane parameters of the chalcogen atoms, only 16 pm in **1** and 42 pm in **2**, are close to the results of the crystal-structure determination. The calculation with the smaller phosphane ligands supports our assumption: the sulfur atom in **3** is more pyramidal, and the out-of-plane parameter of 63 pm illustrates this.

The ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra (–15 °C) of molecular complexes **1** and **2** in solution show typical resonances of the $InMe_3$, $SiMe_3$, and P*i*Pr$_3$ groups (Figures S3 and S4, Supporting Information). However, the ^{31}P signals with chemical shifts close to those of pure P*i*Pr$_3$ are relatively broad, which is indicative of ligand-exchange processes in solution, and there is additional broadening of the ^{31}P signal caused by the quadrupole moment ($I = 3/2$) of the copper isotopes. This is also observed for other Cu^I phosphane complexes.[16] With decreasing temperature, the ^{31}P signals become even broader and become resolved. The ^{1}H NMR signals of the $InMe_3$ groups are slightly shifted downfield relative to the signals of a solution of pure $InMe_3$ (δ = –0.18 ppm in [D$_6$]benzene), and this is consistent with only weak interactions of the $InMe_3$ group with the donor atoms.[17] At room temperature, solutions of **1** and **2** in toluene turn dark before a dark precipitate forms; the NMR spectra indicate the formation of $S(SiMe_3)_2$ and $Se(SiMe_3)_2$, respectively, whereas signals belonging to P*i*Pr$_3$ and $InMe_3$ remain almost unchanged. The formation of TMS was not observed.

Conclusions

Molecular compounds with a copper–chalcogen–indium binding motif could be synthesized and characterized crystallographically. We applied the concept of stabilizing copper trimethylsilylchalcogenolates at low temperatures.[10] The reaction of [(*i*Pr$_3$P)$_n$CuESiMe$_3$] with $InMe_3$ did not result, as expected, in cleavage of the chalcogen–silicon bond but in the formation of a simple Lewis acid–base adduct. Adducts **1** and **2** have the rare structural feature of a chalcogen donor atom with (almost) planar coordination. This is a consequence of the steric demand of the bulky phosphane ligands that coordinate the copper atom. This explanation is supported by DFT calculations. As the structures of **1** and **2** highlight, [(R_3P)$_n$CuESiMe$_3$] molecules, which are stable only at low temperatures, act as electron donors towards Lewis acidic $InMe_3$. In consecutive reactions, copper–indium chalcogenide clusters are formed; a manuscript reporting their synthesis and structures is in preparation.

Experimental Section

Materials, Equipment, and Experimental Methods: All experiments were performed under an inert atmosphere of nitrogen. Standard Schlenk techniques or glove box methods were applied. *i*Pr$_3$P was prepared by reaction of PCl_3 with the *i*PrMgCl Grignard reagent. $(Me_3Si)_2E$ was synthesized from Na_2E and Me_3SiCl. CuOAc was accessible by comproportionation of dehydrated $Cu(OAc)_2$ and copper powder in Ac_2O/AcOH as described by Edwards et al.[18] $InMe_3$ was synthesized according to Brauer.[19] NMR experiments were performed with a Bruker Avance DRX 400 spectrometer in [D$_8$]toluene at –15 °C; the toluene CD_2H signals (δ =2.08 ppm) were used as reference for the ^{1}H resonances.

[(*i*Pr$_3$P)$_2$Cu(μ-ESiMe$_3$)(InMe$_3$)]: *i*Pr$_3$P (3.2 mmol) was added dropwise to a suspension of copper(I)acetate (184 mg, 1.5 mmol) in THF (5 mL) at 0 °C. The obtained colorless solution was cooled to –60 °C and added to $S(SiMe_3)_2$ (0.4 g, 2.2 mmol) at –60 °C. The reaction solution remained colorless. After stirring for 1 h at –60 °C, a precooled solution of $InMe_3$ (1 M in THF, 1.5 mL, 1.5 mmol) was added slowly. The solution was stirred and allowed to reach –20 °C over a period of 3 h. After storing the reaction mixture at this temperature for about 48 h, the solvent and volatile side products (Me_3SiOAc) were removed in vacuo at temperatures below –20 °C to leave a colorless oil. For crystallization, the oil was dissolved in precooled THF (3 mL) and then cold acetonitrile (20 mL) was carefully added as a separate layer. After several days at –20 °C, colorless crystals of **1** appeared, which decomposed immediately under atmospheric conditions or if warmed up to ambient temperature, yield 30–50%. The product can be stored at low temperatures. ^{1}H NMR (400 MHz, [D$_8$]toluene, –15 °C): δ = –0.10 [s, 9 H, In(CH_3)$_3$], 0.48 [s, 9 H, Si(CH_3)$_3$], 0.99 [m, 36 H, PCH(CH_3)$_2$], 1.74 [m, 6 H, PCH(CH$_3$)$_2$] ppm. ^{13}C NMR (100.6 MHz, [D$_8$]toluene, –15 °C): δ = –7.7 [s, In(CH_3)$_3$], 6.6 [s, Si(CH_3)$_3$], 19.7 [d, $^2J_{P,C}$ = 4 Hz, PCH(CH_3)$_2$], 21.8 [d, $^1J_{P,C}$ = 9 Hz, PCH(CH$_3$)$_2$] ppm. ^{31}P{^{1}H} NMR (161.9 MHz, [D$_8$]toluene, –15 °C): δ = 16 (br. s) ppm. ^{29}Si NMR (79.5 MHz, [D$_8$]toluene, –15 °C): δ = 9 (br. s) ppm.

2: Prepared by a procedure similar to that used for **1**; $Se(SiMe_3)_2$ was used instead of $S(SiMe_3)_2$. ^{1}H NMR ([D$_8$]toluene, –15 °C): δ = –0.14 [s, 9 H, In(CH_3)$_3$], 0.55 [s, 9 H, Si(CH_3)$_3$], 0.98 [m, 36 H, PCH(CH_3)$_2$], 1.76 [m, 6 H, PCH(CH$_3$)$_2$] ppm. ^{13}C NMR ([D$_8$]toluene, –15 °C): δ = –8.0 [s, In(CH_3)$_3$], 6.8 [s, Si(CH_3)$_3$], 19.6 [s, PCH(CH_3)$_2$], 21.8 [br. s, PCH(CH$_3$)$_2$] ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene, –15 °C): δ = 14.4 (br.s) ppm. ^{29}Si NMR ([D$_8$]toluene, –15 °C): δ = 7 (br. s) ppm.

X-ray Crystal Structure Determination: Crystals were selected, prepared, and mounted on a glass fiber in mineral oil below –20 °C under an N_2 atmosphere. The mounted crystal was transferred immediately into the cold flush at the diffractometer's goniometer head. The measurements were performed with a STOE IPDS 2T at 180 K with Mo-K_α radiation monochromated with a graphite single crystal. The structures were solved by direct methods (SIR-92).[20] The obtained starting model was then refined with the least-squares method (SHELXL-97).[21]

Due to the instability of **1** and **2** it was difficult to prepare single crystals for structure determination. Slight decomposition on the crystal surface was not avoidable during preparation. This reduced the quality of the collected datasets. The crystal of complex **1** was twinned non-merohedrically with a weighted intensity contribution above 90% of the major domain. Because multidomain integration of the diffracted intensities and *hkl*-f5-refinement did not improve the result significantly, we decided to use just the reflections of the major domain. The Flack parameter of the crystal of complex **2** indicated inversion twinning (ratio 0.6:0.4). The selenium atom is disordered over two sites with occupancies of 0.6 and 0.4.

CCDC-756645 (for **1**) and -756646 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: The molecular structures of **1**, **2**, and hypothetical adduct **3** were optimized at the B3LYP[22] level of density functional theory without symmetry restrictions and were confirmed to be minima on the potential energy surface by frequency analyses (no negative force constants). The calculations were performed by using the Gaussian03 program package.[23] Basis sets employed were 6-31G for hydrogen atoms; 6-311G(d) for carbon, silicon, phosphorus, sulfur, copper, and selenium atoms; and the LANL2DZ effective core potential basis set for indium atoms.[24]

Supporting Information (see footnote on the first page of this article): Unit cell plot of **1**; depiction of the molecular structure of **2**; ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of solutions of **1** and **2**.

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[11] Crystal data and structure refinement: **1** ($C_{24}H_{60}CuInP_2SSi$): STOE IPDS-2T diffractometer, M_m = 649.17 g mol^{-1}, crystal size 0.2 × 0.2 × 0.05 mm^3, orthorhombic, space group $Pna2_1$ (No. 33), a = 1699.64(4) pm, b = 1147.66(3) pm, c = 5260.2(2) pm, $V = 10260.6(5)\times 10^6$ pm^3, Z = 12, T = 180(2) K, ρ_{ber} = 1.261 g cm^{-3}, μ = 1.495 mm^{-1}, λ = 71.073 pm (Mo-K_α), $2\theta_{max}$ = 52°, 32786 measured, 15909 independent reflections, R_{int} = 0.135, 13540 with $I > 2\sigma(I)$, 807 parameters, H atoms in idealized positions, R_1 (observed reflections) = 0.089, wR_2 (all data) = 0.247, Flack parameter x = 0.11(3), max./min. residual electron density peaks 2.83/–1.45 e$^-$/10^6 pm^3. **2** ($C_{24}H_{60}CuInP_2SeSi$): STOE IPDS-2T diffractometer, M_m = 696.07 g mol^{-1}, crystal size 0.5 × 0.4 × 0.3 mm^3, monoclinic, space group Cc (No. 9), a = 1904.9(2) pm, b = 1174.40(6) pm, c = 1740.2(1) pm, β = 118.880(6)°, $V = 3409.0(4)\times 10^6$ pm^3, Z = 4, T = 180(2) K, ρ_{ber} = 1.356 g cm^{-3}, μ = 2.507 mm^{-1}, λ = 71.073 pm (Mo-K_α), $2\theta_{max}$ = 50°, 9479 measured, 5460 independent reflections, R_{int} = 0.102, 4758 with $I > 2\sigma(I)$, 284 parameters, H atoms in idealized positions, R_1 (observed reflections) = 0.055, wR_2 (all data) = 0.145, inversion twinning, max./min. residual electron density peaks 1.82/–0.76 e$^-$/10^6 pm^3.

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Lewis Acid–Base Adducts

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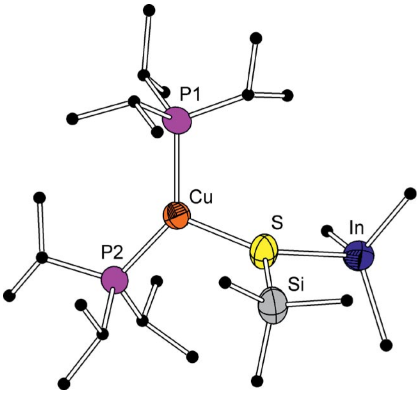
Synthesis and Crystal Structures of [(iPr$_3$P)$_2$Cu(μ-ESiMe$_3$)(InMe$_3$)] (E = S, Se): Lewis Acid–Base Adducts with Chalcogen Atoms in Planar Coordination

Keywords: Lewis acids / Lewis bases / Chalcogens / Density functional calculations / Structure elucidation



Lewis acid–base adducts of trimethylindium and phosphane-stabilized copper(I) (trimethylsilyl)chalcogenolates were synthesized and characterized by X-ray crystal structure determination. They are very unstable under atmospheric conditions and decompose at ambient temperatures. DFT calculations reveal that the unusual planar coordination of the chalcogen atoms is due to steric crowding.