disordered solvent molecules (Et_2O), but which cannot be unambiguously assigned. Compound **7a** is isotypic with **8a**, but the quality of the crystals was very low. The intensities were measured with a Bruker-axs-SMART diffractometer (**5**, **3a**, **7a**) and with a Siemens-P4 diffractometer (**6**, **8a**) ($Mo_{K\alpha}$ radiation, $\lambda = 0.71707$ Å, ω scan, $T = 203$ K). The structures were solved by direct methods (SHELXS97), and refined against F^2 with all measured reflections (SHELXL97). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-119661 (**3a**), CCDC-119662 (**5**), and CCDC-119663 (**8a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[$In_3(In_2)_3(PhP)_4(Ph_2P_2)_3Cl_7(PEt_3)_3$]–A New Molecular III/V Compound Featuring an Unusual 19-Atom Cage

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In the last few years, enormous interest has been generated in the synthesis of molecular III/V cages owing to the diverse optical and electronic properties of binary III/V materials. For the In/P system, several compounds containing In_2P_2 four-membered rings,[1] In_3P_3 six-membered rings,[2] or In_4P_4 heterocubanes[3] as central structural units have been synthesized and characterized by X-ray structure analysis. Furthermore, the generation of nanometer-sized particles of the binary InP phase was investigated intensively, for example, by reaction of $InCl_3$ or $InCl(C_2O_4)$ and $P(SiMe_3)_3$ at high temperatures[4] or by thermolysis of molecular InP compounds.[5] The resulting products were characterized by X-ray powder diffraction and by transmission electron microscopy (TEM) experiments. It was possible to synthesize InP nanoparticles in a size range of 2 to 10 nm.[6]

We report here the synthesis and structure determination[7] of the InP cluster compound **1** (Figure 1), which consists of a 19-atom cage with a diameter of about 0.7 nm.[8] Compound **1** was obtained from the reaction of $InCl_3$ with PEt_3 and $PhP(SiMe_3)_2$ [Eq. (1)]. Besides the loss of Me_3SiCl and the formation of In–P bonds, redox processes occur during the reaction which lead to the formation of additional P–P and In–In bonds.

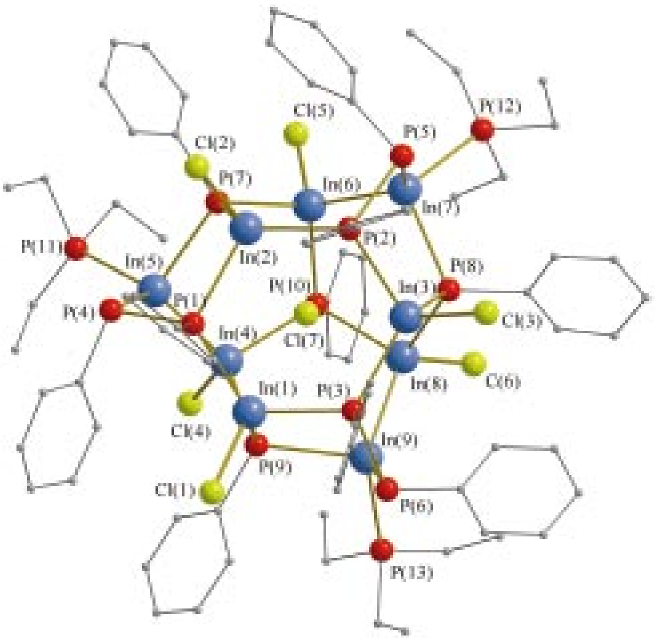

Figure 1. Molecular structure of **1** in the crystal. Selected bond lengths [pm] and angles [°]: In–Cl 241.2–245.0, In–P 253.3–261.6, In–In 273.5–275.1, P–P 220.1–223.1; P-P-In 99.2–116.3 (P(1), P(2), and P(3)), P-P-In 96.0–96.3 (P(4), P(5), and P(6)), P-In-P 101.1–126.1, In-P-In 97.3–113.1, In-In-P 102.1–126.3.

$$9\,InCl_3 + 3\,PEt_3 + 10\,PhP(SiMe_3)_2 \rightarrow \underset{\mathbf{1}}{[In_3(In_2)_3(PhP)_4(Ph_2P_2)_3Cl_7(PEt_3)_3]} + 20\,Me_3SiCl \quad (1)$$

Compound **1** crystallizes in the space group $P\bar{1}$ as a racemate with both enantiomers appearing in the unit cell. The 19-atom polyhedron is built up by nine In and ten P atoms. If the ligands are considered as four PPh^{2-} groups (P(7) to P(10)), three $P_2Ph_2^{2-}$ groups (P(1)–P(4), P(2)–P(5), P(3)–P(6)), and seven Cl^- ligands, a total charge of 21+ can be calculated for the nine In atoms of the cluster. In(1), In(2), and In(3) show no In–In bonds and can be assigned the formal oxidation state 3+, whereas atoms In(4) to In(9) have the formal charge 2+ and correspondingly form In_2 pairs (In(4)–In(5), In(6)–In(7), In(8)–In(9)). Assuming that lone pairs are present at P atoms P(4), P(5), and P(6), the polyhedron possesses 54 valence electrons for 27 bonds and features exclusively two-electron, two-center bonds. All interatomic distances lie in the usual range for single bonds. The In–P distances range between 253.3 and 261.6 pm, the In–In bonds are 274.1 pm on average. These values correspond well to analogous bonds occurring in other In/P compounds; for example, in [$\{(tBu_2P)_2InCl\}_2$] or [$MesInPMes]_4$ (Mes = 2,4,6-$Me_3C_6H_2$) the In–P bonds range between 258.2 and 266.0 pm[1–3] and in [$Trip_4In_2$] (Trip = 2,4,6-$iPr_3C_6H_2$)[9] or [$In_2I_4(nPr_3P)_2$][10] the In–In single bonds are 277.5 and 274.5 pm, respectively. In contrast, longer In–In distances of

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280 to 320 pm are observed in electron-deficient In clusters, such as $R^*_8In_{12}$ ($R^* = SitBu_3$)[11] synthesized recently by Wiberg and co-workers, and in the indium tetrahedron R_4In_4 ($R = C(SiMe_3)_3$).[12] Average P–P bond lengths of 222.0 pm in **1** are similar to those in other compounds containing $(RP)_n$ ligands.[13]

The cluster core has near C_3 symmetry, the idealized threefold axis runs through the center of the In_3P_3 six-membered ring, formed by In(1) to In(3) and P(1) to P(3) as well as through atoms Cl(7) and P(10). Altogether the cluster core is built up by four In_3P_3 six-membered rings, three In_3P_2 five-membered rings, and three In_2P_3 five-membered rings. Considering the view of **1** given in Figure 1, the above-mentioned In_3P_3 ring (In(1) to In(3), P(1) to P(3)) acts as the top surface and the remaining three In_3P_3 rings and three In_2P_3 rings are alternately positioned as lateral limits. Finally, the three In_3P_2 rings, each connected by two In–P(10) bonds, form the bowl-shaped bottom.

Three of the In atoms (In(5), In(7), In(9)) are coordinated by PEt_3 groups, the six remaining In atoms are each bound to one terminal Cl ligand. Cl(7) is located at the center of the cluster cage and has to be viewed as Cl^- for reasons of cluster neutrality and in agreement with quantum chemical calculations. The closest neighboring atoms to Cl(7) are the atoms In(1), In(2), and In(3) at distances of 306.5, 303.2, and 300.8 pm. Intercalation compounds of halides similar to **1** have already been reported for polyoxovanadates[14] and polyoxovanadiumorganophosphates.[15]

The PPh groups (P(7) to P(10)) act as μ_3-bridging ligands, thus phosphorus atoms of these ligands are four-coordinate and exhibit near tetrahedral coordination geometries. The two P atoms of the P_2Ph_2 groups show different coordination geometries. The phosphorus atoms P(1), P(2), and P(3) are four-coordinate and bond in nearly tetrahedral fashion to two In atoms, one carbon atom of a phenyl group, and one phosphorus atom. The phosphorus atoms P(4), P(5), and P(6), however, are three-coordinate and bond to one C atom of a phenyl group, one P atom, and one In atom. These P atoms show nearly trigonal-pyramidal coordination geometries. All In atoms in **1** reside in slightly distorted tetrahedral environments, in which the four binding partners are either three P atoms and one In atom or two P atoms, one In atom, and one Cl ligand, or three P atoms and one Cl ligand.

In order to better understand the bonding and stability of **1**, quantum chemical ab initio calculations were carried out using the program package TURBOMOLE within the resolution of the identity (RI) approximation to the density functional theory (RI-DFT) method.[16] To reduce the computational effort, ethyl and phenyl ligands were replaced by methyl groups. Additionally, C_3 symmetry was assumed for the structure optimization.[17] The deviation between calculated and experimental structural parameters was as expected. As usual, the bond lengths are somewhat overestimated by DFT, as shown by the following (experimental data in parentheses): In–Cl 244.4 (242.9), P–P 224.3 (222.0), In–P (without R_3P–In) 260.6 pm (257.8 pm). Larger deviations occur for the weak, dative R_3P–In contacts; the calculated values were 9.5 pm too long. Computed In–In distances are 6.0 pm longer than experimental ones, probably because the DFT method does not take (attractive) dispersion effects, which play a considerable role, into consideration.

Removal of the central Cl^- ion leads, using the same computational method, to only slightly different structural parameters: bond lengths (In–In, P–P, In–P, In–Cl) less than 4 pm, angles less than 6.0°. Thus, the following two points are to be considered. First, the cationic cage $[In_3(In_2)_3(MeP)_4(Me_2P_2)_3Cl_6(PMe_3)_3]^+$ is stable and encapsulates the Cl^- ion without strain in its center. Second, the interaction of the Cl^- ion with its neighboring In atoms is purely ionic. In both the calculated and the crystal structure of **1**, the nearest neighbors of the interstitial Cl^- ion are In atoms (In(1) to In(3)) in the formal oxidation state III.

By performing additional calculations it was possible to investigate the cluster behavior with F^-, Br^-, or I^- as the central halide ion. The distances of the halide ion to the indium atoms In(1) to In(3) increases with increasing ionic radius but remains the shortest of the indium–halide distances (In–Cl 309.4, In–Br 316.6, In–I 325.3 pm). The bond lengths between the atoms of the cage remain almost constant in the clusters with Cl^-, Br^-, and I^- as the central halide, whereas the angles widen, yielding a more spherical shape for the cationic cage. A second-order Jahn–Teller effect occurs for the F^- case distorting the cluster to C_1 symmetry and giving an energy gain of 4.7 kJ mol^{-1}(In(1)–F 230, In(2)–F 234, In(3)–F 337 pm). Complexation energies of the anions inside the cationic cage ($\Delta E = E_{\text{cluster}} - (E_{x^-} + E_{\text{cation}})$) amount to 638.8 ($F^-$), 494.3 ($Cl^-$), 438.2 ($Br^-$), and 334.1 kJ mol^{-1} (I^-). For a more complete characterization, vertical electronic excitations were calculated by using time-dependent density functional theory (TD-DFT). The computed singlet spectrum consists of a series of bands ending with the longest wavelength signal at 461 nm.[18] The measured electronic excitation spectrum of the yellow compound **1** showed a structureless signal that starts at the long wavelength side at 500 nm, in agreement with the calculation, and rises in intensity to the limit of the spectrometer at 200 nm.[19]

Experimental Section

All manipulations were performed with the rigorous exclusion of oxygen and moisture on a Schlenk line under nitrogen. Solvents were dried according to literature procedures and freshly distilled before use.

A solution of $InCl_3$ (0.22 g, 1.0 mmol) and PEt_3 (0.12 g, 1.0 mmol) was stirred in THF (10 mL) for 30 min. Then $PhP(SiMe_3)_2$ (0.25 g, 1.0 mmol) was added. After 3 h all volatile compounds were removed in vacuo, and the yellow residue was suspended in diethyl ether (5 mL). The suspension was stirred for 16 h and subsequently filtered. A yellow powder was obtained that was redissolved in THF (5 mL). The solution was again filtered in order to remove small amounts of insoluble powder, and was subsequently layered with toluene (20 mL). After a few days, very small crystals of **1** appeared. The formation of **1** was very dependent on the reaction conditions (temperature, concentration, etc.). Yield: 5–15%. ^{31}P NMR (250 MHz, C_6D_6/THF): Very broad signals were observed due to many different P–P couplings and the nuclear spin of In. IR (KBr): $\tilde{\nu} =$ 3048 (m), 2961 (m), 1577 (m), 1478 (s), 1432 (s), 1259 (m), 1136 (m), 1096 (vs), 1042 (m), 841 (m), 737 (vs), 692 (vs), 558 (m), 475 (m), 377 cm^{-1} (w); C, H analysis (%) calcd for $C_{78}H_{95}Cl_7In_9P_{13} \cdot 2.5\,C_7H_8$ (2946.9): C 38.94, H 3.91; found: C 38.20; H 3.89; UV/Vis: $\lambda = 370$ (sh), 280 nm (m).

$PhP(SiMe_3)_2$[20] and PEt_3[21] were synthesized according to literature procedures, $InCl_3$ was purchased from Aldrich.

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[7] **1**·2.5 toluene: crystal dimensions $0.04\times0.03\times0.01$ mm^3, $a = 1509.7(5)$, $b = 1518.5(4)$, $c = 2623.0(5)$ pm, $\alpha = 92.98(3)$, $\beta = 94.21(3)$, $\gamma = 91.37(3)^\circ$, $V = 5986(3)\times10^6$ pm^3; triclinic $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 1.596$ g cm^{-1}, $\mu(Mo_{K\alpha}) = 2.067$ mm^{-1}, STOE IPDS, Siemens rotating anode, graphite monochromator, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 190$ K, $2\theta_{max} = 45^\circ$; a total of 19264 reflections measured, 13093 independent reflections ($R_{int} = 0.0605$), 9568 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2, 749 parameters (In, P, Cl, refined anisotropically, C atoms of the phenyl groups refined anisotropically, C atoms of ethyl groups and solvent molecules were refined isotropically with split positions; H atoms were calculated for the phenyl groups only), $R1 = 0.0832$; $wR2 = 0.2153$, residual electron density 3.004 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118782. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Asymmetric Synthesis of Overcrowded Alkenes by Transfer of Axial Single Bond Chirality to Axial Double Bond Chirality[**]

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Sterically overcrowded alkenes have attracted considerable interest in view of their unique photochromic and thermochromic properties. In addition the beautiful architecture of these structures is as fascinating as their potential applications.[1] Although they lack a stereogenic center they can exist as stable, optically active stereoisomers as a consequence of the presence of substituents that cause sufficient hindrance between the upper and lower half of the alkene and enforce a helical distortion to the entire molecule. Unsymmetrical *cis* and *trans* isomers of overcrowded alkenes were shown to act as chiroptical molecular switches suitable for reversible data storage,[2] while other applications include photomodulation of liquid-crystalline materials[3] and thin polymer films.[4] A practical synthetic route towards enantiomerically pure over-

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