Envelope Clusters

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A Main-Group Analogue of Housene: The Subtle Influence of the Inert-Pair Effect in Group 15 Clusters**

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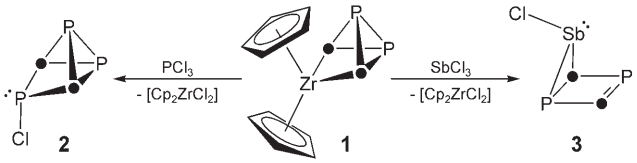
Dedicated to Professor John F. Nixon

The Binger and Regitz groups have described the reaction of zirconocene 1,3-diphosphabicyclo[1.1.0]butane (**1**) with PCl_3 (*n*-hexane, 110 °C) to give the tricyclic *P*-chloro triphosphacyclopentane **2** (Scheme 1),[1] and we have recently shown



Scheme 1. Syntheses of tricyclic *P*-chloro triphosphacyclopentane **2** and envelope compound **3**. ● = C*t*Bu.

that this compound is a valuable precursor for both *nido*-1,2,4-P_3C_2 cationic species and the cyclic 1,3,4-P_3C_2 anion.[2–4] Against this background it was clearly of interest to attempt the incorporation of other heteroatoms into the P_2C_2 manifold through reactions of **1** with group 15 trihalides, such as

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$SbCl_3$, because this particular reaction could provide selective access to the *nido*-SbP_2C_2 cation[5] and the cyclic 1-Sb-3,4-P_2C_2 anion.[6] In the event the reaction proceeded in an unexpected and interesting way to form the envelope compound **3** (Scheme 1), which exhibited unusual solid-state and solution-phase behavior. Herein, we report the synthesis and structural characterization of **3**, along with its variable-temperature NMR spectra. Density functional theory provides a framework for the interpretation of these results.

Addition of two molar equivalents of $SbCl_3$ to a stirred orange-red solution of **1** in *n*-hexane at room temperature led, after 2 h, to the formation of a gray-white precipitate and a change in color of the solution to bright yellow. Filtration followed by recrystallization (−15 °C) of the hexane-soluble material afforded, in good yield, yellow crystals of the only phosphorus-containing product, **3** (according to $^{31}P\{^1H\}$ NMR spectroscopic analysis). A single-crystal X-ray diffraction study of the extremely air-, moisture-, and temperature-sensitive crystals revealed that, although **3** is related to **2** via replacement of one phosphorus center with antimony, the two species have completely different structures, with **3** adopting the envelope-type topology illustrated in Figure 1.

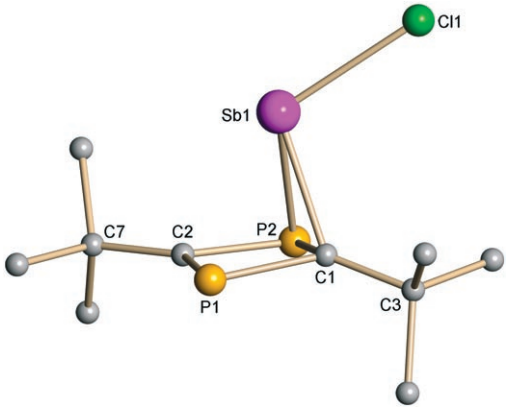

Figure 1. Molecular structure of **3** in the solid state (hydrogen atoms have been omitted for clarity). The molecule is disordered over two sites (relative occupancy 90:10); the disordered units are ostensibly identical and only the major site is shown and discussed. Selected bond lengths [Å] and angles [°]: Sb1–C1 2.241(4), Sb1–P2 2.562(2), Sb1–Cl1 2.511(1), P1–C1 1.844(4), P2–C2 1.807(4), P2–C1 1.831(4), P1–C2 1.725(4); C1-Sb1-P2 44.21(9), Cl1-Sb1-P2 114.92(4), Cl1-Sb1-C1 104.5(1), Sb1-C1-P1 84.8(2), Sb1-P2-C2 74.5(1), P1-C1-P2 94.4(2), C1-P2-C2 81.8(2), P2-C2-P1 99.5(2), C2-P1-C1 83.7(2).

The structure shown in Figure 1 reveals a number of rather unusual features that suggest that the bonding in **3** is more subtle than indicated in the Lewis structure shown in Scheme 1. Most notably, although the Sb–Cl fragment bridges a single carbon–phosphorus bond, the plane defined by the C1-Sb1-P2 triangle is tilted significantly inwards towards the center of the C1-P2-C2-P1 ring, such that the angle between the triangle and the ring is only 80.6°. The Sb1–Cl1 and P1–C2 bonds (2.511(1) and 1.725(4) Å, respectively) are also considerably longer than normal (Sb–Cl is 2.33 Å in $SbCl_3$[7] and P=C bonds in phosphaalkenes range from 1.60 to 1.70 Å).[8] These structural parameters are consistent with the presence of significant interactions between the P=C double bond and the Sb–Cl fragment.

The adoption of completely different structural motifs by the Sb and P analogues has encouraged us to explore the fundamental electronic differences between the two species using density functional theory (DFT). For the two model compounds, $ClP_3(CH)_2$ and $ClSbP_2(CH)_2$, we have located distinct minima corresponding to the envelope and tricyclic structures (Figure 2). The optimized envelope structure for

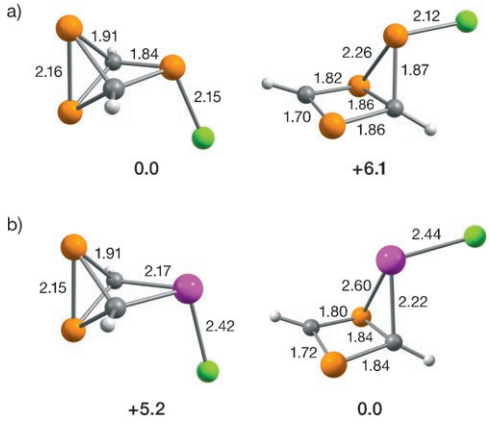

Figure 2. Optimized tricyclic and envelope structures for a) $ClP_3(CH)_2$ and b) $ClSbP_2(CH)_2$. Relative energies in kcal mol^{-1} are given in bold. Sb pink, P orange, Cl green, C gray, H white.

$ClSbP_2(CH)_2$ reproduces the key features of the X-ray structure of **3**, including the inward tilt of the SbCl fragment towards the C2–P1 bond and the rather long Sb–Cl and P=C bonds. Critically, the tricyclic structure is favored by 6.1 kcal mol^{-1} for the phosphorus system, but the order is reversed for the antimony analogue, in which the envelope structure is more stable by 5.2 kcal mol^{-1}.[9]

A natural bond orbital (NBO) analysis[10] reveals the origin of this reversal of stability on moving from phosphorus to antimony. For both $ClSbP_2(CH)_2$ and $ClP_3(CH)_2$, the lone pair at the bridgehead atom (Sb or P) has significantly greater s character in the envelope structure (Sb: 89 %, P: 77 %) than in its tricyclic counterpart (Sb: 79 %, P: 65 %) as a result of the very tight angles (θ) at the bridgehead (envelope: θ = 257°(Sb)/260°(P); tricyclic: 267°(Sb)/284°(P)), which favor greater p orbital participation in the bonding orbitals at the bridgehead atom in the envelope structure. Thus, the reluctance of the antimony center to participate in sp^n hybridization destabilizes the tricyclic structure and drives the switch to the envelope topology. The change in structure is therefore a manifestation of the well-known inert-pair effect.

Although the envelope structure of **3** was unexpected in light of our previous work on the tricyclic compounds $C_2tBu_2P_2ECl$ (E = P, As),[5] it is a relatively well-known structural motif, most notably in the hydrocarbon species bicyclo[2.1.0]pent-2-ene (housene)[11] and its triphospha-derivative, 1,2-$(CH(SiMe_3)_2)$P-1,3-$P_2(CtBu)_2$.[12] Despite the apparent isomorphism of these three compounds, the inward tilt of the apical SbCl fragment noted above is conspicuously

absent in the other two species. Thus, whereas the angle between the C1-Sb1-P2 and C1-P2-C2 planes is acute (80.6°) in **3**, the corresponding angles in bicyclo[2.1.0]pent-2-ene and 1,2-HP-1,3-$P_2(CH)_2$ are 124.5° and 103.7°, respectively. Furthermore, although the formally bonded (2.562(2) Å) and nonbonded (2.770(2) Å) Sb–P distances in **3** are similar, there is a much sharper distinction in 1,2-HP-1,3-$P_2(CH)_2$ (2.24 and 3.02 Å).

A natural bond orbital (NBO) analysis clearly reveals that the inward tilt of the SbCl group in **3** is a result of two significant donor–acceptor interactions, both of which are intimately connected to the unusual structure of **3**. The first corresponds to a σ→π* donation from the Sb1–P2 bond to the empty π* natural orbital of the P1=C2 double bond (Figure 3a), which lengthens Sb1–P2 and P1=C2 while

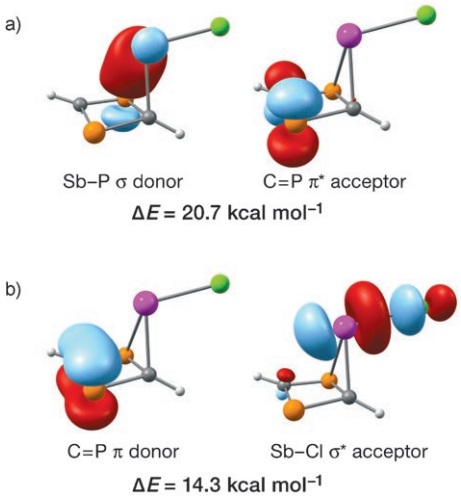

Figure 3. Natural bond orbitals and stabilization energies for the dominant donor–acceptor interactions of 1,2-ClSb-1,3-$P_2(CH)_2$. a) Sb–P σ donor orbital (left) and P=C π* acceptor orbital (right). b) P=C π donor orbital (left) and Sb–Cl σ* acceptor orbital (right). Sb pink, P orange, Cl green, C gray, H white.

reducing the Sb1–P1 distance. The second interaction is a π→σ* donation from the P1=C2 double bond to the Sb–Cl σ* orbital (Figure 3b), which pulls the SbCl fragment towards the double bond while lengthening both Sb1–Cl1 and P1=C2. The associated stabilization energies of 20.7 and 14.3 kcal mol^{-1} indicate a substantial departure from the idealized Lewis structure, in marked contrast to 1,2-HP-1,3-$P_2(CH)_2$. The first of these interactions (donation from P–P σ to C=P π*) is considerably reduced in magnitude (7.1 kcal mol^{-1}), while the second (donation from C=P π to P–H σ*) is almost completely absent (3.0 kcal mol^{-1}), consistent with the much higher energy of the P–H σ* orbital relative to Sb–Cl σ*. Hence, the NBO analysis identifies compact "cluster-like" bonding for $ClSbP_2(CH)_2$ that is quite distinct from the phosphorus analogue, 1,2-HP-1,3-$P_2(CH)_2$.

Despite the presence of phosphorus atoms in two distinct environments in the solid-state structure of **3**, its room-temperature $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 reveals only a single resonance at $\delta = 174.9$ ppm (singlet), which remains sharp even on cooling to 193 K. Similarly, the ^1H NMR spectrum (CD_2Cl_2) shows only a single resonance ($\delta =$ 1.12 ppm), the shape of which is also temperature-invariant, and the signals for the C*t*Bu groups in the ^{13}C NMR spectrum are both triplets as a result of bonding to two P atoms that are equivalent on the NMR timescale. The NMR data therefore indicate the presence of one or more processes that average both the phosphorus and C*t*Bu environments in solution.

We considered several dynamic processes that may account for this fluxionality,[13] and concluded the most likely mechanism was conceptually related to the "walk rearrangement" which has been extensively discussed for both housene and 1,2-HP-1,3-$P_2(CH)_2$. Here, the bridgehead group migrates in a series of 1,3 sigmatropic shifts around the edge of the ring and C_s-symmetric transition states lead to inversion of configuration at the bridgehead atom.[14,15] In the case of housene, the barrier to this 1,3 shift is rather large (31 kcal mol^{-1}) and the transition state has strong biradical character with one unpaired electron on the CH_2 fragment, the other delocalized in the allyl unit of the C_4 ring.[16] In contrast, we calculated barriers for migration of the PH unit over P and C of 10.8 and 31.0 kcal mol^{-1}, respectively, in the model system 1,2-HP-1,3-$P_2(CH)_2$.[15,17,18] The rather low barrier for the first process (**TS_a** in Figure 4) is certainly consistent with the reported presence of only a single resonance in the ^{31}P NMR spectrum of 1,2-[$CH(SiMe_3)_2$]P-1,3-$P_2(CtBu)_2$ down to 163 K.[12] The rather high-lying transition state for the 1,3 shift via the phosphorus center (**TS_b**) should, however, be sufficient to prevent free movement of the PR fragment around the entire C_2P_2 ring, leaving the C*t*Bu

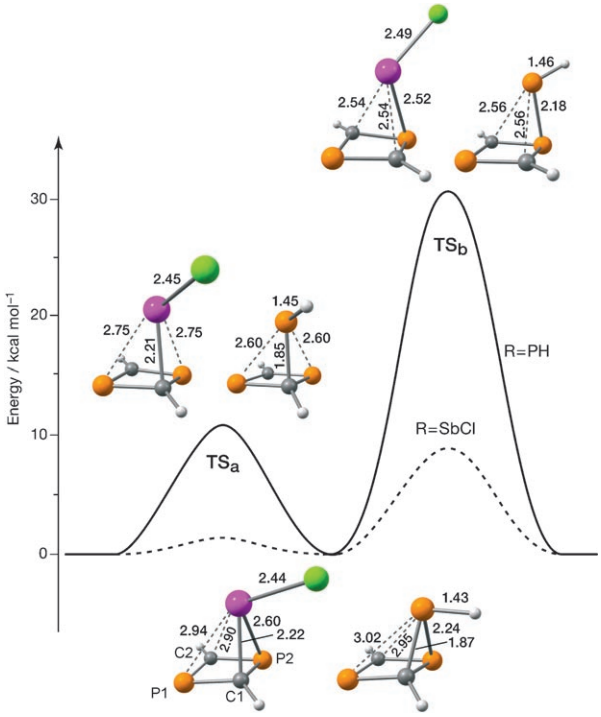

Figure 4. Comparison of the potential-energy surfaces for migration of PH (full line) and SbCl fragments (dashed line) around the C_2P_2 ring. All structures shown were optimized using DFT.

groups inequivalent on the NMR timescale. The initial communication reports only the ^{31}P NMR spectrum and not the complementary ^{1}H and ^{13}C NMR data, so we are unable to confirm this by comparison to experiment.

In the model antimony species, 1,2-ClSb-1,3-$P_2(CH)_2$, the barrier to migration via a carbon center on the ring is reduced to only 0.6 kcal mol^{-1} (**TS$_a$**), indicating that the SbCl fragment is free to move almost unimpeded around the P-C-P unit. To understand this reduction in the barrier from 10.8 kcal mol^{-1} in 1,2-HP-1,3-$P_2(CH)_2$ to less than 1 kcal mol^{-1} for the antimony analogue, we need look no further than the equilibrium structure of **3**, and in particular its compact cluster-like geometry. As a result of the inward tilt, the two Sb–P bonds are very similar even at equilibrium (Figure 2), and so although the motion can be categorized formally as a 1,3 sigmatropic shift, in reality only a very minor displacement of the Sb center is required to interconvert the two isomers.[19] The more delocalized bonding in the antimony case has an even more profound influence on the alternative migration pathway involving cleavage of the Sb–C bond. The barrier of 28.7 kcal mol^{-1} in 1,2-HP-1,3-$P_2(CH)_2$[17] is reduced to only 8.6 kcal mol^{-1} in 1,2-ClSb-1,3-$P_2(CH)_2$ (**TS$_b$** in Figure 4). The structure of **TS$_b$** is quite distinct from the corresponding stationary state in its phosphorus analogue 1,2-HP-1,3-$P_2(CH)_2$ because the antimony center remains centrally located above the C_2P_2 ring, and so the loss of bonding to one carbon center is significantly compensated by enhanced overlap with the other.

Thus, although the 1,3 sigmatropic shifts in 1,2-HP-1,3-$P_2(CH)_2$ and 1,2-ClSb-1,3-$P_2(CH)_2$ are superficially similar, the nature of the electron redistribution in the two cases is fundamentally different. In the case of 1,2-HP-1,3-$P_2(CH)_2$, the 1,3 sigmatropic shift is probably best considered as localized P–P bond cleavage process, and the rather strong P–C bond prevents free movement of the PH unit around the entirety of the P_2C_2 moiety. In contrast, the corresponding process in 1,2-ClSb-1,3-$P_2(CH)_2$ is more accurately envisaged as the migration of an SbCl unit around a continuous ring of electron density formed by the C_2P_2 unit. In the case of **3**, therefore, the SbCl unit is able to migrate around the whole circumference of the C_2P_2 ring with a maximum barrier of only 9 kcal mol^{-1}, which leads to the equivalence of both phosphorus and C*t*Bu units on the NMR timescale. The observed disorder in the crystal structure of **3** may be an experimental manifestation of this fluxionality.

In summary, the synthesis and structural characterization of **3**, along with a detailed analysis of its electronic structure, has revealed a number of distinct differences in the bonding and topology induced by the replacement of a PH or PCl fragment with isolobal SbCl. The relative weakness of the Sb–P bonds and the electron-deficiency of the Sb center lead to a compact, cage-like structure, and also to facile migration of the bridging SbCl unit.

Experimental Section

All experimental procedures were performed under an atmosphere of nitrogen or argon by using standard Schlenk line and glovebox techniques.

3: Compound **1** (0.21 g, 0.5 mmol)[1] was dissolved in *n*-hexane (10 mL) and reacted with two equivalents of antimony trichloride (0.22 g, 1 mmol) for 2 h. The by-product, [Cp_2ZrCl_2], was separated from the reaction mixture by filtration through Celite, and storage of the resulting yellow solution for 16 h at −15 °C afforded yellow cubic crystals of **3**. The yield was quantitative (according to NMR spectrosopic analysis). These crystals decomposed upon attempted isolation which resulted in limited physical data on the crystalline material. The following data were obtained from solutions of **3** and the single-crystal X-ray diffraction study.

$^{31}P\{^1H\}$ NMR (121.45 MHz, 21 °C, CD_2Cl_2): $\delta = 174.9$ ppm; ^1H NMR (270.16 MHz, 21 °C, CD_2Cl_2): $\delta = 1.12$ ppm (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100.54 MHz, 21 °C, CD_2Cl_2): $\delta = 31.8$ (t, $^3J_{CP}$ 4 Hz, $C(CH_3)_3$), 35.9 (t, $^2J_{CP}$ 5 Hz, $C(CH_3)_3$), $C_2tBu_2P_2$ not observed. MS (EI): *m*/*z*: observed 355.9617 [M^+], calculated 355.9610.

Single-crystal X-ray diffraction data for **3**: $C_{10}H_{18}ClP_2Sb$, $M_r = 357.38$ g mol^{-1}, crystal dimensions $0.05 \times 0.05 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$, $a = 6.2063(1)$, $b = 10.1944(2)$, $c = 12.2553(2)$ Å, $\alpha = 73.797(1)$, $\beta = 77.887(1)$, $\gamma = 73.967(1)$°, $V = 708.15(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.676$ Mg m^{-3}, $\mu = 19.039$ mm^{-1}, $\theta = 3.80$–69.96°, 5492 measured reflections, 2401 independent reflections, $R_{int} = 0.0386$, $R_1(I > 2\sigma)$ 0.0388, wR_2 (all data) = 0.1132. Diffraction data were collected at 100(2) K on a Bruker PROTEUM CCD three circle diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The structure was solved by direct methods and refined by full-matrix least squares using the SHELX suite of programs (v5.1, Sheldrick, 1998).[26] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. The two P and the Sb atoms are disordered over two sites which were refined with partial occupancies (90:10). Because the occupation of the minor occupancy site is low, equivalent distances were constrained to be similar to ensure a stable refinement. CCDC-606634 contains 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 methods: Full geometry optimizations were performed with the B3LYP functional[20] using flexible polarized basis sets of the cc-pVTZ family.[21] For Sb we used Peterson's cc-pVTZ-PP basis set that incorporates the small-core MCDHF-adjusted relativistic pseudopotential of Metz, Stoll, and Dolg.[22] Transition states were located with the STQN algorithm,[23] and all stationary points were characterized as minima or first-order saddle points by their harmonic vibrational frequencies. All calculations as well as the NBO analysis[24] were carried out with the Gaussian 03 series of programs.[25]

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[13] We have considered other possible dynamic processes, notably autoionization to give the known $[C_2tBu_2P_2Sb]^+$ cation (see reference [5]) and Cl^-, and a "back-flip" mechanism in which the SbCl unit migrates from one side of the C_2P_2 ring to the other. For autoionization, the computed heterolytic Sb–Cl bond dissociation energy in CH_2Cl_2 solution is rather high (+25 kcal mol^{-1}), casting some doubt on the viability of this pathway. For the "back-flip" mechanism, the pyramidal (C_{2v}-symmetric) structure that lies at the midpoint of this pathway is a second-order saddle point, as distinct from a transition state.
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