Molecular structure of tris(pentafluoroethyl)phosphane P(C_2F_5)_3

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The structure of tris(pentafluoroethyl)phosphane, P(C_2F_5)_3, has been determined in the solid state by in-situ single crystal growth and subsequent X-ray diffraction and in the gas phase by electron diffraction. The experimental structure determinations have been supported by and compared with quantum chemical calculations at different levels of theory. P(C_2F_5)_3 prefers a conformation of C_3 symmetry with the CF_3 groups of the three C_2F_5 units oriented to the same side of the molecule as the phosphorus lone pair of electrons, leading to an estimated Tolman cone angle of 193° (solid) and 191° (gas), whereas a second stable conformer of C_3 symmetry, (only 5 kJ mol\(^{-1}\) higher in energy) has a smaller Tolman cone angle of 171°. The structures are discussed in context with related molecules E(CF_3)_3 (E = N, P, As, Sb) as well as N(C_2F_5)_3 and P(C_2H_5)_3.

Dedicated to Professor David W. H. Rankin on the occasion of his 65\(^{th}\) birthday

Introduction

Electron poor ligands such as perfluoroorganophosphane ligands are useful tools to tune the redox potential as well as the Lewis-acidity of corresponding transition metal complexes.\(^{1}\) One of the most electron poor and therefore strong 𝛾-acidic perfluoroorganophosphane ligands is tris(trifluoromethyl)phosphane, P(CF_3)_3, which is known to form stable transition metal complexes.\(^{2}\) The synthesis of P(CF_3)_3 complexes requires special safety precautions because P(CF_3)_3 (b. p. 17°C)\(^{3}\) reacts violently on contact with air,\(^{4}\) while the less volatile homologue P(C_2F_3)_3 (b. p. 62°C)\(^{5}\) can be handled by standard Schlenk techniques. Therefore it is reasonable to substitute the potentially hazardous P(CF_3)_3 ligand by the P(C_2F_5)_3 ligand which is easy to handle as well as easily accessible. Tris(pentafluoroethyl)phosphane is accessible on a large scale via the reduction of P(CF_2H_5)_3 by the reaction of Me_3SiC_F_3 with P(OPh)_3.\(^{5}\)

Based on DFT calculations, the electronic nature of the P(CF_3)_3 and P(C_2F_5)_3 ligand should be comparable. The Tolman electronic parameter (TEP) is defined as the A_1 CO-valence mode of the corresponding [Ni(CO)_5PR_3] complexes. For P(CF_3)_3 and P(C_2F_5)_3, the calculated TEPs of 2104.4 and 2102.9 cm\(^{-1}\), respectively, are nearly identical.\(^{6}\)

The reaction of [Mo(CO)_5(nbd)] (nbd = norbornadiene) with P(CF_3)_3 leads within hours at room temperature to a nearly quantitative formation of the literature known complex [Mo(CO)_5(P(CF_3)_3)].\(^{8}\) By contrast, the reaction with P(C_2F_5)_3 proceeds much slower and results after a prolonged reaction time mainly in the formation of decomposition products. To demonstrate the different coordination properties of P(CF_3)_3 and P(C_2F_5)_3, [Mo(CO)_5(nbd)] was treated with an excess of a mixture of P(CF_3)_3 and P(C_2F_5)_3 yielding only the bis[tris(trifluoromethyl)phosphane] complex [Mo(CO)_5[P-CF_3H_3][P-C_2F_5H_3]]. Based on these observations, sterical reasons may be the cause of the different coordination properties of the P(CF_3)_3 and P(C_2F_5)_3 ligand.

Herein we report the molecular structure of tris(pentafluoroethyl)phosphane, P(C_2F_5)_3, in the gas and solid phases. The structures explain the significantly different coordination properties of the P(CF_3)_3 and P(C_2F_5)_3 ligand.

Results and discussion

Crystal Structure

P(C_2F_5)_3 crystallises in the trigonal space group R3, with a molecular structure belonging to the C_3 point group, as shown in Figure 1 and 2. The lone pairs on phosphorin in adjacent molecules oppose one another, but the P···P distance is longer than the sum of van-der-Waals radii. The values of structural parameters are presented in the following discussion, alongside those for the theoretical and experimental structures in the gas phase.

Figure 1 Crystal structure of P(C_2F_5)_3 showing the atom numbering and the unit cell viewed along the c-axis.
Ab initio and Hybrid Density-Functional Calculations

The electronic structure calculations were performed, primarily, to assist the determination of the experimental gas-phase structure by GED. In particular, potential energy scans were used to search for probable conformers. Geometry optimisations were performed to estimate the relative energies of local minima on the potential-energy surface (PES) and as flexible restraints on some geometric parameters in the GED refinement. Finally, frequency calculations were used to confirm the nature of the stationary points on the PES and, in combination with the program SHRINK, to provide approximate values for the amplitudes of vibration, \( u \), and distance corrections for curvilinear perpendicular motion, \( k_{h1} \).

Predicted Conformations of \( \text{P}(\text{C}_2\text{F}_5)_3 \) in the Gas Phase

The three \(-\text{C}_2\text{F}_5\) groups allow a large number of possible conformations, making a systematic search of all conformations by \textit{ab initio} methods impractical. However, as this molecule adopts \( C_3 \) symmetry in the solid phase, and does not possess any inter-atomic contacts shorter than the sum of van-der-Waals radii, it is likely that the lowest-energy gas-phase structure also has this symmetry. Potential energy scans were performed for torsion around the \( \text{P}–\text{C} \) bonds, allowing all other parameters to relax within the constraint of \( C_3 \) symmetry, as shown in Figure 3.

This reveals two low-energy local minima at ca. 30° and 65°, denoted A and B, with a potential energy barrier of ca. 10 to 20 kJ mol\(^{-1}\) between them. A is close to the crystal structure, for which the corresponding dihedral angle is 29.8(1)°. Both A and B were confirmed as minima on the full potential-energy surface by further geometry optimisations and frequency analyses, without symmetry constraints. Such close minima, separated by only 35°, but with an appreciable energy barrier between them are unusual and appears to be a result of steric repulsion between fluorine atoms on adjacent \( \text{C}_2\text{F}_5 \) groups. The correlation between the calculated energy and the shortest non-bonded \( \text{F}···\text{F} \) distance on neighbouring fluoroethyl groups can be seen by comparing Figures 3 and 4. This reveals that all three local minima in the potential energy curve correspond to structures where the shortest non-bonded \( \text{F}···\text{F} \) distance is longer than the sum of the van-der-Waals radii of two fluorine atoms.
A search for asymmetric conformers representing minima on the potential-energy surface was carried out by identifying conformers for which repulsive F····F contacts would be minimised. Potential structures were optimised at the HF/6-31G* level of theory and subjected to frequency analysis. In this way, three asymmetric conformers were found, with energies calculated to be 9.2, 7.2 and 11.6 kJ mol⁻¹ higher than that of A. These energies are relatively high and, if correct, these conformers are unlikely to be observable in the GED experiment, despite the lower symmetry compared to A. The highest energy conformer was therefore not subjected to further study, but the geometries of the remaining two structures (C and D) are shown in Figure 5 alongside those of the C₃ symmetric conformers, A and B.

Relative Energies of conformers A, B, C and D

As can be seen from Table 3, the relative electronic energies of A and B vary with the level of theory applied. Considering that an energy difference of 1 kJ mol⁻¹ can significantly change the population of a species, the discrepancy of ca. 8 kJ mol⁻¹ between HF and MP2 theory is a large disagreement. Fluorine is known to be problematic for calculating electron correlation and the apparent importance of steric F····F interactions in this compound may exacerbate this problem. However, the 6-31G* basis is not well balanced for MP2 and this may also be playing a role. The MP2 method was found to be prohibitively expensive for larger basis sets, but it was possible to optimise the geometry using the RI-MP2 method¹⁰⁻¹³ with the larger TZVPP basis set,¹⁴ yielding the energies in Table 1.

In addition to the problem of calculating the electronic energy, the zero-point energy corrections and thermal contributions to the free energy may be quite different for each conformer. The free energy differences were calculated for all four conformers at the HF/6-31G* and B3LYP/6-311G* levels using the harmonic-oscillator and rigid-rotor approximations, and are shown alongside the electronic energy in Table 1. The differences between the values of ΔE and ΔG are almost entirely due to the thermal contributions to the free energy, as the calculated zero-point-energy corrections differ by no more than 0.4 kJ mol⁻¹ (at a given level of theory).

Table 1: Calculated relative electronic and free energies (ΔE and ΔG, respectively) in kJ mol⁻¹, at various levels of theory, and the corresponding abundances for the MP2 calculation.

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Sym</th>
<th>HF/6-31G*</th>
<th>B3LYP/6-311G*</th>
<th>RI-MP2/TZVPP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE</td>
<td>ΔG</td>
<td>ΔE</td>
<td>ΔG</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>7.14</td>
<td>10.88</td>
<td>3.23</td>
<td>4.75</td>
</tr>
<tr>
<td>C</td>
<td>9.21</td>
<td>10.33</td>
<td>5.45</td>
<td>4.14</td>
</tr>
<tr>
<td>D</td>
<td>7.23</td>
<td>8.56</td>
<td>4.82</td>
<td>2.68</td>
</tr>
</tbody>
</table>

* Calculated using ΔE at the RI-MP2/TZVPP level of theory.

Theoretical geometries

The convergence of the calculated geometric parameter values (for conformer A) can be seen from Table 2. The effect of increasing the basis-set size can be gauged by comparing the HF/6-31G* and HF/TZVPP parameter values as well as those at the B3LYP level of theory, where different basis sets have been used. These effects are small, with bonded distances changing by little more than 1 pm as the basis set is increased from double- to triple-zeta quality. In terms of the effect of the level of theory, the agreement between HF and MP2 is remarkably good, the only significant disagreement being the average C–F distance, which HF is expected to underestimate. The hybrid density functionals predict longer bonded C–P and C–C distances and, given the good agreement between HF and MP2, are unreliable. The remaining parameter values are, however, in good agreement. The calculated (RI-MP2/TZVPP) geometries and energies of all four conformers are provided as supporting information.

Table 2: Values of selected geometric parameters for conformer A at various levels of theory. Distances are in Å and angles are in degrees.¹⁵

<table>
<thead>
<tr>
<th></th>
<th>HF 6-31G*</th>
<th>HF TZV</th>
<th>MP2 6-31G*</th>
<th>MP2 TZV</th>
<th>B3LYP 6-31G*</th>
<th>B3LYP TZV</th>
<th>B3PW 6-31G*</th>
<th>B3PW TZV</th>
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<tr>
<td>r_CCF</td>
<td>1.900</td>
<td>1.912</td>
<td>1.909</td>
<td>1.924</td>
<td>1.931</td>
<td>1.937</td>
<td>1.928</td>
<td></td>
</tr>
<tr>
<td>r_CCP</td>
<td>1.533</td>
<td>1.545</td>
<td>1.547</td>
<td>1.548</td>
<td>1.554</td>
<td>1.556</td>
<td>1.554</td>
<td></td>
</tr>
<tr>
<td>r_CFP</td>
<td>1.320</td>
<td>1.312</td>
<td>1.337</td>
<td>1.347</td>
<td>1.344</td>
<td>1.342</td>
<td>1.337</td>
<td></td>
</tr>
<tr>
<td>∠_CCF</td>
<td>99.0</td>
<td>99.9</td>
<td>98.2</td>
<td>97.9</td>
<td>98.5</td>
<td>98.8</td>
<td>99.1</td>
<td></td>
</tr>
<tr>
<td>∠_CCP</td>
<td>113.3</td>
<td>112.6</td>
<td>111.3</td>
<td>111.7</td>
<td>111.6</td>
<td>111.8</td>
<td>111.3</td>
<td></td>
</tr>
<tr>
<td>∠_FFP</td>
<td>30.6</td>
<td>30.2</td>
<td>30.3</td>
<td>30.7</td>
<td>30.3</td>
<td>30.4</td>
<td>29.8</td>
<td></td>
</tr>
</tbody>
</table>

* The TZVPP basis set is similar in size and construction to cc-pVTZ.
Gas Electron Diffraction (GED)

GED Model. C₃ symmetry was assumed in the molecular model, which reduces the number of required parameters from 60 to 20. In addition, local C₃ᵥ symmetry was assumed for the CF₃ group and, on the basis of the ab initio calculations, all F–C–F angles were assumed to be equal. The geometry was therefore described in terms of 13 independent parameters, as shown in Table 3. Parameters p₉ to p₁₁ are deviations of the – CF₃ group from local C₃ᵥ symmetry (with respect to the bond angles) and each of these was defined as a rotation around one of three orthogonal vectors centred at C(1). The ‘rock’ (p₉) denotes a rotation of the fluorine atoms around a vector normal to the P–C–C plane, where a positive value is an increase in the P–C–F angles at the expense of the C–C–F angles. The ‘twist’ angle (p₁₀) is a rotation around the bisector of the unit vectors in the directions of the C–P and C(1)–C(2) bonds, a positive value indicating increases in the angles ∠P–C–F(2) and ∠C–C–F(1). The ‘wag’ is therefore a rotation around a vector approximately normal to the F–C–F plane, where a positive value is defined as an increase in the angles ∠P–C–F(2) and ∠C–C–F(2).

Table 3 Refined gas-phase geometric parameters and applied restraints. Distances are in Å and angles are in degrees.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GED(r₉)</th>
<th>GED(r₃)</th>
<th>RI-MP2(r₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p₁</td>
<td>1.904(3)</td>
<td>1.901(3)</td>
<td>1.909</td>
</tr>
<tr>
<td>p₂</td>
<td>r–C–C</td>
<td>1.533(3)</td>
<td>1.524(4)</td>
</tr>
<tr>
<td>p₃</td>
<td>r–C–F average</td>
<td>1.339(1)</td>
<td>1.338(1)</td>
</tr>
<tr>
<td>p₄</td>
<td>r–C–F diff. (CF₃– CF₃)</td>
<td>0.016(2)</td>
<td>0.017(2)</td>
</tr>
<tr>
<td>p₅</td>
<td>r–C–F diff. (CF₃ group)</td>
<td>0.007(2)</td>
<td>0.006(2)</td>
</tr>
<tr>
<td>p₆</td>
<td>∠C–P–C</td>
<td>100.1(2)</td>
<td>99.9(3)</td>
</tr>
<tr>
<td>p₇</td>
<td>∠P–C–C</td>
<td>113.9(3)</td>
<td>113.2(3)</td>
</tr>
<tr>
<td>p₈</td>
<td>∠F–C–F</td>
<td>108.0(1)</td>
<td>108.0(1)</td>
</tr>
<tr>
<td>p₉</td>
<td>∠CF₃ rock</td>
<td>3.5(3)</td>
<td>3.9(4)</td>
</tr>
<tr>
<td>p₁₀</td>
<td>∠CF₃ twist</td>
<td>0.5(3)</td>
<td>0.4(4)</td>
</tr>
<tr>
<td>p₁¹</td>
<td>∠CF₃ wag</td>
<td>4.3(4)</td>
<td>4.8(4)</td>
</tr>
<tr>
<td>p₁²</td>
<td>ϕ–P–C–C</td>
<td>30.8(5)</td>
<td>31.0(5)</td>
</tr>
<tr>
<td>p₁³</td>
<td>ϕ–P–C–C–F</td>
<td>182.2(9)</td>
<td>182.1(10)</td>
</tr>
<tr>
<td>R₀</td>
<td>4.70%</td>
<td>7.18%</td>
<td>–</td>
</tr>
</tbody>
</table>

GED Refinement. The GED refinement was performed according to the SARCEN method, allowing all thirteen independent geometric parameters to be refined, eight of which refined unrestrained. The resulting parameter values are shown in Table 3. In addition, ten groups of amplitudes of vibration were refined, each corresponding to a single peak in the radial-distribution curve. These were restrained to the B3LYP/6-311G* values, with uncertainties of 10 % of the calculated values. A full list of inter-nuclear distances, camera-to-nozzle distances, electron wavelengths, data cut-offs and weighting points; the least-squares correlation matrix can be found in supplementary information (Tables S1, S2 and S3). The single-conformer model gave a good fit to the experimental data, as shown by the molecular-intensity and radial-distribution curves (Figures 7 and 8, respectively).
Whilst the refined parameter values are similar for the $r_e$ and $r_{ab}$ refinements (Table 3), the quality of fit is substantially better for the $r_{ab}$ structure type, reducing the $R$-factor from 7.18 to 4.70%.

Figure 8 Experimental and difference (experimental minus theoretical) radial-scattering curves. Prior to Fourier transformation, the molecular-scattering intensities were multiplied by $s \exp(-0.00003c(yZ_C - f_C)(Z_D - f_D))$.

**Discussion**

The molecular-structure parameters determined by the three methods used (single crystal XRD, ab initio calculations and GED) are compared in Table 4. These three methods are in good agreement, indicating that the effects of crystal packing are small. Even the torsional angle around the P–C bond ($\phi$...P–C–C) is virtually the same in the solid phase 29.8(1)° and in the gas phase 30.8(5)°. A couple of small differences can also be seen between the calculated equilibrium geometry and the experimental GED structure, where the XRD structure is most similar to the calculated geometry, namely, the C–C distance and the P–C–C angle. As can be seen from Table 3, the C–C distance is one of the few parameters that is dependent on the structure type and increases from 1.524(3) to 1.533(3) with the inclusion of curvilinear distance corrections in the structure refinement. As the distance corrections are fixed, the uncertainty on this value is larger than the standard deviation obtained from the least-squares fit. The P–C bond length is overestimated by ca. 3 pm by B3LYP and ca. 2 pm by B3PW91 (with the relatively large cc-pVTZ basis set). In general, however, the parameter values predicted by B3PW91 are slightly better than those predicted by B3LYP (where the solid- and gas-phase structures are in good agreement).

Data for comparison of the structure of P(CF$_3$)$_3$ with related compounds are presented in Table 5. Such include the trifluoromethylpnictogenes N(CF$_3$)$_3$, P(CF$_3$)$_3$, As(CF$_3$)$_3$, and Sb(CF$_3$)$_3$, the pentafluoroethyl nitrogen analogue N(CF$_3$)$_3$, and the non-fluorinated analogue P(CH$_3$)$_3$. The value for the P–C bond length for P(CF$_3$)$_3$ at 1.937(17) Å seems somewhat larger than that in P(CF$_3$)$_2$ at 1.904(3) (gas phase), but is equal considering the large standard deviation for P(CF$_3$)$_2$ (and Sb(CF$_3$)$_2$) due to the structure determinations have been done at that time without least squares fitting and rotating sector device in the diffractometer (we have recently reinvestigated the structure of As(CF$_3$)$_3$ with modern instr-
mentation and advanced data analysis procedures and could drastically improve the accuracy). Expectedly one observes for the trifluoromethylpnicogenes $E\{CF\}_3, E = N, P, As, Sb$ a drastic decrease of the C-E-C angle from $E = N$ to $P$. There is a slight widening of this C-N-C angle from N($CF\)_3 to N($CF\)_5, but both are unusually large, even for amines, reflecting the unusual steric and electronic situation in such almost planarised nitrogen compounds. However, the C-P-C angles in P($CF\)_3 and P($CF\)_5 (solid and gas) are remarkably similar, showing the very comparable demand for space directly at the phosphorus atom (but again, an exact comparison is hampered by the low accuracy of the old P($CF\)_3 structure). Interestingly this angle is not affected by fluorination of the ethyl groups, as P($C\)H\)_3 has almost the same value for this structural parameter.

The most interesting parameter to look at is the torsion of the ethyl groups, as this defines the orientation of the latter and ultimately the accessibility of the pnicogen atom expressed by the Tolman angle for the purpose of describing their binding properties as Lewis-basic ligands towards metal atoms. This torsion, defined relative to the lone pair of electrons position, i.e. relative to the axis of symmetry (where applicable). In this respect, there is a marked difference between the nitrogen and phosphorus compounds, as for N($C\)F\)_3, its almost planar nitrogen coordination geometry the torsion angle is 147.0(5)°, whereas for the phosphorus analogue it is 30.8(5)°, both in the gas phase. As pointed out earlier, the conformation of P($CF\)_3 seems to be determined by intergroup F-F contacts and thus a difference should be expected in this structural feature between P($C\)F\)_3 and the non-fluorinated P($C\)H\)_3. Indeed there is a larger torsional angle for P($C\)H\)_3 at 48°–50° for the three crystallographically different ethyl groups.

**Conclusion**

The Tolman cone angle is one of the most established models to describe the steric bulk of phosphine ligands. The cone angle of the conformer A of P($C\)F\)_3 (comp. Figure 5) was calculated to be 193° in the solid state (XRD) and 191° in the gas phase (GED) (calculated for a hypothetical P-M distance of 2.28 Å and a F van-der-Waals radius of 1.50 Å). Based on DFT calculations, the P($C\)F\)_3 ligand will favour a B type conformer (conf. Figure 5) in the coordination sphere of a Ni(CO)\(_3\) moiety, which reduces the cone angle to about 171° (based on the calculations on conformer B described above).

These cone angles exceed the cone angle - - the steric bulk - of the P($CF\)_3 ligand significantly and classify the P($C\)F\)_3 ligand as a sterically demanding ligand. Tolman published a cone angle of 137° for the P($C\)F\)_3 ligand, which will be reduced to 128° in the coordination sphere of the iron complex [Fe(CO)\(_3\)][P($CF\)_3]. These considerably different steric bulks might be one reason for the distinctly different reactivity of P($CF\)_3 and P($C\)F\)_3 towards [Mo(CO)\(_3\)(nbd)]. In addition, this fact might also be the reason why no example of a P($C\)F\)_3 transition metal complex is known so far.

At first view the different coordination properties of the P($CF\)_3 and P($C\)F\)_3 ligands may be a surprise because the substitution of only one perfluoroorganogroup by a less sterically demanding non fluorinated alkyl group leads to ligands of nearly comparable cone angles. The estimated cone angles of the most commonly used bidentate bis(perfluoroorganoyl)-phosphane ligands (CF\)_3)(PCH\(_2\)CH\(_2\))(P($CF\)_3) and (C\)F\)_3)(PCH\(_2\)CH\(_2\))(P($C\)F\)_3) are estimated to be 120° and 129°, respectively. Further investigations are in progress to obtain evidence about the complexation ability of P($C\)F\)_3 and to answer the question which of the conformers A and B (or even C and E, see Figure 5) will be presumably favoured by P($C\)F\)_3 in the role of a ligand.

**Experimental**

**Crystal Structure Determination**

A single crystal of tri-pentafluoroethyl phosphane (PFEP), P($C\)F\)_3, was grown in a sealed glass capillary, in situ on a Nonius Kappa CCD diffractometer at ca. 200 K. The crystal was then cooled to 100(2) K for data acquisition.

**Crystal data.** C\(_3\)F\(_3\)P, $M = 388.03$, trigonal, space group $R\overline{3}$. $a = 13.4590$ (4), $c = 10.8110$ (3), $V = 1695.98$ (9) $Å^3$, $T = 100$ (2) K, $Z = 6$, $\mu$(Mo-K\(_α\)) = 0.443 mm\(^{-1}\), 6601 reflections measured, 1086 unique ($R_{int} = 0.028$). Structure solutions and refinements were undertaken with the programs SHELXS-97 and SHELXL-97. Final $R_1$, $wR_2$ values on all data 0.0309, 0.0781. $R_1$, $wR_2$ values on $I > 2\sigma(I)$, 1009 reflections) data 0.0287, 0.0765. CCDC reference number XXX. For crystallographic data in CIF or other electronic format see DOI: XXX/bXXXXx.

**Ab initio and Hybrid DFT Calculations**

The majority of calculations were performed using the Gaussian 03 suite of programs, the exceptions being the RI-MP2/TZVPP calculations, which were performed using the Turbomole\(^{29}\) program. All calculations were restricted and MP2 calculations were performed with frozen cores. The B3LYP and B3PW91 make use of Becke’s three parameter hybrid functional, where the non-local correlation energy is provided by the LYP expression\(^{11}\) in B3LYP and by the Perdew-Wang expression\(^{32}\) in B3PW91.

**GED**

Electron scattering intensities for P($C\)F\)_3 were recorded at room temperature on combination of reusable Fuji and Kodak imaging plates using a Balzers KD-G2\(^{53}\) Gas-Eldigraph (formerly operated in Tübingen by H. Oberhammer\(^{44}\), equipped with a new electron source (STAIB Instruments), operating at ca. 60 kV. The image plates that were exposed at the shorter nozzle-to-plate distance (252.78 mm) were scanned using a Fuji FLA 3000 scanner, whilst those recorded at the longer distance (501.88 mm) were scanned using a Fuji BAS 1800 scanner. In both cases the scanning software yielded digital 16-bit grey-scale image data. These data were reduced to total intensities using T. G. Strand’s program PIMAG\(^{35}\) (version 040827) in connection with a sector curve, which was based on experimental xenon scattering data and tabulated scattering factors of xenon. Further data reduction (yielding
molecular-intensity curves), the molecular structure refinement, and the electron wavelength determination (from benzene data) were performed using versions 2.4 of the ed@ed program. The scattering factors employed were those of Ross et al. Further details about the Bielefeld GED apparatus and methods are to be published elsewhere. Table S1 (see supplementary information) gives the data analysis parameters for each data set: R-factors ($R_p$ and $R_e$), scale factors, correlation parameter values, data ranges, weighting points, nozzle-to-plate distances and electron wavelengths. Amplitudes of vibration, $u$, and distance corrections for curvilinear perpendicular motion, $k_{31}$, were calculated using the program SHIRMD, making use of frequency calculations at the B3LYP/6-311G* level of theory.

### Acknowledgements

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### Notes and references


Molecular Structure of Tris(pentafluoroethyl)phosphane \( \text{P}(\text{C}_2\text{F}_5)_3 \)

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The structures of tris(pentafluoroethyl)phosphane, \( \text{P}(\text{C}_2\text{F}_5)_3 \), determined in the solid and gaseous phases, show it to have a preferred conformation with a sterically shielded binding site; this is expressed by a Tolman angle of ca. 191° (gas) and explains the greater difficulty to act as ligand towards metal atoms as compared with the slimmer \( \text{P}(\text{CF}_3)_3 \).