

The molecular structure of $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$ using gas-phase electron diffraction and DFT calculations†

Derek A. Wann,^a Sarah L. Hinchley,^a Konstantin B. Borisenko,^a Heather E. Robertson,^a Matthew D. Francis,^b John F. Nixon^b and David W. H. Rankin^a

^a School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ.

E-mail: d.w.h.rankin@ed.ac.uk

^b Department of Chemistry, School of Life Sciences, University of Sussex, Falmer, Brighton, UK BN1 9QJ

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The molecular structure of 2,4-di-*tert*-butyl- η^4 -1,3-diphosphacyclobutadiene tin has been determined in the gas phase by electron diffraction using both the DYNAMITE and SARACEN methods. The suitability of many different theoretical methods for the calculation of structures of half-sandwich main-group metal complexes has been investigated, and, by comparison of the results with the experimental structures, suggestions have been made as to the most suitable methods for this class of compound.

Introduction

The past decade has seen a rapid development of a rich new area of organometallic chemistry in which phosphorus atoms replace CH- or CR-fragments in the more familiar unsaturated organic ligands.^{1,2} An extensive range of “phospha-organometallic” compounds containing phospha-alkynes, phospha-alkenes, phospha-dienes, phospha-allyls, phospha-cyclobutadienes, phospha-cyclopentadienyls, phospha-arenes, tetraphospha-cubanes and tetraphospha-barrelenes has been described. Furthermore, these phospha-organometallic compounds have the important additional potential to act as ligands, in view of the availability of their phosphorus lone pair electrons. Activity in this area has been comprehensively reviewed.^{3–12}

We, and others, have been particularly interested in the generation of novel unsaturated ring systems containing more than one phosphorus atom by using the phospha-alkyne, Bu^tCP , as a synthon. Fig. 1 shows the ring systems that have been synthesised to date by a variety of routes.¹²

The first cyclo-dimerisation reactions of phospha-alkynes within the coordination sphere of a transition metal were independently reported in 1986 by Nixon¹³ and Binger,¹⁴ who synthesised and structurally characterised 1,3-diphosphacyclobutadiene compounds of the type $[\text{M}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-P}_2\text{C}_2\text{Bu}^t_2)]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{R} = \text{H} \text{ or } \text{Me}$), **1**. Since this early work, several other 1,2- and 1,3-diphosphacyclobutadiene transition-metal complexes have been reported; of special interest are those complexes containing no other attendant ligands (see Fig. 2).^{15–17}

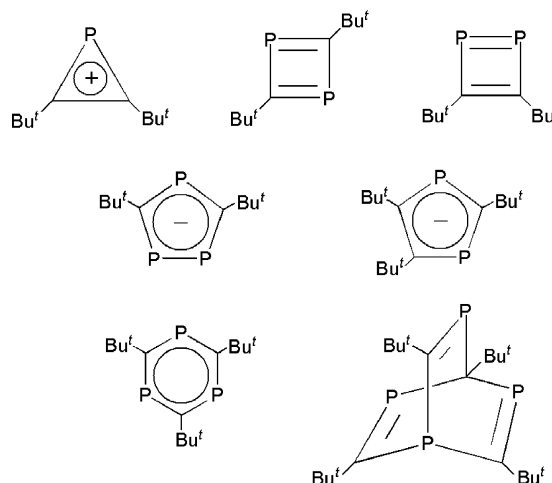


Fig. 1 Some unsaturated ring systems derived from the phospha-alkyne Bu^tCP .

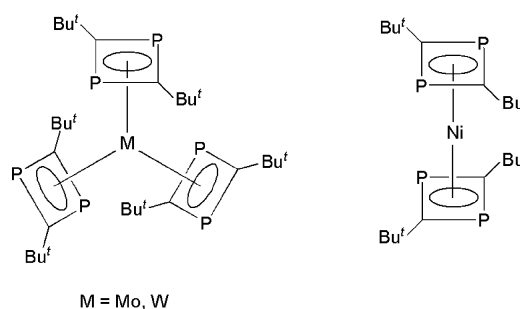
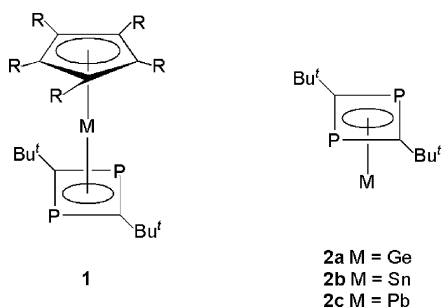


Fig. 2 1,3-diphosphacyclobutadiene complexes of Mo, W and Ni.

The first examples of main-group elements ligated to a 1,3-diphosphacyclobutadiene ring have been described only recently by Francis *et al.*^{18–20} The series of compounds of the type $[\text{M}(\eta^4\text{-P}_2\text{C}_2\text{Bu}^t_2)]$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$), **2a–c**, were made by treating $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2(\text{P}_2\text{C}_2\text{Bu}^t_2)]$ with the appropriate Group 14 metal dihalide. Single crystal X-ray diffraction studies show that in the solid state the 1,3-diphosphacyclobutadiene ring is coordinated to the metal in an η^4 -fashion and the half-sandwich compounds represent 24-electron *nido*-5-vertex structures. Since these compounds are formally derivatives of divalent metals, they can be considered as involving the $[\text{P}_2\text{C}_2\text{Bu}^t_2]^{2-}$ dianion.

† Electronic supplementary information (ESI) available: Table S1: Nozzle-to-film distances (mm), weighting functions (nm^{-1}), scale factors, correlation parameters and electron wavelengths (pm) used in the electron diffraction study of $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**. Table S2: Selected interatomic distances (r_s/pm) and amplitudes of vibration (u_{01}/pm) for the restrained GED structure of $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**. Table S3: Least-squares correlation matrix for $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**. Table S4: GED coordinates for $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**. Table S5: Calculated coordinates (B3PW91/6-31G*/LanL2DZ) for $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**. Table S6: Calculated coordinates (B3PW91/6-31G*/LanL2DZ) for $[\text{Sn}(\text{P}_2\text{C}_2\text{H}_5)_2]$, **3**. Table S7: Calculated coordinates (B3PW91/6-31G*) for $[\text{P}_2\text{C}_2\text{Bu}^t_2]$, **4**. Table S8: Calculated coordinates (B3PW91/6-31G*/LanL2DZ) for $[\text{Sn}(\text{C}_4\text{Bu}^t_2\text{H}_2)]$, **5**. Table S9: Calculated coordinates (B3PW91/6-31G*) for $[\text{Li}_2(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **6**. Fig. S1: Molecular-scattering intensity and final weighted difference curves for $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**, at nozzle-to-film distances of (a) 255 mm and (b) 86 mm. See <http://www.rsc.org/suppdata/dt/b4/b418171a/>



In view of very recent synthesis and structural characterisation of the dilithium salt of the related 1,3-diphosphacyclobutadiene dianion,²¹ $[\text{P}_2\text{C}_2(\text{SiMe}_3)_2]^{2-}$, and theoretical discussions of the aromaticity of the corresponding isoelectronic cyclobutadiene dianion,²² $[\text{C}_4\text{H}_4]^{2-}$, and its structurally characterised derivative $[\text{Li}_2\text{C}_4\text{R}_4]$ ($\text{R} = \text{SiMe}_3$),²³ we wish to report our studies concerning the gas-phase structure of $[\text{Sn}(\eta^1\text{-P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**, as determined by electron diffraction and theoretical methods.

Experimental

Synthesis

A sample of $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**, was prepared from SnCl_2 and $[\text{Zr}(\eta^1\text{-C}_5\text{H}_5)_2(\text{PCBu}^t_2)_2]$ according to the literature method.¹⁸

Theoretical methods

The majority of calculations reported in this work were performed on a Linux 12-Processor Parallel Quantum Solutions (PQS) workstation²⁴ running the Gaussian 98 suite of programs.²⁵ Calculations at the PBE1PBE level were run using the Gaussian 03 programs,²⁶ with the resources of the EPSRC National Service for Computational Chemistry Software, on a cluster of 6 HP ES40 computers. Each Alphaservert ES40 machine has four 833 MHz EV68 CPUs and 8 GB of memory. All MP2 calculations were frozen core.

A search of the potential-energy surface of **2b** was undertaken at the Hartree–Fock level of theory using a 3-21G* basis set²⁷ (HF/3-21G*) in order to locate any minima and a single structure with C_{2v} was identified.

A series of graded calculations was performed in order to gauge the effects of basis set size, use of effective core potentials and treatment of electron correlation on the optimised geometries. At the Hartree–Fock level of theory, where electron correlation is ignored, calculations were performed using the 6-31G* basis set²⁸ on C, P and H and, firstly, the LanL2DZ basis set²⁹ on Sn, then the Stuttgart/Dresden/Dunning (SDD) basis set,³⁰ and finally the SDB-aug-cc-pVTZ basis set,³¹ in order to investigate their suitability. Such basis sets were chosen for the tin atom because of their ability to provide a pseudopotential, as relativistic effects become important with heavier atoms, and, given that the effective core potential (ECP) reduces the number of electrons that must be considered, they reduce the time taken for the calculations.

The DFT methods that were used in this work are based on Becke's B3 electron-exchange functional³² and both the PW91³³ and LYP³⁴ correlation functionals. The PBE1PBE exchange–correlation functional of Perdew, Burke and Ernzerhof³⁵ was also used. Calculations comparing LanL2DZ, SDD and SDB-aug-cc-pVTZ on Sn were performed using the B3PW91, B3LYP and PBE1PBE functionals with various basis sets on C, P and H (6-31G*, 6-311G*, 6-311+G* and 6-311++G**).

Calculations at the MP2 level of theory³⁶ were performed using the same combinations of ECPs on Sn and other basis sets on the lighter atoms as described previously.

Based on the effects of different levels of theory and basis sets on the geometry of **2b**, the analytical force field was calculated at the B3PW91/6-31G* (LanL2DZ on Sn) level. This was used

to provide estimates of the amplitudes of vibration (u_{h1}) and the curvilinear corrections (k_{h1}), from the SHRINK program,³⁷ using in the gas-phase electron diffraction refinements.

An identical approach to that described above was adopted for geometry optimisation calculations to investigate the structures of three related molecules and fragments: $[\text{Sn}(\text{P}_2\text{C}_2\text{H}_2)]$, **3**, $[(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **4**, $[\text{Sn}(\text{C}_4\text{Bu}^t_2\text{H}_2)]$, **5**, and $[\text{Li}_2\text{P}_2\text{C}_2\text{Bu}^t_2]$, **6**.

Gas-phase electron diffraction (GED)

Data were collected for $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, **2b**, using the Edinburgh gas-phase electron diffraction apparatus.³⁸ An accelerating voltage of around 40 kV was used, equating to an electron wavelength of approximately 6.0 pm. Scattering intensities were recorded on Kodak Electron Image films at nozzle-to-film distances of 86.08 and 255.26 mm, with sample and nozzle temperatures held at 431 and 452 K respectively for the shorter distance and 424 and 429 K for the longer distance.

The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for both camera distances are given in Table S1 (ESI†). Also included are the exact electron wavelengths as determined from the scattering patterns for benzene that were recorded immediately after the patterns for **2b**. The scattering intensities were measured using an Epson Expression 1600 Pro Flatbed Scanner and converted to mean optical densities as a function of the scattering variable, s , using an established program.³⁹ The data reduction and the least-squares refinement processes were carried out using the ed@ed program⁴⁰ employing the scattering factors of Ross *et al.*⁴¹

Results and discussion

A large amount of work has been directed towards calculating the structures of transition-metal complexes incorporating ring systems. A review⁴² of the computational chemistry of metallocenes investigated the application of *ab initio* and DFT methods to model transition-metal complexes and in particular ferrocene. The M–Cp distance was identified as an appropriate parameter on which to judge the suitability of a calculation for such a molecule. *Ab initio* studies⁴³ of ferrocene at the HF level gave Fe–ring distances that were overestimated by up to 15% compared to experimental parameters and this phenomenon was shown to be independent of basis set. A further study⁴⁴ of transition-metal sandwich and half-sandwich compounds was carried out and aimed to investigate the correlation effects involved in optimising the M–Cp distance. This concluded that the bond length was insensitive to an improvement in basis set beyond double- ζ quality. A later study⁴⁵ applied MP2 perturbation theory to the problem with similarly unsatisfactory results. In that instance the Fe–Cp bond length in ferrocene was underestimated by more than 10 pm.

In contrast to the unsuccessful efforts to optimise the geometry of metallocenes *ab initio*, the application of DFT methods to these compounds has proved promising. In a study of ferrocene,⁴⁶ the use of a DFT method (LDA/NL) returned an Fe–Cp distance to within 1 pm of experimental values (electron diffraction). DFT methods have also been used to investigate the structures of substituted ferrocenes with good results.⁴⁷

Recently, photoelectron spectroscopic measurements and/or DFT calculations have given information about the electronic structures of the following phospho-metallocenes $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)]$ ($\text{M} = \text{Ti}, \text{Fe}, \text{Ru}$); $[\text{M}(\eta^5\text{-P}_2\text{C}_3\text{Bu}^t_3)]$ ($\text{M} = \text{Fe}$); $[\text{Sc}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2-\mu-(\eta^2\text{-P}_3\text{C}_2\text{Bu}^t_2)]\text{Sc}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)]$ and the half-sandwich compounds $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)(\text{CO})_3]$ ($\text{M} = \text{Mn}, \text{Re}$); and $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)]$ and $[\text{M}(\eta^5\text{-P}_2\text{C}_3\text{Bu}^t_3)]$ ($\text{M} = \text{In}$).^{48–52}

Much less research has been directed towards calculating structures of p-block metallocenes or phospho-metallocenes. In the recently published paper investigating the electronic structure of $[\text{Sn}(\text{P}_2\text{C}_2\text{Bu}^t_2)]$, Green *et al.* describe the use of one DFT method.²⁰ They compare the calculated parameters

with the crystal structure¹⁸ in order to assess the reliability of the calculations. While these values compare reasonably, it would have been especially interesting to compare the theoretical parameters with ones determined in the gas phase, where molecules are free from intermolecular interactions.

In this paper we describe such a structure determination of [Sn(P₂C₂Bu'₂)], **2b**, using gas-phase electron diffraction and *ab initio* molecular-orbital calculations and density functional theory. Many methods have been tested, and several different effective core potentials have also been evaluated.

The structure of [Sn(P₂C₂Bu'₂)] was investigated using the various levels of theory and basis sets described in the Experimental section. With respect to the ECP to be used on the Sn atom, there was little to choose between the LanL2DZ and SDB-aug-cc-pVTZ pseudopotentials. Both produced Sn–ring bond lengths to within a couple of picometres of the experimental (GED and X-ray) values. The SDD pseudopotential was less successful, generating Sn–P bond lengths that were approximately 5 pm too long. Results for each of the three ECPs that were tested for the tin atom are given in Table 1. From this point on, all calculations will use the LanL2DZ ECP on the Sn atom unless otherwise stated.

Selected principal parameters taken from the geometries calculated at the different levels of theory used in this study are given in Table 2, alongside experimental data for comparison. In general, an improvement in the results of the calculations was noted as the basis set was increased from 6-31G* to 6-311G*. Only a very slight further difference was observed upon the addition of diffuse functions to the non-hydrogen atoms

(6-311+G*) and no gain was made by adding diffuse and polarisation functions to the hydrogen atoms (6-311++G**).

It was noted that while the MP2 level of theory did not perform as badly as reported for transition-metal complexes, it had a tendency to overestimate the Sn–P length by up to 9 pm, depending on the pseudopotential used on Sn. Only when using SDB-aug-cc-pVTZ on tin did MP2 give results that were consistent with those determined experimentally. It should also be noted that these calculations took more than four times as long as B3PW91/LanL2DZ to complete on our workstation.

The gas-phase structure has been determined using the DYNAMITE Interaction of Theory and Experiment (DYNAMITE) method.⁵³ This new technique has been successfully applied to the gaseous structure determination of sterically crowded molecules⁴⁰ and allows ligands to be fully asymmetric during the gas electron diffraction refinement. This is achieved by incorporation of theoretical methods [in this case molecular mechanics (MM)] into the least-squares refinement program. This theoretical method allows the differences in light-atom positions to be defined accurately, whilst the less-accurate absolute distances, angles and torsions are scaled back to the single refining parameters from the original description. This allows groups to possess C₁ symmetry without the need for many or any extra refining parameters, which would all require restraint in the SARACEN method.⁵⁴ If there is steric strain present within a molecule, then assumptions of local symmetry for light-atom groups (*e.g.* methyl groups) affect the heavy-atom positions as they compensate for the inflexibility of the light-atom groups. The application of the DYNAMITE method to

Table 1 Calculated geometries (*r_c*) at different levels of theory using the 6-31G* basis set on C, P and H atoms and comparing the LanL2DZ, SDD and SDB-aug-cc-pVTZ pseudopotentials on Sn^a

	LanL2DZ	MP2	B3PW91	B3LYP	PBE1PBE	PW91PW91
Sn–C _{ring}		242.2	242.6	243.7	242.0	244.0
Sn–P		266.5	263.3	264.8	262.8	265.5
P–C		181.0	181.2	181.1	180.8	182.0
Ring deformation ^b		10.4	8.4	8.7	8.5	8.5
SDD						
Sn–C _{ring}		247.0	246.3	247.6	245.6	247.8
Sn–P		269.8	266.0	267.6	265.4	268.2
P–C		181.4	181.2	181.8	180.8	182.7
Ring deformation ^b		9.4	7.7	8.0	7.8	7.8
SDB-aug-cc-pVTZ						
Sn–C _{ring}		240.9	243.5	244.7	242.9	244.8
Sn–P		262.4	262.9	264.4	262.3	264.9
P–C		182.3	181.3	181.8	180.7	182.7
Ring deformation ^b		8.2	7.5	7.8	7.5	7.6

^a Distances are in pm, angles in degrees. ^b Refers to the angle of deformation from the position where all four ring atoms are coplanar. The C atoms move towards the Sn atom and the P atoms move away from Sn. For definition, see text regarding *p*₂₀.

Table 2 Comparison of selected ring parameters for various experimental and theoretical methods^a

	GED	X-Ray ^b	MP2	B3PW91	B3LYP	PBE1PBE
Sn–C _{ring}	241.0(11)	243.2(3)	242.8	242.9	244.0	243.1
Sn–P	261.6(7)	261.1(1)	266.4	262.8	264.3	262.7
P–C _{ring}	180.1(3)	179.8(3) ^c	181.3	180.9	181.5	180.6
P–C _{ring} –P	97.1(8)	97.5(2)	98.9	98.1	98.0	98.0
C _{ring} –P–C _{ring}	82.0(7)	82.1(2)	80.3	81.4	81.5	81.5
Ring deformation ^d	6.4(16)	6.9	9.7	7.7	8.1	7.6

^a All calculations were performed using the 6-311+G* basis set on all atoms except Sn, where LanL2DZ was used. ^b Taken from Ref. 18. ^c Average value. ^d Refers to the angle of deformation from the position where all four ring atoms are coplanar. The C atoms move towards the Sn atom and the P atoms move away from Sn. For definition, see text regarding *p*₂₀.

[Sn(P₂C₂Bu'₂)] allows us to examine whether there are structural consequences of steric strain within this molecule, and also to examine its potential application to other main-group metal half-sandwich complexes.

On the basis of the calculations described above, a geometrical model describing **2b** was written allowing the ring to be non-planar and also permitting two different C_{ring}-P distances. For the initial SARACEN refinement,⁵⁴ the geometry was described in terms of 21 independent parameters (see Table 3 and Fig. 3 for atom numbering). These comprised five bond lengths, which included the average C-C bond distance (the simple average of the mean C_{tert}-C_{Me} bond and the C_{tert}-C_{ring} distance) and the corresponding difference between these two (*p*₁₋₂). Fixed differences were used to define the separate bond lengths of the three C_{tert}-C_{Me} bonds away from their mean value. A single common C-H length was used throughout (*p*₃) and the Sn-C_{ring} and C_{ring}-P bond lengths were also included (*p*₄₋₅). Although symmetry implies that two distinct C_{ring}-P distances are possible, all calculations with this symmetry found all C-P distances to be the same and therefore only one C-P distance is actually required. The model also used seven angle parameters. The average C-C-C angle (*p*₆) is the average of the three values C(3)-C(6)-C(7/8/9). As C(3)-C(6)-C(8) and C(3)-C(6)-C(9) were calculated to have the same value, the C-C-C difference

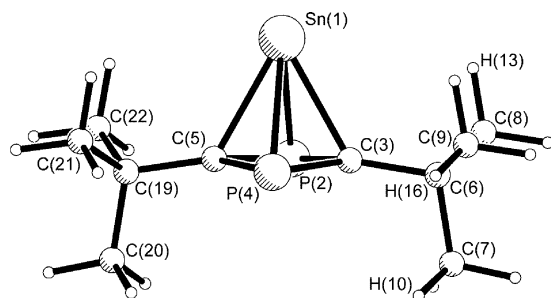


Fig. 3 Structure of [Sn(P₂C₂Bu'₂)], **2b**, showing the atom numbering used in calculations and the GED refinement.

parameter (*p*₇) is the difference between this value and that for C(3)-C(6)-C(7). An average value (*p*₈) of all the C-C-H angles in the molecule is combined with fixed differences to describe each individual angle. Other angles that are used are ∠P-C_{ring}-C_{tert}, ∠Sn-C_{ring}-C_{tert}, ∠P-C_{ring}-P and ∠C_{ring}-P-C_{ring} (*p*₉₋₁₂). The drop of the butyl groups relative to the PPC half-ring plane is defined as the angle between the mid-point of the two P atoms (PP_{mid}) and the C_{ring} and C_{tert} atoms, ∠PP_{mid}-C(3)-C(6) (*p*₁₃). The remaining nine parameters are dihedral angles required to place all atoms in position. In all cases, a positive dihedral angle indicates clockwise rotation when viewed along the central bond. The twist of the first methyl group is defined by φC(3)-C(6)-C(7)-H(10) (*p*₁₄), with the other two hydrogen atoms added with the assumption of C_{3v} local symmetry. The twists of the other two methyl groups are defined similarly, using φC(3)-C(6)-C(8)-H(13) and φC(3)-C(6)-C(9)-H(16) (*p*₁₅₋₁₆), respectively. The *tert*-butyl groups were of approximate C_s local symmetry and therefore the positions of the methyl groups were determined relative to the C(7) methyl group using φC(8)-C(6)-C(3)-C(7) and φC(9)-C(6)-C(3)-C(7) (*p*₁₇₋₁₈) to move the respective methyl groups in opposite directions. The twist of the *tert*-butyl group is described by φP(2)-C(3)-C(6)-C(7) (*p*₁₉). Dihedral angle C(3)-P(2)-C(5)-P(4) (*p*₂₀) is used to define the deformation of the ring from planar to a position where the carbon atoms move towards the tin atom and the phosphorus atoms move away from it. The final dihedral angle that is used in the model is φSn(1)-C(3)-C(6)-C(7) (*p*₂₁), which describes the twist of the *tert*-butyl group in relation to the position of the Sn atom. By allowing the *tert*-butyl groups to rotate, the molecule can adopt either C₂ or C_{2v} symmetry. A value for *p*₂₁ of 180° corresponds to C_{2v} symmetry.

In total 21 geometric parameters and 14 groups of amplitudes of vibration were refined in the least-squares process. See Table S2 (ESI†) for the list of amplitudes of vibration. Flexible restraints were employed, using the SARACEN method,⁵⁴ for fourteen parameters and nine amplitudes. For the purposes of SARACEN, the parameter values were set to be those obtained from calculations performed using the B3PW91 level of theory with the LanL2DZ basis on Sn and 6-311+G* on all other atoms. The uncertainty on each restraint was then based on the

Table 3 Refined (*r*_{h1}) and calculated (*r*_c) geometric parameters for [Sn(P₂C₂Bu'₂)] from the GED study using DYNAMITE^{ab}

Independent	Parameter	<i>r</i> _{h1}	<i>r</i> _c	Restraint
<i>p</i> ₁	<i>r</i> C-C average	153.6(2)	152.4	152.4(3)
<i>p</i> ₂	<i>r</i> C-C difference	3.0(5)	2.5	2.5(5)
<i>p</i> ₃	<i>r</i> C _{Me} -H average	110.3(3)	109.5	109.5(5)
<i>p</i> ₄	<i>r</i> P-C _{ring}	180.1(3)	180.9	—
<i>p</i> ₅	<i>r</i> Sn-C _{ring}	241.0(11)	242.9	—
<i>p</i> ₆	∠C _{ring} -C _{tert} -C _{Me} average	109.6(5)	109.4	—
<i>p</i> ₇	∠C _{ring} -C _{tert} -C _{Me} difference	2.7(5)	2.6	2.6(5)
<i>p</i> ₈	∠C _{tert} -C _{Me} -H average	111.1(8)	111.1	111.1(10)
<i>p</i> ₉	∠P-C _{ring} -C _{tert}	129.4(11)	129.8	129.8(10)
<i>p</i> ₁₀	∠Sn-C _{ring} -C _{tert}	126.8(8)	126.6	126.6(10)
<i>p</i> ₁₁	∠C _{ring} -P-C _{ring}	82.0(7)	81.4	—
<i>p</i> ₁₂	∠P-C _{ring} -P	97.1(8)	98.1	—
<i>p</i> ₁₃	∠PP _{mid} -C(3)-C(6)	166.4(16)	167.5	—
<i>p</i> ₁₄	φH(10)-C(7)-C(6)-C(3)	59.9(17)	60.0	60.0(15)
<i>p</i> ₁₅	φH(13)-C(8)-C(6)-C(3)	64.0(17)	63.8	63.8(15)
<i>p</i> ₁₆	φH(16)-C(9)-C(6)-C(3)	56.3(17)	56.6	56.6(15)
<i>p</i> ₁₇	φC(8)-C(6)-C(3)-C(7)	118.3(16)	119.1	119.1(15)
<i>p</i> ₁₈	φC(9)-C(6)-C(3)-C(7)	-118.2(16)	-119.1	-119.1(15)
<i>p</i> ₁₉	φP(2)-C(3)-C(6)-C(7)	-78.0(28)	-79.4	—
<i>p</i> ₂₀	Ring deformation	-6.4(16)	-7.7	-0.7(15)
<i>p</i> ₂₁	φSn(1)-C(3)-C(6)-C(7)	180.3(23)	180.0	180.0(20)
Dependent				
<i>p</i> ₂₂		261.6(7)	262.8	—

^a Refers to B3PW91 calculation with a LanL2DZ basis set on Sn and 6-311+G* on C, P and H atoms. ^b Distances are in pm, angles in degrees. See text for parameter definitions and Fig. 3 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

change in value of that parameter during a series of graduated calculations. Within experimental error, the molecule was found to have C_{2v} symmetry.

On completion of the SARACEN refinement, the DYNAMITE code⁵³ was activated within the ed@ed program,⁴⁰ upon which the above parameter definitions relating to $rC-H$, $\angle C-C-H$ and the methyl torsions changed. For example, the $C-H$ bond length (p_s) no longer represented the actual bond length for all the $C-H$ distances, but rather the mean of them, while differences between them were updated continually in the course of the refinement.

The success of the final DYNAMITE refinement, for which $R_G = 0.049$ ($R_D = 0.049$), can be assessed on the basis of the radial-distribution and experimental – theoretical difference curves (Fig. 4) and the molecular-scattering intensity curves (Fig. S1, ESI†). The least-squares correlation matrix is given in Table S3 (ESI†) and coordinates for the GED structure are given in Table S4 (ESI†).

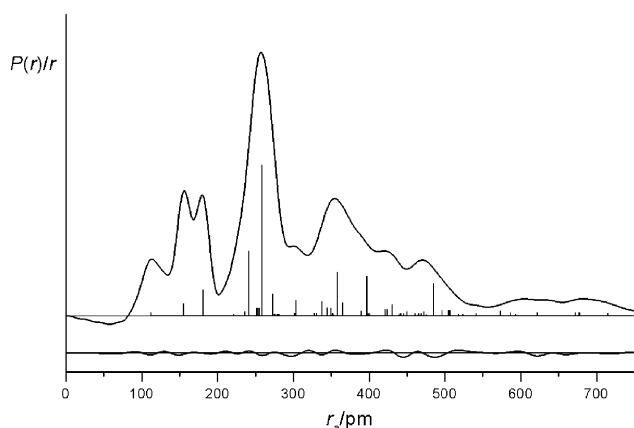


Fig. 4 Experimental and difference (experimental – theoretical) radial-distribution curves for $[Sn(P_2C_2Bu'_2)]$, **2**. Before Fourier inversion, the data were multiplied by $\text{sexp}(-0.00002s^2)/(Z_{Sn} - f_{Sn})(Z_C - f_C)$.

Obtaining a reliable GED structure determination, as judged by the goodness of fit to the data, makes this an ideal case for calibrating the various calculations that were performed. The calculated geometry of $[Sn(P_2C_2Bu'_2)]$ at the B3PW91 level of theory with the LanL2DZ pseudopotential on Sn and the 6-311+G* basis set on all other atoms was close to that determined from the GED experiment. The parameters obtained by using the MP2 level of theory with the SDB-aug-cc-pVTZ basis on the tin atom were also close to the experimental values, but the geometry optimisation took significantly longer to complete. The force field that is required to provide vibrational quantities for use in the GED refinement is also much more readily calculated using DFT methods than with MP2. For these reasons, B3PW91/LanL2DZ was used as the method of calculating the geometry of **2b**.

The R_G values from the SARACEN and DYNAMITE refinements were identical (0.049) and examination of the parameter values from each refinement revealed that those from one were within the esd range of the other. From this we can conclude that no improvement to the structure or refinement has been gained by using the DYNAMITE method in this particular case, but it is no worse either. As the *tert*-butyl groups are not in close contact with each other in this molecule, it is perhaps not surprising that there is no steric crowding within the groups.

It is important to note that the DYNAMITE and SARACEN refinements return essentially the same parameter and amplitude values. It is very positive to note that if no steric crowding exists in a molecule, activation of the DYNAMITE method will indicate this. Therefore, we are unlikely to “improve” a structure artificially by implementing this method. Also, any improvement in the goodness of fit and any change in parameter values for a refinement can be attributed to better modelling of the light-atom positions *via* the DYNAMITE method. There are other molecules to be studied in this series of main-group half-sandwich complexes, including $[In(P_2C_3Bu'_3)]$,⁵⁵ for which *ab initio* and DFT investigations indicate that a large degree of distortion and steric crowding exists. A gas-phase investigation of this structure using the DYNAMITE method would be prudent.

In an attempt to understand better the steric properties and structure of **2b**, calculations were performed on various related molecules. All calculations were performed at the B3PW91 level of theory with the 6-31G* basis set on all atoms except for Sn, where LanL2DZ was used where appropriate. Table 4 lists selected parameters for all structures, including **2b**, at this level of computation and Table S5 (ESI†) contains coordinates for **2b**. The geometry of $[Sn(P_2C_2H_2)]$, **3**, principal geometric parameters for which are included in Table 4 and coordinates in Table S6 (ESI†), differed very little from the *tert*-butyl analogue. With a similar ring deformation and the hydrogen atoms bending away from Sn, the Sn–ring bond lengths were within about 1 pm of those obtained for **2b**. This suggests that the non-planarity of the ring is caused by the tin atom complexing to the ring atoms and is not a steric effect caused by the *tert*-butyl groups.

The calculated geometry (see Table 4 for parameters; coordinates given in Table S7, ESI†) for neutral diphosphabutadiene ligand, $[P_2C_2Bu'_2]$, **4**, exhibited two separate P–C_{ring} distances (169.0 and 192.4 pm), unlike its tin complex, where only one distance was observed in the calculations and GED refinement. This is as would be expected for a non-aromatic molecule. Notably, this fragment was calculated to be planar, suggesting that the non-planarity of **2b** is caused simply by the Sn–P bond lengths requiring to be longer than Sn–C.

To investigate this further, an analogue with a purely organic ring was explored. For $[Sn(C_4Bu'_2H_2)]$, **5**, the cyclobutadiene ring was very nearly planar and again all the bonds within the ring were found to be equal in length. (See Table S8, ESI† for coordinates and Table 4 for principal parameters.) The Sn–C bonds were calculated to be shorter than for the diphospho derivative, due to the smaller ring involved.

Table 4 Comparison of calculated ring parameters for various derivatives of $[Sn(P_2C_2Bu'_2)]$, **2b**^{a,b}

Parameter	$[Sn(P_2C_2Bu'_2)]$, 2b	$[Sn(P_2C_2H_2)]$, 3	$[P_2C_2Bu'_2]$, 4	$[Sn(C_4Bu'_2H_2)]$, ^c 5	$[Li_2(P_2C_2Bu'_2)]$, 6
$rP/C-C$	181.2	180.2	169.0/192.4	146.5	182.0
$rM-P/C^d$	263.3	263.7	—	235.1	231.6
$rM-C^d$	242.6	241.3	—	235.3	221.4
$\angle C-P/C-C$	81.4	80.2	80.7	90.8	81.0
$\angle P/C-C-P/C$	98.0	99.1	99.3	89.2	99.0
$\phi X-C-P/C-C^e$	171.4	176.3	180.0	161.4	175.3
$\phi C-P/C-C-P/C$	8.4	8.9	0.0	0.5	1.0

^a Calculations performed at the B3PW91 level of theory with the 6-31G* basis set on all atoms except Sn, where LanL2DZ was used where appropriate.

^b Distances are in pm, angles in degrees. ^c In this instance atom P has been replaced by a CH fragment. ^d M refers to Sn in **2b**, **3** and **5** and to Li in **6**.

^e X refers to the *tert*-C atom in **2b**, **4**, **5** and **6** and the H atom in **3**.

As mentioned in the Introduction, in formal terms complex **2b** should be considered to involve the diphosphabutadiene dianion, $[\text{P}_2\text{C}_2\text{Bu}'_2]^{2-}$. The dianion $[\text{C}_4\text{H}_4]^{2-}$ is known to be unstable, existing as a resonance state with a short lifetime, and therefore standard computational methods cannot be used to model this.²² The neutral ligand $[\text{Li}_2\text{C}_4\text{H}_4]$ is used instead to express the aromaticity of the cyclobutadiene ring and here we have also calculated the structure of $[\text{Li}_2\text{P}_2\text{C}_2\text{Bu}'_2]$, **6**. The molecule contains an essentially planar ring with all four P–C bonds of equal length (Table 4), suggesting that this ring system is aromatic. (Coordinates for the calculated geometry are given in Table S9, ESI.†) As with $[\text{Li}_2\text{C}_4\text{H}_4]$, this should be thought of as a 2π -aromatic system, because, although there are 6π electrons, four of them occupy non-bonding orbitals.

The dilithium salt of the related 1,3-diphosphacyclobutadiene dianion, $[\text{P}_2\text{C}_2(\text{SiMe}_3)_2]^{2-}$, has recently been synthesised and characterised by X-ray crystallography.²¹ That study found the P–C bonds to be equivalent (within experimental error) and quoted the ring angles as $83.8(1)^\circ$ for $\angle\text{P–C–P}$ and $96.2(1)^\circ$ for $\angle\text{C–P–C}$. When these values are compared with those theoretical values obtained for **6** it can be seen that $\angle\text{P–C–P}$ is approximately 3° wider in the trimethylsilyl analogue, while $\angle\text{C–P–C}$ was narrower by the same amount. For **6** the distance between the lithium atom and the centre of the ring is calculated to be 186.0 pm, considerably shorter than the 206.6(2) pm distance observed for $[\text{Li}_2\text{P}_2\text{C}_2(\text{SiMe}_3)_2]$.

The Sn–C bond lengths in other compounds were examined for comparison with our half-sandwich complex, **2b**. In the sandwich complex stannocene, $[\text{Sn}(\text{C}_5\text{H}_5)_2]$, where the cyclopentadienyl groups are not parallel, the bond distance in the gas-phase structure was 270.6(24) pm,⁵⁶ and in the X-ray crystal structure they ranged from 256(2) to 285(3) pm,⁵⁷ compared to 241.0(11) pm in the present study. In a theoretical study of stannocene, B3PW91 calculations gave an Sn–C bond length of 271.8 pm.⁵⁸ It is perhaps not surprising that the Sn–C bonds are longer in stannocene, where the Sn is η^5 -coordinated to each ring, as opposed to η^4 in **2b**. In $[\text{Sn}(\text{CH}_3)_4]$, Sn is bonded to four carbon atoms through simple σ bonds, but in this instance the Sn–C bond length in the gas phase is 214.4(3) pm.⁵⁹

Attempts were made to optimise a geometry for **2b** in which the Sn was less than η^4 -coordinated to the ring. No minima were found to correspond to such structures and it was concluded that Sn must interact with each of the ring atoms. This coordination was also found in the crystal structure,¹⁸ where no parameters were found to be significantly different from those obtained from the GED study.

It might be expected that a compound such as this, with a metal atom exposed on one face of a ring, might exhibit significant intermolecular interactions. In fact any interactions are so small that the crystal and gas-phase structures are effectively indistinguishable. This similarity makes this an ideal molecule for the assessment of computational methods for main-group complexes of this type.

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