

Acyclic Dialkylstannylene and -Plumbylene Compounds That Are Monomeric in the Solid State

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The new phosphine-borane adduct $(Me_2PhSi)CH_2P(BH_3)Me_2$ is prepared by the reaction between $Me_2PhSiCl$ and *in situ*-generated $Me_2P(BH_3)CH_2Li$; the adduct undergoes clean deprotonation on treatment with *n*-BuLi to give the phosphine-borane-stabilized carbanion complex [(Me_2PhSi)-{Me_2P(BH_3)}CH]Li. The reaction between 2 equiv of [(Me_2PhSi){Me_2P(BH_3)}CH]Li and either Cp_2Sn or Cp_2Pb gives the acyclic dialkylstannylene and -plumbylene compounds *rac*-[(Me_2PhSi)-{Me_2P(BH_3)}CH]_2E [E = Sn (13), Pb (14)]. Similarly, the reaction between 2 equiv of [(Me_3Si){Me_2P(BH_3)}CH]_2E [E = Sn (15), Pb (16)]. X-ray crystallography reveals that compounds 13-16 crystallize as discrete monomers that are stabilized by two agostic-type $B-H\cdots E$ contacts in each case; multielement NMR spectroscopy and UV/visible spectroscopy indicate that these agostic-type contacts are preserved in solution. DFT calculations reveal that these $B-H\cdots E$ contacts stabilize compounds 13-16 by between 38.0 and 43.7 kcal mol⁻¹. Calculations suggest that the dimerization of 15, which is isoelectronic with the archetypal dialkylstannylene {(Me_3Si)_2CH}_2Sn, to the corresponding distannene [(Me_3Si){Me_2-P(BH_3)}CH]_2Sn=Sn[CH{P(BH_3)Me_2}(SiMe_3)]_2 (15_2) is disfavored by some 30.5 kcal mol⁻¹.

Introduction

There is a great deal of current interest in the chemistry of heavier group 14 element analogues of alkenes, alkynes, and carbenes. Of these compounds the heavier group 14 carbene analogues (tetrylenes) hold a special fascination, as these compounds are potentially useful ligands for transition metal centers.¹ Although much progress has been made in this field over the past decade, especially in the synthesis of diaminotetrylenes, $(R_2N)_2E$ (E = Si, Ge, Sn, Pb), and their cyclic counterparts, the N-heterocyclic tetrylenes,² the number of hydrocarbyl-substituted tetrylenes remains relatively low. In particular, although the chemistry of diaryltetrylenes, Ar_2E , has become reasonably well established over the

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past few years,³ few dialkyltetrylenes, $(R_3C)_2E$, have been isolated.^{1,4–10} Such diaryl- and dialkyltetrylenes do not benefit from stabilization by $p\pi$ – $p\pi$ interactions between the group 14 center and adjacent heteroatoms (cf. diaminocarbenes and their heavier group 14 analogues), but are typically stabilized solely by the presence of sterically demanding substituents.

The archetypal dialkylstannylene and -plumbylene, { $(Me_3Si)_2CH$ }₂E [E = Sn (1), Pb (2)], were first reported by Lappert and co-workers in the 1970s.⁴ However, whereas **1** is monomeric in the gas phase, this compound dimerizes to the corresponding distanene (1₂) in the solid state; in solution compounds **1** and **1**₂ are in dynamic equilibrium.^{4b} Compound **2** also crystallizes with a dimeric structure (2₂), although the long Pb···Pb distance suggests that the plumbylene subunits are only weakly bonded.^{1e} The few known monomeric dialkyltetrylenes (**3–8**) are stabilized toward dimerization in the solid state by the steric bulk of the alkyl substituents.



We recently isolated a series of new cyclic dialkyltetrylenes (9-12), which exhibit unusual agostic-type B-H···E interactions [E = Sn, Pb], and showed that such interactions may potentially serve as an alternative method for the stabilization of dialkylstannylenes and -plumbylenes.¹¹⁻¹³ However, although 9-12 are monomeric in the solid state, stabilization of these compounds is afforded by a *combination* of agostictype interactions and the steric bulk of the ligands; for these compounds it is not possible to separate the two distinct stabilization effects. The question therefore remains as to whether such agostic-type interactions alone are sufficiently stabilizing that the dimerization of dialkyltetrylenes to the corresponding tetraalkylditetrenes, R₂E=ER₂, is inhibited. In order to address this issue, we have now prepared direct isoelectronic analogues of 1 and 2 containing phosphineborane substituents and show that these are indeed monomeric in the solid state.

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Scheme 1



Results and Discussion

The new phosphine-borane adduct (Me₂PhSi)CH₂P(BH₃)-Me₂ was prepared by the reaction between *in situ*-generated Me₂P(BH₃)CH₂Li and Me₂PhSiCl and was obtained as colorless crystals in good yield after crystallization from cold methylcyclohexane. Treatment of (Me₂PhSi)CH₂P(BH₃)Me₂ with *n*-BuLi in THF leads to quantitative deprotonation, as determined by ³¹P{¹H} and ¹H NMR spectroscopy. The lithium salt [(Me₂PhSi){Me₂P(BH₃)}CH]Li is isolated as a colorless, viscous oil that is soluble in ether and toluene, but that we have been unable to isolate in a state suitable for detailed analysis; however, the identity of this compound is confirmed by its ready metathesis reactions (see below).

The reaction between either Cp_2Sn^{14} or $Cp_2Pb^{12,15}$ and 2 equiv of [(Me₂PhSi){Me₂P(BH₃)}CH]Li in toluene cleanly gives the corresponding dialkyltetrylenes rac-[(Me₂PhSi)- ${Me_2P(BH_3)}CH_2E [E = Sn (13), Pb (14)] (Scheme 1).$ Similarly, the reaction between either Cp₂Sn or Cp₂Pb and 2 equiv of the known alkyllithium $[(Me_3Si){Me_2P(BH_3)}-$ CHILi¹⁶ in toluene yields rac-[(Me₃Si){Me₂P(BH₃)}CH]₂E [E = Sn (15), Pb (16)]. Compounds 13-16 are isolated in good to excellent yields as yellow, air- and moisture-sensitive crystals that decompose to the free phosphine-borane and elemental Sn or Pb on exposure to ambient light for extended periods or on heating above ca. 50 °C. Once isolated, compounds 13 and 14 exhibit limited solubility in hydrocarbon solvents, but are soluble in ethereal and halocarbon solvents; in contrast, compounds 15 and 16 are soluble in most common aprotic solvents, including light petroleum and toluene.

All four compounds 13–16 are isolated solely as the *rac* isomer; there is no evidence from ${}^{31}P{}^{1}H$ NMR spectra of the crude reaction solutions for the formation of the alternative meso diastereomers. This contrasts markedly with the cyclic compounds 9 and 10,^{11,12} which are isolated as mixtures of the rac and meso diastereomers in ratios of 1:1 and 3:2, respectively; for 11, which contains a seven-membered ring, there is evidence for the formation of the meso diastereomer in up to 25% yield, but there is no evidence for the formation of the meso diastereomer of the corresponding dialkylplumbylene 12.13 Since racemization of the chiral carbanions in both [(Me₂PhSi){Me₂P(BH₃)}CH]Li and $[(Me_3Si){Me_2P(BH_3)}CH]Li$ is likely to be rapid in solution, we attribute the selective formation of the *rac* isomers of 13-16 to the stabilization afforded to these compounds by the two agostic-type $B-H\cdots E$ interactions in each case (see below).

Single crystals of **13** and **14** suitable for X-ray crystallography were obtained from cold toluene/THF or cold diethyl ether/THF, respectively; single crystals of **15** and **16** were

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(a)



(b)

Figure 1. Molecular structures of (a) rac-[(Me₂PhSi){Me₂P(BH₃)}CH]₂Sn (13) and (b) rac-[(Me₂PhSi){Me₂P(BH₃)}CH]₂Pb (14) with 40% probability ellipsoids and with methyl and aryl H atoms omitted for clarity.

obtained by crystallization from cold diethyl ether. Compounds 13 and 14 adopt similar, but not identical, structures, whereas compounds 15 and 16 are both isostructural and isomorphous. The molecular structures of 13 and 14 are shown in Figure 1, and the molecular structure of 15 is shown in Figure 2; selected bond lengths and angles for 13 and 14 and for 15 and 16 are given in Tables 1 and 2, respectively.

The structures of 13 and 14 differ solely in the orientation of one of the two Me₂PhSi groups. Whereas in 14 both of these groups are oriented such that the phenyl rings are at the extremes of the molecule, in 13 one of the Me₂PhSi groups is rotated by approximately 120°, such that the phenyl ring in this group lies proximal to the tin atom.

Compounds 13-16 crystallize as discrete dialkyltetrylenes. The shortest Sn \cdots Sn distances in 13 and 15 are 4.401 and 6.685 Å, respectively, whereas the shortest Pb \cdots Pb distances in 14 and 16 are 7.165 and 6.661 Å, respectively; in no case is the vector between the two group 14 elements consistent with an $E \cdots E$ bonding interaction (see Supporting Information for crystal packing diagrams). The Sn \cdots Sn and Pb \cdots Pb distances in 13–16 are substantially longer than the corresponding distances of 2.768(2) and 4.129 Å in dimeric 1₂ and 2₂, respectively.^{4,1e} This clearly suggests that the two agostic-type B-H \cdots Sn interactions observed in each of compounds 13–16 are sufficiently stabilizing that dimerization to the corresponding distances or diplumbene is inhibited; this suggestion is supported by DFT calculations (see below).

The Sn–C distances of 2.296(5) and 2.308(5) A in **13** and 2.3149(16) and 2.2864(16) Å in **15** are similar to the corresponding distances in the few previously reported dialkyl-stannylenes; for example, the Sn–C distances in **7** are 2.284(3) and 2.286(3) Å, ⁹ and the Sn–C distances in *rac-9* are 2.2984(14)



Figure 2. Molecular structure of rac-[(Me₃Si){Me₂P(BH₃)}CH]₂-Sn (15) with 40% probability ellipsoids and with methyl H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 13 (E = Sn) and 14 (E = Pb)

13	14
2.296(5)	2.363(2)
2.308(5)	2.424(2)
1.797(5)	1.786(2)
1.794(5)	1.783(2)
1.875(5)	1.862(2)
1.885(5)	1.858(2)
1.913(6)	1.905(3)
1.905(7)	1.902(3)
2.35(6)	2.48(2)
2.41(8)	2.50(2)
99.60(17)	97.42(8)
	13 2.296(5) 2.308(5) 1.797(5) 1.794(5) 1.875(5) 1.885(5) 1.913(6) 1.905(7) 2.35(6) 2.41(8) 99.60(17)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 15 (E = Sn) and 16 (E = Pb)

	15	16
E-C(1)	2.3149(16)	2.408(2)
E - C(7)	2.2864(16)	2.383(2)
C(1) - P(1)	1.7877(16)	1.783(2)
C(7) - P(2)	1.7919(18)	1.792(2)
C(1) - Si(1)	1.8777(18)	1.879(2)
C(7) - Si(2)	1.8778(19)	1.876(2)
P(1) - B(1)	1.909(3)	1.916(3)
P(2) - B(2)	1.918(2)	1.921(3)
$E \cdots H(1A)$	2.38(2)	2.51(3)
$E \cdots H(2A)$	2.29(2)	2.36(2)
C(1) - E - C(7)	98.26(6)	97.51(8)

and 2.3046(14) Å.¹¹ Similarly, the Pb–C distances of 2.363(2) and 2.424(2) Å in **14** and 2.408(2) and 2.383(2) Å in **16** are comparable to the corresponding distances in **8** [2.397(6) and 2.411(5) Å]¹⁰ and *rac*-**10** [2.390(4) and 2.402(4) Å].¹²

The C–Sn–C angles of 99.60(17)° and 98.26(6)° in 13 and 15, respectively, are similar to the C–Sn–C angle observed in the gas phase structure of 1 [97(2)°];⁴ however, the C– Pb–C angles of 97.42(8)° and 97.51(8)° in 14 and 16, respectively, are substantially narrower than the C–Pb–C angle in the corresponding gas phase structure of 2 [103.6°],^{1e,17} although in the loosely dimeric solid state structure of 2₂ the C–Pb–C angle is 93.6°.^{1e} The differences in C–E–C angles

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between the isoelectronic pairs 15/1 and 16/2 may, at least in part, be attributed to the different orientations of the alkyl ligands in the two systems: in the gas phase structures of 1 and 2 the ligands adopt a *syn,anti*-configuration, which minimizes steric interactions between the bulky substituents, whereas in 15 and 16 (and also in 13 and 14) the ligands adopt a *syn,syn*-configuration.



The adoption of a *svn.svn*-configuration in 13-16 is a consequence of the two short, agostic-type $B-H\cdots E$ contacts in each compound, one to each of the two BH₃ groups, which essentially lock the two alkyl substituents into this configuration. The B-H···E distances of 2.41(8) and 2.35(6) Å (13), 2.48(2) and 2.50(2) Å (14), 2.38(2) and 2.29(2) Å (15), and 2.51(3) and 2.36(2) Å (16) lie well within the sum of the van der Waals radii of H and either Sn or Pb (3.37 and 3.22 Å, respectively). The B-H \cdots Sn distances in 13 and 15 compare with $B-H\cdots$ Sn distances ranging from 2.25(4) to 2.32(2) Å in 9 and 11, 11,13 whereas the B-H···Pb distances in 14 and 16 compare with $B-H\cdots Pb$ distances ranging from 2.25(4) to 2.59(6) Å in 10 and 12.12,13 To the best of our knowledge, outside of our own studies the only example of a short $B-H\cdots$ Sn contact is found in the anion of [10-endo-(SnPh₃)-10-µ-H-7,8-nido-C₂B₉H₁₀][trans-Ir(CO)-(PPh₃)₂(MeCN)], in which the tin(IV) center is directly bonded to the boron atom of a carborane cage [Sn···H 2.349 Å].¹⁸ Similarly, outside of our own studies we are aware of only one other short $B-H\cdots Pb$ contact, which is found in the tris(2-mercaptoimidazolyl)borate complex (Tm^{Ph})₂Pb $[Tm^{Ph} = HB(2-S,3-PhC_3N_2)_3];$ in this compound one of the Tm^{Ph} ligands adopts an inverted η^4 -coordination mode, binding the lead atom through its three S-donors and the central B–H group, and the Pb···H distance is 2.39 Å.¹⁹

In addition to the B-H···E contacts observed in 13–16, there are relatively short distances between the tin or lead centers and the methine hydrogen atoms of each ligand [C-H···Sn 2.76 and 2.79 Å (13), 2.77 and 2.77 Å (15);C-H···Pb 2.84 and 2.89 Å (14), 2.86 and 2.86 Å (16)]; however, DFT studies (see below) indicate that these are a consequence solely of the ligand conformation and are not due to any significant C-H···E interactions.

The ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹¹B{¹H} NMR spectra of **13–16** are as expected and reveal no evidence for dynamic behavior in solution (cf. **9** and **10**). The ¹¹⁹Sn chemical shifts of **13** and **15** (375 and 377 ppm, respectively) and the ²⁰⁷Pb chemical shifts of **14** and **16** (3931 and 3902 ppm, respectively) are to significantly higher field than the corresponding shifts of the monomeric forms of **1** and **2** (2328 and 9112 ppm, respectively)⁴ and of the related cyclic dialkyltetrylenes **6** (2323),⁶ **7** (2299),⁹ and **8** (10050 ppm),¹⁰ but are similar to those of *rac*-**9** (578),¹¹ *rac*-**10** (4580),¹² *rac*-**11** (320), and *rac*-**12** (5920 ppm),¹³ consistent with the B–H···E contacts observed in the solid state persisting in solution.

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This proposal is supported by the UV-visible spectra of solutions of **13–16**, which exhibit absorption maxima between 324 and 370 nm [cf. 546 and 610 nm for **7** and **8**, respectively], which may be assigned to the $n \rightarrow p$ transition in each case; the significant blue shift for **13–16** is consistent with retention of the agostic-type interactions in solution. The solid state infrared spectra of **13–16** exhibit absorptions in the range 2079–2170 cm⁻¹, which may be attributed to B–H stretching vibrations of the H atoms involved in the agostic-type B–H···E interactions.

DFT Calculations. The nature of the bonding and the degree of stabilization afforded by the short $B-H\cdots E$ contacts in 13-16 was probed using DFT calculations. Geometries were optimized using the B3LYP hybrid func-tional²⁰ with a Lanl2dz basis set²¹ on Sn and Pb and a 6-31G(d,p) basis set²² on all other atoms. The location of minima was confirmed by the absence of imaginary vibrational frequencies. For the phenyl-substituted compounds 13 and 14 geometries were optimized for both of the possible conformations of each compound; we designate the conformation corresponding to the solid state structure of 14, in which both Me₂PhSi groups are oriented such that the phenyl rings are at the periphery of the molecule, as conformer a, whereas the alternative conformation, in which one of the Me₂PhSi groups is rotated through ca. 120°, corresponding to the solid state structure of 13, is designated as conformer b. Calculations reveal that the difference in energy between conformers 13a and 13b is only 1.4 kcal mol⁻ whereas the difference in energy between conformers 14a and **14b** is just 1.3 kcal mol⁻¹; in each case the more symmetrical **a** conformer is the lowest energy minimum.

The calculated minimum-energy structures of 13-16 correlate extremely well with those determined by X-ray crystallography (Table 3); in each case the calculated C-E distances are overestimated by approximately 0.02–0.06 Å, although there is a close correspondence between the calculated and experimental C-E-C angles. The B-H···E contacts observed crystallographically are replicated extremely well in the calculated structures; in each calculated structure there are two short $B-H\cdots E$ contacts, one to each BH_3 group. The calculated and experimental $B-H\cdots$ Sn distances in 15 [2.38/2.31 and 2.38(2)/2.29(2) Å, respectively] are identical within experimental error, whereas the calculated B-H···Pb distances in 16 [2.40 and 2.43 Å] are close to those determined crystallographically [2.36(2) and 2.51(3) Å]. There is a similarly close correspondence between the calculated and experimental B-H···E distances in the phenyl-substituted stannylenes 13 and 13b and plumbylenes 14 and 14a. It should be noted that bond lengths to H atoms are generally underestimated by X-ray crystallography; if all the B-H bond lengths in these structures are reset to 1.23 Å (consistent with the calculated results), without changing their directions, the adjusted E···H distances, given in square brackets in Table 3, give an even better agreement overall with the calculated distances.

 Table 3. Comparison of Selected Calculated and Experimental Bond Lengths and Angles for 13–16

	E-C (Å)	$E \cdots H$ (Å)	B-H (Å)	C-E-C (deg)
15(expt)	2.3149(16)	2.38(2)[2.31]	1.07(2)-1.17(2)	98.26(6)
	2.2864(16)	2.29(2)[2.25]		
15(calc)	2.3503	2.38	1.21-1.25	99.56
	2.3134	2.31		
13 (expt)	2.296(5)	2.35(6)[2.31]	1.01(9) - 1.17(6)	99.60(17)
	2.308(5)	2.41(8)[2.26]		
13a	2.3102	2.33	1.21-1.25	99.16
	2.3545	2.33		
13b	2.3096	2.38	1.20 - 1.25	99.44
	2.3588	2.30		
16 (expt)	2.383(2)	2.36(2)[2.36]	0.99(2) - 1.23(2)	97.51(8)
	2.408(2)	2.51(3)[2.44]		
16 (calc)	2.4423	2.40	1.21 - 1.24	99.13
	2.3979	2.43		
14(expt)	2.363(2)	2.48(2)[2.43]	1.03(2) - 1.18(2)	97.42(8)
(1)	2.424(2)	2.50(2)[2.47]		
14a	2.3947	2.41	1.21 - 1.24	99.05
	2.4476	2.41		
14b	2.4537	2.39	1.21-1.25	98.65
	2 3928	2 43		20100

Table 4. Selected NBO Energies for 13-16

	13a	13b	15	14a	14b	16
$E(2)^a/\text{kcal mol}^{-1}$	20.8	20.2	20.4	18.4	17.3	17.4
$E_{\rm DEL}^{b}/{\rm kcal}~{\rm mol}^{-1}$	43.7	42.6	42.9	38.4	38.0	38.0

^{*a*} E(2) energy from NBO calculations for the elements corresponding to B-H···E delocalizations. ^{*b*} Energy difference between the ground state structure and the structure in which the elements responsible for the principal B-H···E delocalizations have been deleted (see text).

Natural bond orbital analyses²³ of 13-16 reveal that the HOMO and LUMO in each case consist of an essentially s-type lone pair on the tin or lead center and a vacant tin or lead p orbital lying perpendicular to the C-E-C plane, respectively. The short $B-H\cdots E$ contacts in 13-16 are associated with significant delocalization of electron density from one of the B–H σ -bonds in each BH₃ group into the vacant p orbital on the tin or lead atom. The E(2) energy associated with this interaction, calculated via second-order perturbation theory, provides a measure of the degree of stabilization afforded by these contacts (Table 4). For the tin compounds 13a, 13b, and 15 the E(2) energies fall in a narrow range from 18.3 to 20.8 kcal mol^{-1} , whereas for the plumbylenes 14a, 14b, and 16 the calculated E(2) energies lie in the range 16.4 to 18.4 kcal mol⁻¹. The overall stabilization energy afforded by the $B-H\cdots E$ contacts may be calculated by selective deletion of the elements associated with the agostic-type interactions and recalculation of the energy of the system.²⁴ This method yields stabilization energies (E_{DEL}) between 42.6 and 43.7 kcal mol⁻¹ for the three stannylenes and between 38.0 and 38.4 kcal mol⁻¹ for the three plumbylenes. The values of E(2) and E_{DEL} for 13–16 are in keeping with the corresponding energies calculated for the cyclic stannylenes and plumbylenes 9-12. As expected, stabilization via agostic-type $B-H\cdots E$ interactions in the

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Scheme 2. Dimerization of 15 to 15_2^a



^a Optimized geometry of 15₂ shown with H atoms omitted for clarity.

plumbylenes 14 and 16 is less than for the corresponding stannylenes 13 and 15, consistent with poorer orbital overlap in the latter case due to the increased size and diffuse nature of the 6p orbital on lead compared to the 5p orbital on tin.

One of the key questions we set out to address through the synthesis of 13-16 was whether agostic-type $B-H\cdots E$ interactions were sufficiently stabilizing to prevent the dimerization of dialkyltetrylenes to the corresponding tetraalkylditetrenes. The isoelectronic nature of 15 and 1 makes these ideal compounds for comparison in this regard; whereas 1 dimerizes to the distannene 1_2 in the solid state, compound 15 is isolated as a dialkylstannylene. In order to gain further insight into the relative energies of the monomeric and dimeric forms of 15, we have calculated the energy of the dimerization reaction shown in Scheme 2.

Initial attempts to locate a local minimum-energy geometry for 15_2 failed: irrespective of the starting geometry, calculations consistently yielded a pair of monomers in which the B-H...Sn contacts had re-established themselves and in which there was no evidence for any $Sn \cdots Sn$ interaction. However, a minimum energy geometry for 152 (Scheme 2) was successfully located by initially constraining the Sn-Sn distance in the dimer to the value observed in 1_2 (2.768 Å) and then reoptimizing the resulting geometry in the absence of any constraints. There are only marginal differences between the overall structures of the constrained and unconstrained dimers, with the exception of the Sn-Sn distance, which increased to 2.902 Å in the latter, clearly suggesting a reduction in the Sn-Sn bond order in 15_2 compared to 1_2 . Consistent with this, the Wiberg bond index of 1.28 for the Sn=Sn bond in 15_2 is somewhat lower than in a traditional double bond; for comparison, the bond order for the model complex $H_2Sn=SnH_2$ has been calculated as 1.46.²⁵

In all other respects, the optimized geometry of 15_2 is very similar to the solid state structure of 1_2 and has the typical *trans*-bent motif common to distance. The bending angle of 34.1° in 15_2 (i.e., the angle by which the C-Sn-C planes deviate from the Sn-Sn vector) compares with a corresponding angle of 32.2° in 1_2 .⁴ It is notable that in 15_2 the four borane groups are oriented away from the tin atoms and so there are no short B-H···Sn contacts in the dimer.

In keeping with the stabilizing nature of the $B-H\cdots E$ contacts observed in **15**, the energy for the dimerization reaction shown in Scheme 2 is calculated to be +30.5 kcal mol⁻¹. This clearly suggests that the energy gained on formation of the Sn=Sn bond in the dimer is insufficient to compensate for the loss of the two $B-H\cdots$ Sn interactions in each monomer unit and, thus, that these interactions provide a substantial barrier toward dimerization.

Conclusions

In contrast to the archetypal dialkyltetrylenes 1 and 2, the readily accessible isoelectronic dialkyltetrylenes 15 and 16 crystallize as discrete monomers, with no close $Sn \cdots Sn$ or $Pb \cdots Pb$ contacts. The closely related compounds 13 and 14 similarly crystallize as discrete monomers. Each of the compounds 13–16 is stabilized by two short, agostic-type $B-H\cdots E$ contacts, one to each of the two BH_3 groups in each case. The $B-H\cdots E$ contacts appear to be preserved in solution and significantly affect the spectroscopic properties of these compounds. DFT calculations suggest that the $B-H\cdots E$ contacts stabilize compounds 13-16 by between 38.0 and 43.7 kcal mol⁻¹. There is no evidence for the dimerization of these species in solution, and DFT calculations reveal that the dimerization of 15 to 15_2 is significantly disfavored.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or in a nitrogen-filled glovebox. Toluene, THF, and diethyl ether were distilled under nitrogen from sodium, potassium, or sodium/potassium alloy, respectively, and were stored over either a potassium film or activated 4 Å molecular sieves, as appropriate. Deuterated toluene and THF were distilled under nitrogen from potassium, and CDCl₃ was distilled under nitrogen from CaH₂; NMR solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4 Å molecular sieves. The compounds Me₃P(BH₃),²⁶ {Me₂P(BH₃)}-(SiMe₃)CH₂,¹⁶ Cp₂Sn,¹⁴ and Cp₂Pb^{12,15} were prepared by previously published procedures; *n*-BuLi was purchased as a 2.5 M solution in hexanes.

¹H, ¹¹B{¹H}, ¹³C{¹H}, ³¹P{¹H}, ¹¹⁹Sn{¹H}, and ²⁰⁷Pb{¹H} NMR spectra were recorded on a JEOL Eclipse500 spectrometer operating at 500.16, 160.35, 125.65, 202.35, 186.50, and 104.32 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane (¹H and ¹³C), external BF₃(OEt₂) (¹¹B), external 85% H₃PO₄ (³¹P), external Me₄Sn (¹¹⁹Sn), or external Me₄Pb (²⁰⁷Pb), as appropriate. The positions of the BH₃ signals in the ¹H NMR spectra and J_{PH} for these signals were determined using a selective ¹H{¹¹B} experiment. Infrared spectra were recorded as neat powders on a Varian 800 FTIR spectrometer; UV–visible spectra were recorded as 1.0 mM solutions in matched quartz cells on a Hitachi F4500 spectrophotometer. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

 $(Me_2PhSi)CH_2P(BH_3)Me_2$. To a cold (0 °C) solution of $Me_3P(BH_3)$ (1.90 g, 21.1 mmol) in THF (30 mL) was added *n*-BuLi (8.45 mL, 21.1 mmol). The resulting solution was allowed

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Table 5. Crystanographic Data for 15, 14, 15, and 10.	Table 5.	Crystallographic	Data for	13, 14,	, 15, and 16:
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	13	14	15	16
formula	$C_{22}H_{42}B_2P_2Si_2Sn$	C ₂₂ H ₄₂ B ₂ P ₂ PbSi ₂	$C_{12}H_{38}B_2P_2Si_2Sn$	$C_{12}H_{38}B_2P_2PbSi_2$
$M_{ m w}$	565.0	653.5	440.9	529.4
cryst size/mm	$0.30 \times 0.20 \times 0.20$	$0.42 \times 0.20 \times 0.10$	0.40 imes 0.30 imes 0.30	$0.30 \times 0.20 \times 0.20$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	C2/c	$P2_1/c$	$P2_1/c$
a /Å	11.8589(5)	30.4056(6)	6.68543(14)	6.66086(15)
b /Å	18.8499(9)	12.4203(2)	21.6435(3)	21.7767(5)
c /Å	13.0329(6)	16.7601(4)	15.9783(4)	15.9405(3)
β/deg	101.717(4)	112.894(3)	100.905(2)	100.237(2)
$V/\text{\AA}^3$	2852.7(2)	5830.8(2)	2270.24(7)	2275.40(8)
Ż	4	8	4	4
μ/mm^{-1}	1.100	5.986	1.361	7.650
transmn coeff range	0.735-0.810	0.188-0.590	0.612-0.686	0.207-0.310
reflns measd	16839	27 608	24 088	16219
unique reflns	5569	7256	5661	5515
R _{int}	0.045	0.033	0.032	0.025
reflns with $F^2 > 2\sigma$	4372	5387	4520	4405
refined params	294	294	206	206
R (on $F, F^2 > 2\sigma)^a$	0.052	0.021	0.023	0.019
$R_{\rm w}$ (on F^2 , all data) ^a	0.144	0.035	0.049	0.033
goodness of fit ^a	1.086	0.900	1.021	0.929
max., min. electron density/e $Å^{-3}$	1.99, -1.28	0.84, -0.64	0.51, -0.46	0.86, -0.72

^{*a*} Conventional $R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}; S = [\sum w(F_o^2 - F_c^2)^2 / (\text{no. data} - \text{no. params})]^{1/2}$ for all data.

to attain room temperature and was stirred for 3 h, then added to a cold (-78 °C) solution of Me₂PhSiCl (3.61 g, 21.1 mmol) in THF (10 mL). This mixture was allowed to attain room temperature and was stirred for 16 h. Water (50 mL) was added, the organic layer was extracted into diethyl ether (3×30 mL), the combined organic extracts were dried over MgSO₄ and filtered, and the solvent was removed *in vacuo* from the filtrate to give (Me₂PhSi)CH₂P(BH₃)Me₂ as a white solid, which was purified by crystallization from cold (-30 °C) methylcyclohexane (20 mL). Isolated yield: 2.55 g, 54%. Anal. Calcd for C₁₁H₂₂BPSi: C 58.94, H 9.89. Found: C 59.04, H 10.03. ¹H{¹¹B} NMR (CDCl₃, 25 °C): δ 0.49 (s, 6H, SiMe₂), 0.58 (d, ²J_{PH} = 16.1 Hz, 3H, BH₃), 1.14 (d, ²J_{PH} = 14.7 Hz, 2H, CH₂), 1.18 (d, ²J_{PH} = 10.6 Hz, 6H, PMe), 7.34–7.60 (m, 5H, Ph). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ –1.06 (d, J_{PC} = 1.9 Hz, SiMe₂), 14.89 (CH₂), 14.93 (d, J_{PC} = 37.4 Hz, PMe₂), 128.16 (*m*-Ph), 129.67 (*p*-Ph), 133.60 (*o*-Ph), 137.99 (d, J_{PC} = 3.84, *ipso*-Ph). ¹¹B{¹H} NMR (CDCl₃, 25 °C): δ –37.3 (d, J_{PB} = 61 Hz). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ 3.8 (q, J_{PB} = 61 Hz).

rac-[{Me₂P(BH₃)}(Me₂PhSi)CH]₂Sn (13). To a solution of (Me₂PhSi)CH₂P(BH₃)Me₂ (1.24 g, 5.53 mmol) in THF (20 mL) was added n-BuLi (2.21 mL, 5.53 mmol). The resulting solution was stirred for 1 h, and then solvent was removed in vacuo to yield a colorless oil. This oil was dissolved in toluene (20 mL) and added to a solution of freshly sublimed Cp₂Sn (0.69 g, 2.77 mmol) in toluene (20 mL). This mixture was stirred for 30 min, then filtered. The solvent was removed in vacuo from the filtrate to yield a yellow solid, which was dissolved in toluene/THF (30 mL of a 1:1 mixture) and cooled to $-30 \text{ }^{\circ}\text{C}$ for 16 h to yield 13 as yellow blocks. Isolated yield: 1.34 g, 86%. Anal. Calcd for C₂₂H₄₂B₂P₂Si₂Sn: C 46.77, H 7.49. Found: C 46.85, H 7.53. ¹H{¹¹B} NMR (d_8 -THF, 25 °C): δ 0.41 (s, 3H, SiMe), 0.45 (d, ${}^{2}J_{\text{PH}} = 11.9 \text{ Hz}, 3\text{H}, \text{BH}_{3}$, 0.63 (s, 3H, SiMe), 1.13 (d, ${}^{2}J_{\text{PH}} =$ ^{10.1} Hz, 3H, PMe), 1.19 (d, ${}^{2}J_{PH} = 10.5$ Hz, 3H, PMe), 1.36 (d, ${}^{2}J_{PH} = 14.2$ Hz, 1H, CH), 7.29–7.62 (m, 5H, Ph). ${}^{13}C{}^{1}H$ NMR (d_8 -THF, 25 °C): δ – 1.53 (SiMe), 1.14 ($d_7^{3}J_{PC} = 4.8$ Hz, SiMe), 15.47 ($d_7^{1}J_{PC} = 34.5$ Hz, PMe), 17.41 ($d_7^{1}J_{PC} = 34.5$ Hz, PMe), 19.70 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz, CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz; CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz; CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz; CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz; CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz; CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{SnC} = 418$ Hz; CH), 127.75 ($d_7^{1}J_{PC} = 11.5$ Hz; $d_7^{1}J_{PC} = 11.5$ Hz; dPh), 128.81 (*p*-Ph), 133.77 (*o*-Ph), 141.48 (*ipso*-Ph). $^{11}B{}^{1}H{}$ NMR (d_8 -THF, 25 °C): δ -34.5 (d, J_{PB} = 76 Hz). $^{31}P{}^{1}H{}$ NMR (d_8 -THF, 25 °C): δ 6.8 (q, J_{PB} = 76 Hz). $^{119}Sn{}^{1}H{}$ NMR (d₈-THF, 25 °C): δ 375 (br). UV/vis (1.0 mM in dichloromethane): λ_{max} 324 nm ($\varepsilon = 250 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). IR (solid, cm⁻¹): 3055 (w), 2950 (w), 2904 (w), 2565 (w), 2354 (s), 2170 (m), 2082 (m), 2039 (m), 1977 (m), 1920 (w), 1832 (w),

1411 (m), 1254 (m), 1096 (s), 922 (s), 829 (s), 809 (s), 731 (s), 687 (s).

rac-[{Me₂P(BH₃)}(Me₂PhSi)CH]₂Pb (14). To a solution of (Me₂PhSi)CH₂P(BH₃)Me₂ (0.51 g, 2.28 mmol) in THF (20 mL) was added n-BuLi (0.91 mL, 2.28 mmol). The resulting solution was stirred for 1 h, and then solvent was removed in vacuo to yield a colorless oil. This oil was dissolved in toluene (20 mL) and added to a solution of freshly sublimed Cp₂Pb (0.38 g, 1.14 mmol) in toluene (20 mL). The solution was stirred for 30 min, then filtered. The solvent was removed in vacuo from the filtrate to yield a yellow solid, which was dissolved in diethyl ether/THF (15 mL of a 1:1 mixture) and cooled to $-30 \degree$ C for 16 h to yield 14 as yellow blocks. Isolated yield: 0.54 g, 72%. Anal. Calcd for C₂₂H₄₂B₂P₂Si₂Pb: C 40.43, H 6.48. Found: C 40.50, H 6.51. ¹H{¹¹B} NMR (d_8 -THF, 25 °C): δ 0.00 (d, ² $J_{PH} = 10.1$ Hz, 3H, BH_3 , 0.38 (s, 3H, SiMe), 0.56 (s, 3H, SiMe), 0.87 (d, ${}^2J_{PH} = 13.8$ Hz, 1H, CH), 1.09 (d, ${}^{2}J_{PH} = 10.1$ Hz, 3H, PMe), 1.16 (d, ${}^{2}J_{PH} =$ 10.5 Hz, 3H, PMe), 7.28–7.59 (m, 5H, Ph). $^{13}C{^{1}H}$ NMR (d_{8} -THF, 25 °C): $\delta -0.84$ (SiMe), 1.35 (d, ${}^{3}J_{PC} = 5.8$ Hz, SiMe), 19.60 (d, ${}^{1}J_{PC} = 34.5$ Hz, PMe), 20.78 (d, ${}^{1}J_{PC} = 35.5$ Hz, PMe), 52.52 (d, ${}^{1}J_{PC} = 11.5$ Hz; ${}^{1}J_{PbC} = 744$ Hz, CH), 127.8 (*m*-Ph), 128.77 (*p*-Ph), 133.75 (*o*-Ph), 143.21 (d, ${}^{3}J_{PC} = 1.9$ Hz, *ipso*-Ph). ¹¹B{¹H} NMR (d_8 -THF, 25 °C): δ -40.4 (d, J_{PB} = 77 Hz). ³¹P{¹H} NMR (d_8 -THF, 25 °C): δ 6.8 (q, J_{PB} = 77 Hz). ²⁰⁷Pb NMR (d₈-THF, 25 °C): δ 3931 (br s). UV/vis (1.0 mM in toluene): λ_{max} 370 nm ($\varepsilon = 738 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). IR (solid, cm⁻¹): 2962 (w), 2356 (w), 2156 (w), 2104 (w), 1569 (w), 1412 (w), 1258 (m), 1088 (s), 1029 (s), 916 (m), 800 (s), 727 (m), 692 (m), 622 (m).

rac-[{**Me**₂**P**(**BH**₃)}(**Me**₃**Si**)**CH**]₂**Sn** (15). To a solution of (Me₃Si)CH₂P(BH₃)Me₂ (1.06 g, 6.54 mmol) in THF (30 mL) was added *n*-BuLi (2.60 mL, 6.54 mmol). This mixture was stirred for 1 h, and then the solvent was removed *in vacuo*. The resulting colorless oil was dissolved in toluene (20 mL) and added to a solution of freshly sublimed Cp₂Sn (0.81 g, 3.27 mmol) in toluene (20 mL). This solution was stirred for 30 min and then filtered. The solvent was removed *in vacuo* from the filtrate to yield a yellow solid, which was dissolved in diethyl ether (10 mL) and cooled to $-30 \,^{\circ}$ C for 16 h to yield **15** as yellow needles. Isolated yield: 1.35 g, 94%. Anal. Calcd for C₁₂H₃₈-B₂P₂Si₂Sn: C 32.69, H 8.69. Found: C 32.62, H 8.59. ¹H{¹¹B} NMR (*d*₈-toluene, 25 °C): δ 0.26 (s, 9H, SiMe₃), 0.82 (d, ²*J*_{PH} = 10.1 Hz, 3H, PMe), 1.07 (d, ²*J*_{PH} = 10.5 Hz, 3H, PMe). ¹³C{¹H} NMR (*d*₈-toluene, 25 °C): δ 2.45 (d, ³*J*_{PC} = 2.9 Hz, SiMe₃), 16.18

(d, ${}^{1}J_{PC} = 34.5$ Hz, PMe), 18.29 (d, ${}^{1}J_{PC} = 34.5$ Hz, PMe), 20.75 (d, ${}^{1}J_{PC} = 10.6$ Hz, ${}^{1}J_{SnC} = 417.5$ Hz, CH). ${}^{11}B{}^{1}H{}$ NMR (d_{8} -toluene, 25 °C): $\delta - 34.2$ (d, $J_{PB} = 79$ Hz). ${}^{31}P{}^{1}H{}$ (d_{8} -toluene, 25 °C): $\delta 5.9$ (q, $J_{PB} = 79$ Hz; ${}^{2}J_{SnP} = ca.$ 200 Hz). ${}^{119}Sn{}^{1}H{}$ NMR (d_{8} -toluene, 25 °C): $\delta 377$ (br s). UV/vis (1.0 mM in methylcyclohexane): λ_{max} 316 nm ($\varepsilon = 1848$ dm³ mol⁻¹ cm⁻¹). IR (solid, cm⁻¹): 2936 (m), 2363 (m), 2079 (w), 1415 (w), 1250 (m), 1067 (m), 924 (m), 834 (s), 758 (m), 668 (m), 572 (m), 547 (m).

rac-[{Me₂P(BH₃)}(Me₃Si)CH]₂Pb (16). To a solution of (Me₃Si)CH₂P(BH₃)Me₂ (0.89 g, 5.49 mmol) in THF (30 mL) was added n-BuLi (2.20 mL, 5.49 mmol). This mixture was stirred for 1 h and solvent was removed in vacuo. The resulting colorless oil was dissolved in toluene (20 mL) and added to a solution of freshly sublimed Cp₂Pb (0.93 g, 2.75 mmol) in toluene (20 mL). The solution was stirred for 30 min and then filtered. The solvent was removed in vacuo from the filtrate to yield a yellow solid, which was dissolved in diethyl ether (15 mL) and cooled to -30 °C for 16 h to yield **16** as yellow needles. Isolated yield: 1.10 g, 76%. Anal. Calcd for C12H38B2P2PbSi2: C 27.23, H 7.24. Found: C 27.33, H 7.20. ¹H{¹¹B} NMR (d₈toluene, 25 °C): δ 0.21 (s, 9H, SiMe₃), 0.33 (d, ²J_{PH} = 9.7 Hz, 3H, BH₃), 0.50 (d, ²J_{PH} = 13.8 Hz, 1H, CH), 1.01 (d, ²J_{PH} = 10.1 Hz, 3H, PMe), 1.07 (d, ²J_{PH} = 10.1 Hz, 3H, PMe). ¹³C{¹H} NMR SH, PMe), 1.07 (d, $J_{PH} = 10.1$ Hz, 5H, PMe). C{ H} NMR (d_8 -toluene, 25 °C): δ 3.33 (d, ${}^{3}J_{PC} = 2.9$ Hz, SiMe₃), 20.85 (d, ${}^{1}J_{PC} = 34.5$ Hz, PMe), 21.72 (d, ${}^{1}J_{PC} = 33.6$ Hz, PMe), 53.24 (d, ${}^{1}J_{PC} = 12.5$ Hz, ${}^{1}J_{PbC} = 746$ Hz, CH). ¹¹B{¹H} NMR (d_8 -toluene, 25 °C): δ -40.3 (d, $J_{PB} = 79$ Hz, $J_{PbB} = ca. 100$ Hz). ${}^{31}P{}^{1}H{}$ (d_8 -toluene, 25 °C): δ 6.2 (q, $J_{PB} = 79$ Hz, ${}^{2}J_{PbP} = ca.$ 200 Hz). ${}^{207}Pb{}^{1}H{}$ NMR (d_8 -toluene, 25 °C): δ 3902 (br s). UV/ vis (1.0 mM in methylcyclohexane): λ_{max} 360 nm ($\epsilon = 958 \text{ dm}^3$ mol⁻¹ cm⁻¹). IR (solid cm⁻¹): 2959 (w), 2360 (w), 1611 (w), 1407 (w), 1381 (w), 1255 (m), 1018 (s), 926 (m), 791 (s), 690 (m), 604 (w), 570 (w), 534 (m).

Crystal Structure Determinations of 13, 14, 15, and 16. Measurements were made at 150 K on an Oxford Diffraction Gemini A Ultra diffractometer using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semiempirically for absorption, based on symmetryequivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. Further details are given in Table 5. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were constrained with a riding model, while B-bound H atoms were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs were Oxford Diffraction CrysAlisPro for data collection and processing and SHELXTL for structure solution, refinement, and molecular graphics.26

DFT Calculations. Geometry optimizations on the gas-phase molecules were performed with the Gaussian03 suite of programs (revision E.02)²⁷ via the UK National Grid Service or the UK National Service for Computational Chemistry Software (http://www.nsccs.ac.uk). Optimizations were performed using the B3LYP hybrid functional²⁰ with a Lanl2dz effective core potential basis set²¹ for Sn and Pb and a 6-31G(d,p) all-electron basis set²² on the remaining atoms [default parameters were used throughout]. The dimerization energy for 15a was corrected for basis set superposition error using the counterpoise method.² The location of minima was confirmed by the absence of imaginary vibrational frequencies in each case. Natural bond orbital analyses were performed using the NBO 3.0 module of Gaussian03;23 the stabilization energy associated with the B-H···E interactions was calculated using the NBODel routine, in which the elements affording this interaction were selectively deleted.24

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Supporting Information Available: For 13, 14, 15, and 16 details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format; for 13, 14, and 15 crystal packing diagrams. For 13a, 13b, 14a, 14b, 15, 16, and 15₂ details of DFT calculations, final atomic coordinates, and energies. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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