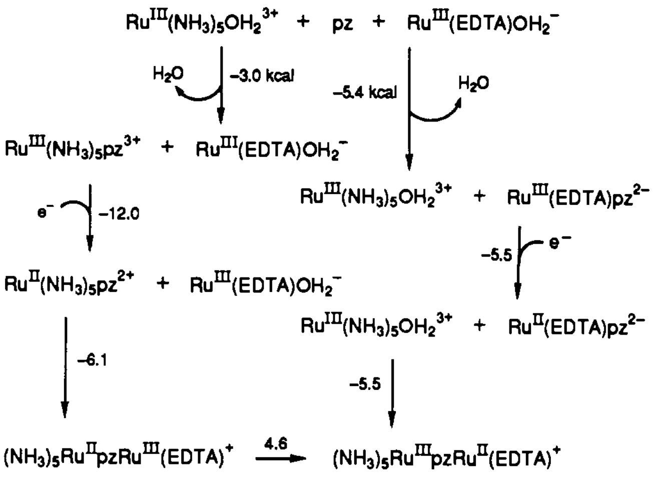
**Scheme III**



in the ammine system as compared to that in the EDTA system has been ascribed[1] to an increased interaction between the Ru(II) $\pi$d and L $\pi^*$ orbitals.

Finally, we examine the dissociation of M into its component mononuclear units (reverse of eq 1 or eq 14). Table V shows that dissociation of M via rupture of the $Ru^{III}$(EDTA)-pz bond is

$$(NH_3)_5Ru^{II}pzRu^{III}(EDTA)^+ + H_2O \rightleftharpoons Ru^{II}(NH_3)_5pz^{2+} + Ru^{III}(EDTA)OH_2^- \quad (14)$$

considerably more favorable than dissociation via the alternate $Ru^{II}(NH_3)_5$-pz bond rupture mode ($\Delta G°$ values of 6.1 and 13.2 kcal/mol, respectively). This results from the substantial stabilization of Ru(II)-pz bonds via Ru(II) d$\pi$-L $\pi^*$ back-bonding. Free energy changes associated with rupture of a Ru(II)-pz bond fall in the range 11.1-13.3 kcal/mol, whereas free energy changes associated with Ru(III)-pz bond-breaking fall in the range 2.6-6.1 kcal/mol. It is noteworthy that the formation of $Ru^{III}$(EDTA)-pz complexes is 1.3-2.4 kcal more exoergonic than the formation of the corresponding $Ru^{III}(NH_3)_5$-pz complexes. A similar trend is seen for the formation of pyridine and isonicotinamide complexes.[11,25,26] Presumably, Ru(III)-pz back-bonding is practically nonexistent for $Ru^{III}(NH_3)_5^{3+}$, whereas for $Ru^{III}(EDTA)^-$, with the accumulation of negative charge on the ruthenium center, its $\pi$ basicity is not negligible and is reflected in its higher affinity, compared to that of $Ru^{III}(NH_3)_5^{3+}$, toward the $\pi$ acidic nitrogen heterocycles.

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(26) $\Delta G°$ values for formation of $Ru^{III}(NH_3)_5$-L and $Ru^{III}$(EDTA)-L complexes are: L = pyridine, -4.7 and -6.8 kcal/mol; L = isonicotinamide, -4.5 and -5.6 kcal/mol.

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Contribution from the Departments of Chemistry, Southern Methodist University, Dallas, Texas 75275,
and The University of Texas at Austin, Austin, Texas 78712

# The First Phosphorus Closo Complex of a Dicarborane System: Synthesis and Characterization of 1-[2,4,6-Tris(*tert*-butyl)phenyl]-2,3-bis(trimethylsilyl)-2,3-dicarba-1-phospha-*closo*-heptaborane

Narayan S. Hosmane,[*,†] Kai-Juan Lu,[†] Alan H. Cowley,[*,‡] and Miguel A. Mardones[‡]

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The reaction between the $Na^+(THF)Li^+[2,3-(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt and $2,4,6-(t-Bu)_3C_6H_2PCl_2$ in a molar ratio of 1:1 in dry THF produced in 38% yield the previously unknown *closo*-phosphacarborane complex, $1-[2,4,6-(t-Bu)_3C_6H_2]-1-P-2,3-(SiMe_3)_2-2,3-C_2B_4H_4$ (I) as an air-sensitive, white, crystalline solid. The new complex was characterized by $^1H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR, IR, and mass spectroscopy. These spectroscopic data are consistent with the proposed pentagonal-bipyramidal structure, which contains 16 skeletal valence electrons.

## Introduction

A group 15 atom is isoelectronic and isolobal with a CH group. Therefore, one would expect that substitution of a group 15 element for a CH group in a dicarborane would yield compounds with similar structures and comparable reactivities. Indeed, all of the group 15 elements have been inserted into monocarborane cages, and the resulting icosahedral heterocarboranes have been characterized.[1] The icosahedral geometries of these heterocarboranes are supported by the X-ray analysis of *closo*-$9,10-Cl_2-1,7-CPB_{10}H_9$.[2] Surprisingly, the chemistry of the $C_2B_9$ carborane system containing group 15 elements has been limited to aza- and arsacarboranes. However, none of the group 15 elements has been incorporated into a $C_2B_4$ carborane as an integral part of the polyhedron. Even though Wallbridge and co-workers have reported in 1979 a brief account of the insertion of a "bare" phosphorus atom into the open face of a $C_2B_8$ carborane to produce *nido*-$9-P-7,8-C_2B_8H_{11}$,[3] the insertions of RP (R = aryl or alkyl group) moieties in an $\eta^5$-fashion into the dicarborane systems to produce the corresponding *closo*-phosphacarborane derivatives have not been reported to date. We report herein the synthesis and characterization of the first *closo*-phosphacarborane based on a dicarborane system.

## Experimental Section

**Materials.** 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) was prepared by the methods of Hosmane et al.[4,5] Solution of the lithium sodium double salt of the *nido*-carborane dianion $Na^+(THF)Li^+[2,3-(SiMe_3)_2-2,3-C_2B_4H_4]^{2-}$ in tetrahydrofuran (THF) was prepared by the method described elsewhere.[6] The supermesityldichlorophosphine $2,4,6-(t-Bu)_3C_6H_2PCl_2$ was prepared and purified according to the literature method.[7] The purity of the phosphorus reagent was checked by IR and NMR spectroscopy and on the basis of the melting point. A 1.7

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† Southern Methodist University.

‡ The University of Texas at Austin.

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M solution of *tert*-butyllithium (*t*-BuLi) in *n*-pentane was obtained from Aldrich Chemical Co., Milwaukee, WI and used as received. NaH (Aldrich) in mineral oil dispersion was washed repeatedly with dry pentane. Benzene and THF were dried over $LiAlH_4$ and doubly distilled before use. All other solvents were dried over 4–8 mesh molecular sieves (Davidson) and either saturated with dry argon or degassed before use.

**Spectroscopic Procedures.** Proton, boron-11, carbon-13, and phosphorus-31 pulse Fourier transform NMR spectra, at 200, 64.2, 50.3, and 81.01 MHz, respectively, were recorded on an IBM-200 SY multinuclear NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer and a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Mass spectral determinations were performed on Finnigan TSQ-70 and ZAB2-E instruments at the University of Texas at Austin.

**Synthetic Procedure.** Syntheses were carried out in Pyrex glass round-bottom flasks of 250-mL capacity, containing magnetic stirring bars and fitted with high-vacuum Teflon valves. Nonvolatile substances were manipulated in either a drybox or evacuable glovebags under an atmosphere of dry nitrogen. All known compounds among the products were identified by comparing their IR and $^1H$ NMR spectra with those of authentic samples.

**Synthesis of *closo*-1-[2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]-1-P-2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_4$ (I).** A 10.15 mmol sample of the $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt was allowed to react with 10.15 mmol of anhydrous 2,4,6-$(t\text{-}Bu)_3C_6H_2PCl_2$ (3.525 g) in dry THF (20 mL) at 0 °C for 2 h, during which time the solution became turbid and its color turned to pale yellow. After removal of THF from the heterogeneous solution in vacuo, the yellow residue was heated to 130 °C, and the product was sublimed out of the reactor into a detachable U-trap that was held at 0 °C. The resulting white solid was identified as 1-P[2,4,6-$(t\text{-}Bu)_3C_6H_2$]-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (I) (1.92 g, 3.89 mmol; 38% yield). After complete removal of I from the reactor, the remaining residue was heated further to 180 °C overnight. The resulting bright orange solid (0.67 g, 1.21 mmol; 12% yield based on 2,4,6-$(t\text{-}Bu)_3C_6H_2PCl_2$ consumed) was identified as the diphosphene $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2P]_2$ by $^1H$, $^{13}C$, and $^{31}P$ NMR and mass spectroscopy.[8] The polymeric material that remained in the reactor after the second sublimation was insoluble in organic solvents and was therefore discarded.

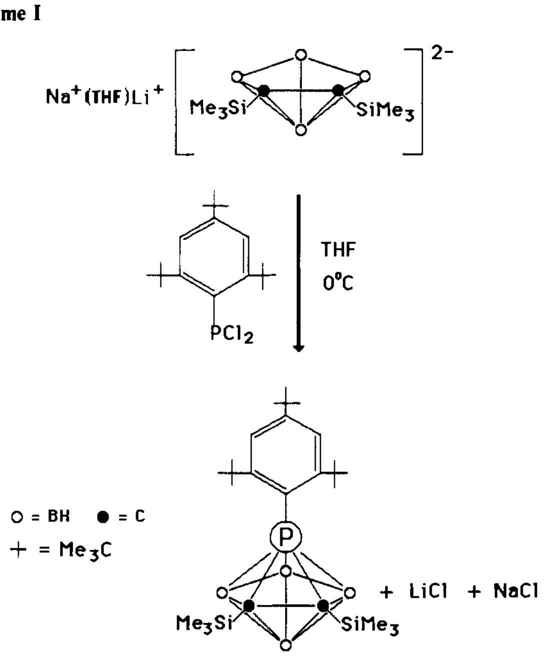
The physical properties and characterization of I are as follows: mp 147–148 °C; sensitive to air and moisture; soluble in both polar and nonpolar organic solvents; $^1H$ NMR ($C_6D_6$, relative to external $Me_4Si$) $\delta$ 7.52 [s (br), 2 H, $C_6H_2$], 1.56 [s (br), 9 H, *p*-$Me_3C$], 1.34 [s (br), 18 H, *o*-$Me_3C$], 0.23 [s (br), 18 H, $SiMe_3$]; $^{11}B$ NMR ($C_6D_6$, relative to external $BF_3{\cdot}OEt_2$) $\delta$ 15.85 [d, 2 B, basal BH, $^1J(^{11}B\text{–}^1H)$ = 165.65 Hz], 7.68 [d, 1 B, basal BH, $^1J(^{11}B\text{–}^1H)$ = 164.88 Hz], −16.63 [d, 1 B, apical BH, $^1J(^{11}B\text{–}^1H)$ = 174.39 Hz]; $^{13}C$ NMR (relative to external $Me_4Si$) $\delta$ 149.75 [d, phenyl C–P, $^1J(^{13}C\text{–}^{31}P)$ = 61 Hz], 123.44 [s, *p*ara-phenyl C], 122.30 [s, ortho phenyl C], 119.66 [d, meta phenyl CH, $^1J(^{13}C\text{–}^1H)$ = 153.5 Hz], 119.25 [d (br), cage carbons (SiCB), $^1J(^{13}C\text{–}^{31}P)$ = 115 Hz], 37.44 [s (br), q-C, $Me_3C$], 34.1 [s (br), q-C, $Me_3C$], 32.66 [q of d, 3 C, $Me_3C$, $^1J(^{13}C\text{–}^1H)$ = 114 Hz, $^6J(^{13}C\text{–}^{31}P)$ = 7.4 Hz], 31.63 [q of d, 6 C, $Me_3C$, $^1J(^{13}C\text{–}^1H)$ = 125 Hz, $^4J(^{13}C\text{–}^{31}P)$ = 14.9 Hz], 0.88 [q (br), $SiMe_3$, $^1J(^{13}C\text{–}^1H)$ = 119 Hz], $^{31}P$ NMR (relative to external $H_3PO_4$) $\delta$ −129.68 [s (br), cage P]; IR ($cm^{-1}$; $C_6D_6$ vs $C_6D_6$) 3225 (m), 2955 (vs), 2861 (vs) [$\nu$(C–H)], 2600 (vs) [$\nu$(B–H)], 1901 (w, br), 1866 (w), 1684 (w), 1619 (s), 1596 (sh), 1549 (w), 1455 (s), 1408 (w) [$\delta(CH)_{asym}$], 1361 (m), 1331 (vs), 1255 (s) [$\delta(CH)_{sym}$], 1161 (s, s), 1067 (s, br), 910 (m, sh), 838 (vs, sh), 808 (vvs, br) [$\rho$(CH)], 761 (w, s), 597 (vs, br).

## Results and Discussion

During the course of our study of the reactivity of $C_2B_4$ carborane dianions toward dihalides of the group 15 elements, the $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}$ double salt was treated with 2,4,6-$(t\text{-}Bu)_3C_6H_2PCl_2$ in a molar ratio of 1:1 in dry tetrahydrofuran (THF) to produce in low yield the previously unknown *closo*-phosphacarborane complex, 1-[2,4,6-$(t\text{-}Bu)_3C_6H_2$]-1-P-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (I) (see Scheme I). This compound was isolated as a white, air-sensitive, solid, which does not form crystals that are suitable for X-ray analysis.

The electron-impact mass spectrum of I exhibited a weak parent ion grouping $[^{31}P(^{12}CH_3)_{15}{}^{28}Si_2{}^{12}C_{11}{}^{11}B_4H_6]^+$ with the major cutoff at *m*/*z* 494. However, the exact mass measurement of 495.3636 for the elemental composition $^{12}C_{26}H_{51}{}^{11}B_4{}^{28}Si_1{}^{29}Si_1{}^{31}P$ is in good agreement with the calculated mass of 495.3634. Thus, the mass

**Scheme I**



spectra unambiguously confirm the molecular composition of I.

The $^1H$ and $^{13}C$ NMR spectra (see Experimental Section) clearly indicate the presence of two equivalent and one nonequivalent *tert*-butyl groups, two equivalent $SiMe_3$ groups, and two equivalent phenyl CH groups in I. The proton-coupled $^{11}B$ NMR spectrum (see Experimental Section) shows two downfield doublets and a third upfield doublet, whose relative areas include a 2:1:1 distribution of basal and apical BH groups, respectively. The 34 ppm downfield shift of the apical BH resonances in I compared with those of the *nido*-carborane precursor is indicative of the stronger interaction between the apical phosphorus and the apical boron transmitted through the basal borons, and thus imply a *closo*-geometry for the title compound. This observation is consistent with the $^{11}B$ NMR spectra of all known heterocarboranes of the $C_2B_4$ system.[9] The splitting of the broad resonances of the cage carbons due to $^{31}P$ coupling and shielding of these resonances as a result of formation of the *closo*-phosphacarborane complex are the most significant features in the $^{13}C$ NMR spectra of I. The proton-coupled and proton decoupled $^{31}P$ NMR spectra show a slightly broad singlet at −129.7 ppm that corresponds to the apical phosphorus atom (see Experimental Section). The upfield shift (by about 283 ppm) of the $^{31}P$ resonance in I from that of the precursor, 2,4,6-$(t\text{-}Bu)_3C_6H_2PCl_2$,[7] is indicative of the $\pi$-complexation that exists between the carborane cage and the phosphorus atom.

The IR (see Experimental Section), NMR, and mass spectroscopic data for I are all consistent with the proposed pentagonal-bipyramidal structure, which contains 16 skeletal valence electrons {assigning two from P[2,4,6-$(t\text{-}Bu)_3C_6H_2$], three from each $C(SiMe_3)$, and two from each BH unit}. Since it has been established[1] that the main-group elements utilize one radially oriented p or sp hybrid and two tangentially oriented p orbitals in bonding, the effective bonding of the heteroatom to the carborane face would generally be accompanied by a slip-distortion of the heterocarborane cage and tilting of the heteroatom-bound *exo*-polyhedral moiety toward the cage carbons. This is evident in the crystal structures of *closo*-heterocarborane derivatives of group 13 elements such as 3,1,2-$Al(Et)C_2B_9H_{11}$,[10] 1,2,3-$Ga(Me)C_2B_4H_6$,[11] and 1,2,3-$Ga(t\text{-}Bu)(SiMe_3)_2C_2B_4H_4$.[12] A similar

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bonding environment of the 2,4,6-($t$-Bu)$_3$C$_6$H$_2$P moiety in I is anticipated.

This work, together with earlier studies in our laboratory,[9] and elsewhere,[13,14] suggests that the reactivity of the $Na^+(THF)Li^+[2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ double salts (R = SiMe$_3$, Me, or H) toward a variety of dihalo compounds of the main-group elements and transition metals should lead to several new carborane compounds. Efforts to incorporate other group 15 elements into the $C_2B_4$ carborane system are currently underway in our laboratories.

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Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60208

# Synthesis of $K_4M_3Te_{17}$ (M = Zr, Hf) and the Structure of $K_4Hf_3Te_{17}$, a New One-Dimensional Solid-State Ternary Polytelluride

Patricia M. Keane and James A. Ibers*

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The compounds $K_4Zr_3Te_{17}$ and $K_4Hf_3Te_{17}$ have been synthesized through the reaction at 900 °C of Zr or Hf with a $K_2Te$/Te melt as a reactive flux. The compounds crystallize in space group $C_{2h}^5$-$P2_1/c$ of the monoclinic system with four formula units in cells: $a$ = 10.148 (6) Å, $b$ = 28.889 (17) Å, $c$ = 11.626 (7) Å, $\beta$ = 115.21 (2)° ($T$ = 107 K) for $K_4Hf_3Te_{17}$; $a$ = 10.146(2) Å, $b$ = 29.98 (1) Å, $c$ = 11.669 (4) Å, $\beta$ = 115.01 (3)° ($T$ = 153 K) for $K_4Zr_3Te_{17}$. The structure of $K_4Hf_3Te_{17}$ has been determined from single-crystal X-ray data. The structure comprises infinite, one-dimensional chains of Hf-centered polyhedra that extend along [101] and are separated from each other by K$^+$ ions. Each Hf atom is eight-coordinate. If the Te–Te maximum bond length is taken to be 2.94 Å, then there are six $Te_2^{2-}$ ligands, one $\mu_2$-$\eta^1$-$Te_2^{2-}$ ligand, and a $\mu$-$Te_3^{2-}$ ligand. The composition of the infinite chain is $^1_\infty[Hf_3(Te_3)(Te_2)_7{}^{4-}]$ with the Hf atoms present in the +4 oxidation state.

## Introduction

Recently, the use of fluxes or molten salts in the synthesis of new ternary polychalcogenides was described.[1] This technique exploits molten salts of the type $A_2Q/Q$ (A = alkali metal, Q = chalcogenide (S, Se, Te)) not only as a flux or crystallizing agent but also as a reactant. The resultant compounds typically exhibit unusual chalcogen–chalcogen bonding and novel structure types. Although there have been several ternary sulfides[1-3] and selenides[2,4,5] reported that make use of this synthetic procedure, no tellurides have been synthesized. In general, the well-characterized intercalation compounds of the type $A_xM_yQ_z$ (M = group IV-VI metal; Q = S, Se, Te) are pervasive in this system.[6,7] The extreme thermodynamic stability of the binary metal tellurides $MTe_3$[8] and $MTe_5$[9] (M = Zr, Hf) hinders the formation of the new ternary polytellurides. We demonstrate here that through utilization of a $K_2Te$/Te flux, the technique, as predicted,[1] can be extended to the tellurides.

## Experimental Section

In order to facilitate the reaction, elemental K (Alfa, 99%) and elemental Te (AESAR, 99.5%) in the stoichiometric ratio of 1:2 were prereacted at 650 °C for 3 days. In a drybox under an Ar atmosphere, 0.157 g of this mixture, 0.025 g of Hf powder (AESAR, 99.6%), and 0.068 g of Te powder were ground together and then loaded into a silica tube. The tube was subsequently evacuated (~10$^{-4}$ Torr) and sealed. It was heated at 650 °C for 6 days and then ramped to 900 °C to heat for 4 days. The tube was then cooled at a rate of 3 °C/h to 450 °C and then to room temperature at 90 °C/h. The product contained air-stable, dull black needle-shaped crystals at the surface and within the melt. Single crystals of what proved to be $K_4Hf_3Te_{17}$ suitable for X-ray diffraction studies were manually extracted from the melt. $K_4Zr_3Te_{17}$ was prepared by the same route with 0.165 g of the K/Te mixture, 0.0135 g of Zr powder (AESAR, 99%), and 0.071 g of Te powder. Similarly, the product consisted of dull black needles within the melt.

Analysis of these compounds with an EDAX-equipped Hitachi S570 scanning electron microscope confirmed the presence of (K, Hf, Te) and (K, Zr, Te) in the approximate ratio of (3.8:3.0:14.4). The exact composition of the Hf compound was established from the X-ray structure determination.

**Table I.** Data Collection and Refinement Details for $K_4Hf_3Te_{17}$

| | | | |
|---|---|---|---|
| formula | $K_4Hf_3Te_{17}$ | density (calcd), g cm$^{-3}$ | 5.96 |
| fw | 2861.06 | | |
| space group | $C_{2h}^5$-$P2_1/c$ | radiation | graphite-monochromated Mo K$\alpha$ ($\lambda(K\alpha_1)$ = 0.7093 Å) |
| $a$, Å | 10.148 (6) | | |
| $b$, Å | 29.889 (17) | linear abs coeff, cm$^{-1}$ | 225 |
| $c$, Å | 11.626 (7) | | |
| $\beta$, deg | 115.21 (2) | transm factors | 0.43–0.52[b] |
| vol, Å$^3$ | 3190 (1) | $R_w(F_o)$ | 0.094 |
| $Z$ | 4 | $R(F)$ for $F_o^2 > 3\sigma(F_o^2)$ | 0.084 |
| $T$, K | 107[a] | | |

[a] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [b] The analytical method was used for the absorption correction (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018).

## X-ray Structure Analysis

$K_4Zr_3Te_{17}$. The cell parameters ($a$ = 10.146 (2), $b$ = 29.98 (1), $c$ = 11.669 (4) Å; $\beta$ = 115.01 (3)°) of a single crystal of $K_4Zr_3Te_{17}$ were determined by a least-squares analysis of 25 reflections centered on an Enraf-Nonius CAD4 diffractometer at 153 K. Systematic absences were

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