of the carbanion **3a**$_1$ affords the intermediate **3a**$_2$ which is alkylated at sulfur leading to **6a** and finally to **5a** (Scheme I).

The carbanion **3a**$_1$ may not be the kinetic product because the methylene protons α to the sulfur linked to Fe(1) probably are more acidic.[11] In addition, masked pathways can exist during all these transformations. Consequently, we have labeled specifically Fe(1) by replacement of a CO ligand with P(OMe)$_3$. Complex **3b** thus obtained[15] has been submitted to the same reaction sequence.[17] As expected, the coordination of P(OMe)$_3$ stabilizes complex **6b** by decreasing the electron demand on sulfur and consequently making the carbon–sulfur single bond less labile.[6] The structure of **6b** has been established by X-ray diffraction.[18] The ORTEP view (Figure 1) clearly shows that ring opening, followed by alkylation at the sulfur atom linked to iron, occurs without alteration of the metallic skeleton. Compound **6b** is analogous to **1b** previously described[2] with a sulfur atom, instead of oxygen linked to the tetragonal carbon atom C(1). When heated, **6b** undergoes the expected fragmentation giving rise to the carbenic complex **5b** which is in all respects identical with the monosubstituted phosphite derivative prepared independently from **5a**.[19] This transformation **5a** → **5b** is similar to **2a** → **2b** previously described in detail, the structure of **2b** being proved by an X-ray study.[20] In **6b** the P(OMe)$_3$ ligand is linked to Fe(1) while C(1) is bonded to Fe(2), but they are both coordinated to Fe(1) in complex **5b**. Consequently, owing to the phosphite ligand's reluctance to migrate, it is obvious that during the rearrangement the carbon atom C(1) discriminates between Fe(1) and Fe(2) to become bonded to the most electron-rich metal atom. This last step can only occur if in the transition state the carbon atom is bonded to both metal atoms.[2,5,6]

Registry No. **3a**, 90697-86-2; **3b**, 118459-31-7; **5a**, 118459-30-6; **5b**, 118459-33-9; **6a**, 118459-29-3; **6b**, 118459-32-8.

Supplementary Material Available: Tables of selected interatomic distances, selected bond angles, positional parameters, anisotropic thermal parameters and hydrogen parameters (6 pages); a listing of observed and calculated structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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(15) To a solution of **3a** (2 g, 4.8 mmol) in dry acetone (15 mL) cooled to −80 °C was added P(OMe)$_3$ (0.56 mL, 4.8 mmol). After 3 h under argon at −80 °C, the solvent was partly removed under vacuum and the residue chromatographed on silica plates. The strip of R_f 0.61 gave 0.2 g of **3a** and the strip of R_f 0.26 afforded 1.5 g of **3b** (68%) after crystallization from hexane. **3b**: mp 90 °C; mass spectrum, m/z calcd 511.820, found 511.821 ($M^{\bullet+}$). ^{1}H NMR (CDCl$_3$) δ 2.12 (m, 1 H), 2.53 (m, 3 H), 3.22 [d, P(OMe)$_3$]; ^{31}P NMR (toluene) δ 174.4; ^{13}C NMR (toluene at −85 °C) δ 36.8, 50.4, 51.3 [P(OMe)$_3$], 76.5 (d, CS, ^3J = 4 Hz), 209.9 (d, J = 6 Hz), 211.4 (d, J = 24 Hz), 212.4 (d, J = 3 Hz), 218.7 (2CO); IR (Nujol) 1932, 1972 (br), 2044 cm^{-1}. Anal. Calcd for $C_{11}H_{13}Fe_2O_8PS_3$: C, 25.80; H, 2.56; P, 6.05. Found: C, 26.01; H, 2.64; P, 5.90. The position of P(OMe)$_3$ was assigned by considering the low value of the $^3J_{P-C}$ coupling[16] and later by an X-ray diffraction study.[8]

(16) Lagadec, A.; Misterkiewicz, B.; Patin, H.; Mousser, A.; Le Marouille, J. Y. *J. Organomet. Chem.* **1986**, *315*, 201.

(17) A solution of **3b** (0.512 g, 1 mmol) in THF (50 mL) was treated at −70 °C, under argon, with a solution of LDA (0.150 g, 1.5 mmol) in 25 mL of THF. The reaction and treatment are conducted as for **3a**,[12] and we obtained 0.25 g (50%) of the orange compound **6b** (R_f 0.45) and 0.08 g (15%) of the red compound **5b** (R_f 0.54). **6b**: mp 103 °C; mass spectrum, m/z calcd 525.836, found 525.839 ($M^{\bullet+}$); ^{1}H NMR (CDCl$_3$) δ 2.27 (s, 3 H), 3.73 [d, P(OMe)$_3$], 5.26 (d, J = 10 Hz, 1 H) 5.31 (d, J = 17 Hz, 1 H), 6.52 (dd, J = 10 Hz, J = 17 Hz, 1 H); ^{13}C NMR (CDCl$_3$ at 36 °C) δ 32.2, 52.5 [P(OMe)$_3$], 67.9 (CS), 115.2, 134.8, 212 (multiplet for 3 CO), 214.2 (multiplet for 2 CO); IR (Nujol) 1947, 1993, 2043 cm^{-1}. Anal. Calcd for $C_{12}H_{15}Fe_2O_8PS_3$: C, 27.37; H, 2.87; P, 5.88; S, 18.27. Found: C, 27.33; H, 2.90; P, 6.00; S, 18.03. Crystals suitable for the X-ray study were obtained from hexane. **5b**: mp 70 °C, mass spectrum, m/z calcd 525.836, found 525.836 ($M^{\bullet+}$); ^{1}H NMR (CDCl$_3$) δ 2.10 (s, 3 H), 3.73 [d, P(OMe)$_3$], 5.47 (d, J = 14 Hz, 1 H), 5.80 (d, J = 17 Hz, 1 H), 6.29 (dd, J = 14 Hz, J = 17 Hz, 1 H); ^{13}C NMR (CDCl$_3$ at −55 °C) δ 23.4, 51.4 [P(OMe)$_3$], 122.7, 137.5, 206.1 (J = 13 Hz), 211.3 (J = 6 Hz), 213.5, 213.7 (J = 19 Hz), 214.9 (J = 4 Hz), 308.1 (carbene), at room temperature the carbene is at δ 309.5 (d, J = 3.7 Hz); ^{31}P NMR (CDCl$_3$) δ 176.7. Anal. Calcd for $C_{12}H_{15}Fe_2O_8PS_3$: C, 27.40; H, 2.87. Found: C, 27.86; H, 2.91.

(18) Crystal data for $C_{12}H_{15}Fe_2O_8PS_3$: space group $P\bar{1}$, a = 7.887 (2) Å, b = 11.756 (2) Å, c = 12.502 (6) Å, α = 110.52 (3)°, β = 100.30 (3)°, γ = 103.04 (2)°, V = 1014.5 Å^3, ρ(calcd) = 1.72 g cm^{-3} for M_r 526.11, Z = 2, μ = 18.38 cm^{-1}, for Mo Kα. A red-orange parallelipipedic crystal of **6b** (approximate dimensions 0.05 × 0.22 × 0.46 mm) was studied on a CAD4 Enraf-Nonius diffractometer at room temperature with a Mo Kα graphite-monochromatized radiation (λ = 0.7107 Å). All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/60 computer using the SDP (structure determination package). A total of 3738 reflections were collected in the range $1° \le \theta \le 25°$. The structure was solved by the direct method using the MULTAN program and difference Fourier syntheses. The last refinement gave R = 0.032 and R_w = 0.043 for 2320 observations ($I > 3\sigma(I)$) and 236 refined parameters; GOF = 1.005. Hydrogen atoms are included as fixed contributors in idealized positions prior to the final least-squares refinement cycles. Their thermal parameters are obtained by multiplying by 1.3 the thermal parameters of the carbon atoms to which they are bonded, before the last refinement. The highest residual peak (0.5 e/Å^3) is located at 1.214 Å from the Fe(2) atom.

(19) A solution of **6b** (0.1 g) in acetone (15 mL) was refluxed under N$_2$ for 8 h. After chromatography the product is in all respects identical with complex **5b**. When **5a** (0.2 g) in acetone (10 mL) was treated with P(OMe)$_3$ (0.06 g) at room temperature under nitrogen for 3 h, we obtained after chromatography 0.17 g (85%) of **5b**, also identical with other samples (mixed melting point and spectroscopic data).

(20) Lhadi, E. K.; Patin, H.; Benoit, A.; Le Marouille, J. Y.; Darchen, A. *J. Organomet. Chem.* **1983**, *259*, 321.

The First Structural Evidence for the Insertion of an Unsubstituted Lead into a Carborane Cage

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Summary: The reaction of the monoanion of the *nido*-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_6$ (I) with anhydrous PbCl$_2$ in a 1:1 molar ratio in tetrahydrofuran (THF) at −23 °C produced a new plumbacarborane, *closo*-1-Pb-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$ (II), as an off-white, sublimable solid, in 25% yield. The X-ray crystal structure of II unambiguously showed that the apical lead atom, formally in a +2 oxidation state, is η^5-bonded to the planar face of the C_2B_4 carborane ligand and is located almost in the centroidal position above the C_2B_3 face. A pair of these plumbacarboranes form a molecular cluster with a crystallographic center of symmetry halfway between the two apical lead atoms in the crystal lattice; the clusters are layered almost symmetrically on top of each other along with benzene molecules of crystallization.

Of all the group 14 heterocarboranes the plumbacarboranes have been least studied.[1] The first icosahedral plumbacarborane was reported nearly 18 years ago by Rudolph et al.[2] Since this heterocarborane was insoluble

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(1) (a) Hosmane, N. S.; Maguire, J. A. *Molecular Structure* and *Energetics*; Greenberg, A., Liebman, J. F., Williams, R. E., Eds.; VCH: New York, 1988; Vol. 5, Chapter 14, pp 297–328 and references therein. (b) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1989**, *30*, 0000.

(2) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351.

in benzene, it was not possible to determine whether the molecule was monomeric or polymeric in solution. No X-ray structural data were reported, presumably due to pronounced tendency of this compound to form disordered lattices upon crystallization. However, on the basis of the ^{11}B NMR spectra, it has been suggested that the Pb atom in $PbC_2B_9H_{11}$ may be "slipped" from an "icosahedral" position toward the three borons of the cage.[2] Wong and Grimes described the synthesis and spectroscopic characterization of smaller cage plumbacarboranes of the type 1-Pb-2,3-(R)$_2$-2,3-$C_2B_4H_4$ (R = Me, H); however, the yields were very low and their solid-state structures have not been reported.[3] Recent Fenske–Hall[4] and MNDO-SCF[5] theoretical calculations on the stannacarborane derivatives suggest that slip distortion should increase going down a periodic series (from Si to Pb). Here we report the synthesis and the first solid-state structure of the benzene-solvated, neutral, unsubstituted plumbacarborane 2,3-bis(trimethylsilyl)-2,3-dicarba-1-plumba-*closo*-heptaborane(6), a covalent compound that exists in extended arrays of dimers with strong dipole–dipole intermolecular force of attraction between the plumbacarborane units.

The title compound *closo*-1-Pb-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (II) was prepared[6] from *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (I)[7] in a procedure identical with that employed in the synthesis of *closo*-stannacarboranes[8] and was crystallized in dry benzene.

The electron-impact (EI) mass spectrum of II exhibited a parent grouping [$^{208}Pb(^{12}CH_3)_6{}^{28}Si_2{}^{12}C_2{}^{11}B_4H_4{}^+$] and a weak parent grouping minus a methyl group [$^{208}Pb(^{12}CH_3)_5{}^{28}Si_2{}^{12}C_2{}^{11}B_4H_4{}^+$] with the major cutoffs at *m/z* 426 and 411, respectively. The strong peaks of Pb^+ ions with local cutoff at *m/z* 209 and Me_3Si^+ ion at *m/z* 73 are the only remaining ion fragments observed in the EI mass spectrum of II. Among the spectroscopic data,[9] the ^{11}B NMR spectrum provides the most important information regarding the structure of the plumbacarborane II. It displays a downfield doublet due to a basal BH unit (37.01 ppm, intensity 1) separated from the other resonance of two equivalent basal BH units (30.25 ppm). By contrast the corresponding *closo*-stanna- and germacarboranes displayed a single doublet corresponding to their three basal BH units.[8,10] The separation of one BH resonance from the remaining basal BH resonances has also been observed previously in the ^{11}B NMR spectra of $PbC_2B_4H_6$,[3] $Pb(CH_3)_2C_2B_4H_4$,[3] and $PbC_2B_9H_{11}$.[2] On the basis of this type of ^{11}B NMR spectral pattern, Rudolph et al.[2] proposed that the Pb atom in $PbC_2B_9H_{11}$ may be "slipped" from the centroidal position above the C_2B_3 face toward the three borons with a greater interaction between the apical Pb and the unique boron. Later, Grimes interpreted that the splitting of the basal BH resonances in the ^{11}B NMR spectra of the plumbacarboranes of both C_2B_4 and C_2B_9 systems as nothing more than a better resolution of the nonequivalent unique BH resonance in the plumbacarboranes than in those of the germa- and stannacarborane analogues.[3] Since the structure of the plumbacarborane, whether slipped or symmetric, monomeric, or polymeric, could not be determined from its IR, NMR, and mass spectral data,[9] we have conducted an X-ray analysis of II.[11]

The crystal packing diagram, shown in Figure 1, is of an extended chain network of [*closo*-Pb-$(CSiMe_3)_2B_4H_4$]$_2$ molecular dimers that are layered almost symmetrically on top of each other. Each cluster consists of two PbC_2B_4 cages with a crystallographic center of symmetry halfway between the two apical Pb atoms. In addition, a benzene molecule of crystallization is found in the crystal lattice between the two extended chains of layered plumbacarborane clusters (see Figure 1). Each apical Pb atom, formally in a +2 oxidation state, is η^5-bonded to the planar face of the C_2B_4 carborane ligand and is located almost in the centroidal position above the C_2B_3 face [the Pb–C(cage) distances are 2.582 (17) and 2.634 (14) Å, while Pb–B distances are 2.601 (16), 2.579 (17), and 2.520 (20) Å] as represented in the thermal ellipsoid diagram of II in Figure 2. These distances indicate a strong covalent interaction of the apical Pb atom with the carborane cage atoms. If any distortion exists, it is one in which the Pb is slipped toward the basal boron that is attached to the C(cage) [B(5)] in Figure 2. This boron, and the unique boron B(4), are also involved in a very strong intermolecular dipole–dipole type of interactions with the neighboring Pb atom [Pb(a)–B(5d) = 3.195 (16) and Pb(a)–B(4d) = 3.375 (15) Å] as shown in Figure 1. If this dimeric structure exists in solution, it may well be that it is this B(5)H unit that is separated from the remaining basal BH resonances in the ^{11}B NMR spectrum of II as this boron has maximum interactions with the apical Pb atom not only of its own cage but also of the neighboring ones. Perhaps these intercluster interactions are also responsible for the slight distortion of the plumbacarborane cage. Although these distances are within the van der Waal's distances, the Pb(a)–Pb(d) distance of 4.165 (14) Å is longer. The closest distance between $(PbC_2B_4)_2$ dimers of 3.868 (16) Å is between Pb(b,d) and B(4a,4e) (see Figure 1). These are sufficiently large so that they should not exert much of an influence on the structure of a PbC_2B_4 unit. Similarly, the intercluster layers of solvated benzene molecules are not within the van der Waal's distances but are presumably responsible for the crystal packing of II. It is of interest to note that the crystal structure of $(\eta^5\text{-}C_5H_5)_2Pb$ is of a polymeric chain structure in which each lead atom has trigonal-planar coordination by bonding to one terminal and two bridging η^5-C_5H_5 ligands with mean Pb–C distances of 2.76 ± 0.1 and 3.06 ± 0.1 Å, respectively.[12,13]

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(3) Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053.

(4) Barreto, R. D.; Fehlner, T. P.; Hosmane, N. S. *Inorg. Chem.* **1988**, *27*, 453.

(5) Maguire, J. A.; Ford, G. P.; Hosmane, N. S. *Inorg. Chem.* **1988**, *27*, 3354.

(6) In a procedure identical with that employed in the synthesis of *closo*-stannacarboranes a 1.70-g (7.74-mmol) sample of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (I) in tetrahydrofuran (THF) (25 mL) was reacted with 0.21 g (8.4 mmol) of NaH in THF to produce Na^+[2,3-$(SiMe_3)_2C_2B_4H_5$]$^-$ which was then allowed to react with anhydrous $PbCl_2$ (2.15 g, 7.74 mmol) in THF at −23 °C with constant stirring for 2 h. After removal of THF at this temperature in vacuo, the reaction flask was attached to a series of detachable U traps. Upon vacuum sublimation of the brown residue at 150 °C, 0.83 g (1.95 mmol, 25% yield) of off-white solid, identified as 1-Pb-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (II) (mp 207–208 °C, highly soluble in polar solvents and slightly soluble in nonpolar solvents), and neutral *nido*-carborane 2,3-$(SiMe_3)_2C_2B_4H_6$ (I) (0.53 g, 2.41 mmol) were collected in U traps held at 0 and −23 °C, respectively.

(7) (a) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359. (b) Hosmane, N. S.; Mollenhauer, M. N.; Cowley, A. H.; Norman, N. C. *Organometallics* **1985**, *4*, 1194.

(8) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665.

(9) Spectroscopic Data. IR (C_6H_6 vs C_6H_6): 3090 (s, s); 3035 (s, s) [ν(C–H)]; 2552 (m, s) [ν(B–H)]; 1959 (s, s); 1815 (s, s); 1526 (m, s); 1478 (m, br) [$\delta(CH)_{asym}$]; 1394 (m, s); 1330 (w, s); 1250 (m,s) [$\delta(CH)_{sym}$]; 1175 (m, s); 1035 (s, s); 842 (vs, br) [ρ(CH)]; 674 (s, br) [ν(Si–C)]; 500 (s, s) cm^{-1}. FT NMR data: ^{1}H NMR (C_6D_6, relative to external Me_4Si) δ 6.48 [q (v br), 1 H, basal H_t, $^1J(^1H-^{11}B)$ = 146 Hz], 5.23 [q (v br), 2 H, basal H_t, $^1J(^1H-^{11}B)$ = 145 Hz], 3.56 [q (v br), 1 H, apical H_t, $^1J(^1H-^{11}B)$ = 160 Hz], 0.40 [s, 18 H, Me_3Si]; ^{11}B NMR (C_6D_6, relative to external $BF_3 \cdot OEt_2$) δ 37.01 [d (br), 1 B, basal BH, $^1J(^{11}B-^1H)$ = 145.62 Hz], 30.25 [d (br), 2 B, basal BH, $^1J(^{11}B-^1H)$ = 145 Hz], 2.106 [d (br), 1 B, apical BH, $^1J(^{11}B-^1H)$ = 158.48 Hz]; ^{13}C NMR (C_6D_6, relative to external Me_4Si) δ 130.62 [s (br), cage carbons], 2.49 [q, Me_3Si, $^1J(^{13}C-^1H)$ = 125.42 Hz]; ^{207}Pb NMR (C_6D_6, relative to external Me_4Pb) δ −1373.8 [s (v br), cage Pb].

(10) Hosmane, N. S.; Islam, M. S.; Pinkston, B. S.; Siriwardane, U.; Banewicz, J. J.; Maguire, J. A. *Organometallics* **1988**, *7*, 2340.

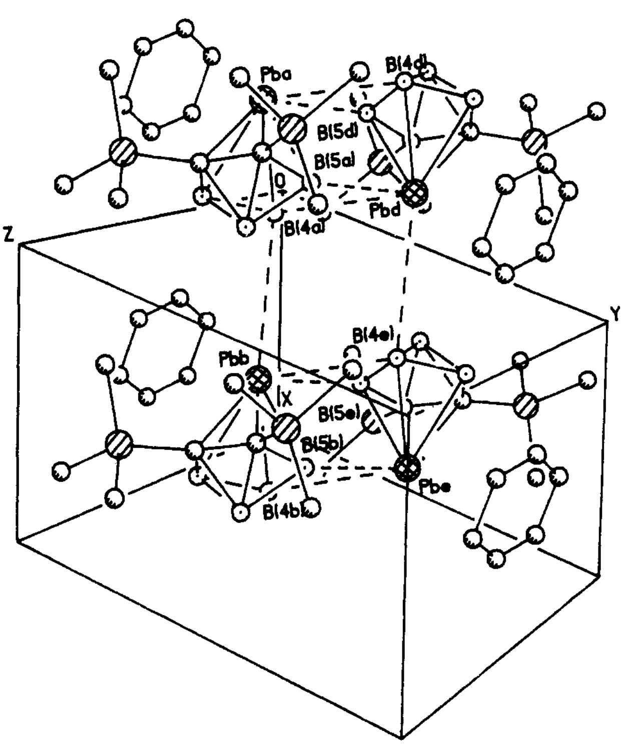

Figure 1. The crystal packing diagram showing the extended chain network of [*closo*-1-Pb-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4]_2$ molecular clusters with benzene molecules of crystallization. The intermolecular Pb(a)-Pb(d), Pb(a)-B(4d), Pb(a)-B(5d), Pb(b)-B(4a), and Pb(b)-B(5a) distances are 4.165 (14), 3.375 (15), 3.195 (16), 3.868 (16), and 4.966 (20) Å, respectively.

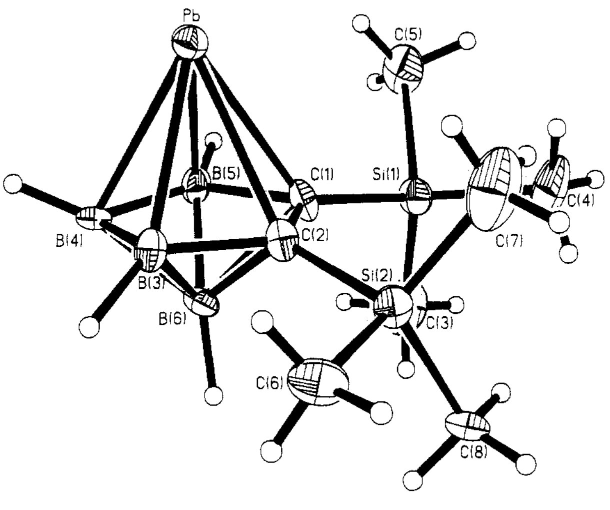

Figure 2. Structure of one of the plumbacarboranes in Figure 1 showing the atom-numbering scheme and thermal ellipsoids at the 30% probability level. Pertinent parameters include Pb-C(1) = 2.582 (17), Pb-C(2) = 2.634 (14), Pb-B(3) = 2.601 (16), Pb-B(4) = 2.579 (17), and Pb-B(5) = 2.520 (20) Å.

However, the solid-state structure of $(Me_5C_5)_2Pb$ was found to be monomeric and slipped.[14] Even the shortest Pb-C distance of 2.69 (1) Å in $(Me_5C_5)_2Pb$ is considerably longer than the longest Pb-cage distance [Pb-C(2) = 2.634 (14) Å] found for the plumbacarborane II. Therefore, it can be stated that the Pb atom is more covalently bonded with the carborane cage than with the cyclopentadienyl ring.

The symmetric structure of the plumbacarborane is quite surprising. At present, it is not known how much the unusual dimeric cluster formation affects the structure of a PbC_2B_4 unit or whether this dimer exists in solution. This and other aspects of the chemistry of *closo*-plumbacarboranes and their derivatives are currently underway in our laboratories.

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Supplementary Material Available: Tables of positional and thermal parameters (Table S1), bond distances (Table S2), bond angles (Table S3), torsion angles (Table S4), anisotropic temperature factors (Table S5), and H-atom coordinates and isotropic displacement parameters (Table S6) (7 pages); a listing of observed and calculated structure factors (Table S7) (9 pages). Ordering information is given on any current masthead page.

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(11) Crystal and Experimental Data. Suitable colorless needle-shaped crystals of II ($C_8H_{22}B_4Si_2Pb\cdot{}^1/_2C_6H_6$, fw 463.9) were grown in C_6H_6 solution. Since the crystals changed to opaque-white upon brief exposure to air, they were coated with an epoxy resin. Data were collected at 233 K, using an automatic Nicolet R3m/V diffractometer, Mo Kα radiation. The space group is $P\bar{1}$ with a = 6.409 (6) Å, b = 10.068 (11) Å, c = 14.86 (2) Å, α = 79.5 (1)°, β = 88.3 (1)°, γ = 74.13 (9)°, U = 907 (2) Å^3, Z = 2, and d_{calcd} = 1.70 g cm^{-3}. A total of 2370 independent reflections in the range $3.0 \leq 2\theta \leq 45$ were collected. Three standard reflections collected after every 100 reflections showed ~16% decay of intensity at the end of the data collection. Data were corrected for decay, Lorentz-polarization, and absorption. Structure was solved by direct methods programs used in SHELXTL-Plus (Sheldrick, G. M. *Structure Determination Software Programs*; Nicolet Instrument Corp., Madison, WI, USA, 1988) and subsequent difference Fourier methods. Final full-matrix least-squares refinement (SHELXTL-Plus) using 2077 observed reflections with $F > 6.0\sigma(F)$ converged to R = 0.048 and R_w = 0.050; S = 1.03, $(\Delta/\sigma)_{max}$ = 0.006, and $\Delta\rho_{max,min}$ = 2.14 (close to Pb), -2.18 e/Å^3. All non-H atoms were refined anisotropically, and silyl methyl H atoms were constrained tetrahedrally. The function minimized being $\sum w(|F_o| - |F_c|)^2$, the weight used being $w^{-1} = \sigma(F^2) + 0.0054F^2$. Scattering factors for C, H, B, Si, and Pb were those stored in SHELXTL-Plus.

(12) Almenningen, A.; Haaland, A.; Motzfeldt, T. *J. Organomet. Chem.* **1967**, *7*, 97.

(13) Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823.

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Relative Sign Determination of Phosphorus-Carbon Coupling Constants by 2D Carbon-13 NMR Spectroscopy

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Summary: The two-dimensional COSY-90 technique is shown to be a viable method for determining the relative signs of heteronuclear couplings. In particular the $^2J_{PMC}$ coupling constants for three phosphido-bridged ruthenium complexes, $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$, $Ru_2(CO)_6[\mu\text{-}CHC(Ph)NEt_3](\mu\text{-}PPh_2)$, and $Ru_2(CO)_6[\mu\text{-}O{=}CCHC(Ph)NEt_2](\mu\text{-}PPh_2)$, have been examined and found to depend on the crystallographic PMC angle.

In assessing the stereochemistry and bonding of a wide range of organometallic complexes, both the magnitude and the relative signs of scalar coupling constants such as $^2J_{PMP}$ and $^2J_{PMC}$ are important. Generally, the assignments for monodentate phosphorus ligands have been made on