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7. General procedure; To a stirred mixture of dialkyl phosphite (1 mmol), triethylamine (1 mmol), tetrakis (triphenylphosphine) palladium (3 mol %) and triphenylphosphine (12 mol%) in toluene (1 ml), was added (*E*)-1-(trimethylsilyl)alkenyl halide (1 mmol). The resultant mixture was stirred at 90-100 °C until the reaction completed (GC, TLC). After cooling to rt, ether (30 ml) was added and ammonium salt was removed by filtration. Filtrate was evaporated to give the products. Pure sample were obtained by SiO₂ column chromatography (EtOAc/*n*-Hex).
8. Representative spectral data of **3** and **4**. **3a**: ¹H-NMR

(CDCl₃); δ 0.27 (s, 9H), 1.37 (t, J = 7Hz, 6H), 4.10 (p, J = 7Hz 4H), 6.34 (dd, J = 58Hz, J = 3.5Hz, 1H), 6.76 (dd, J = 34Hz, J = 3.5Hz, 1H). **4a**: ¹H-NMR (CDCl₃); δ 0.17 (s, 9H), 1.37 (t, J = 7Hz, 6H), 4.10 (p, J = 7Hz 4H), 6.20 (dd, J = 28Hz, J = 20Hz, 1H), 7.15 (dd, J = 35Hz, J = 20Hz, 1H).

9. Representative spectral data of **5** and **6**. **5a**: ¹H-NMR (CDCl₃); δ 0.18 (s, 9H), 1.18 (t, 3H), 1.40 (t, J = 7Hz, 6H), 2.60 (m, 1H), 4.10 (q, J = 7Hz, 4H). **6a**: ¹H-NMR (CDCl₃); δ 0.16 (s, 9H), 1.28 (t, 2H), 1.40 (t, J = 5Hz, 6H), 2.30 (m, 2H), 4.10 (q, J = 7Hz, 4H).
10. Similar rearrangements were reported. B. Cazes, V. Colovray and J. Gore, *Tetrahedron Lett.*, **29**, 627 (1988).

Synthesis and Structural Characterization of a Zwitterionic Triphenylphosphine Derivative of the Dicarbollide Anion: [*nido*-9-P(C₆H₅)₃-7,8-C₂B₉H₁₁]

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Recently, the icosahedral carborane has been employed in the area that ranges from basic inorganic chemistry¹⁻³ to biomedical applications.⁴⁻⁶ The final ligand form used in the former area has the polyhedral framework of C₂B₉ cage of the *nido* dicarbollide anion.⁷ As observed in our recent reports of the synthesis and structure of the unprecedented clustered cluster with a pinwheel ligand array,^{3b,c} reduction of the formal charge of [*nido*-C₂B₉H₁₁]²⁻ (**1**)⁷ by the substitution of a terminal hydride on boron with a neutral Lewis base has been adopted as a way of tuning the reaction conditions. Among the possible Lewis bases, phosphine might be useful in the synthesis of a charge-compensated carborane ligand in which the substituent is not innocent sterically as well as electronically. Here we wish to report the synthesis and structural characterization of [*nido*-9-P(C₆H₅)₃-7,8-C₂B₉H₁₁] (**2**), a zwitterionic triphenylphosphine derivative of the dicarbollide anion.

A slurry of AgBr (2 mmol) and triphenylphosphine (1 mmol) in 40 ml of dichloromethane was allowed to react anaerobically with the dithallium salt⁸ (1 mmol) of **1** at ambient temperature for 12 hrs, producing colorless solution and black precipitate. Recrystallization (CH₂Cl₂/*n*-heptane) of the white crystalline solids obtained by treating the concentrated filtrate with *n*-heptane afforded white crystalline **2** in a yield of 74%.⁹ The nature of **2** was established by single-crystal X-ray analysis¹⁰ as well as other means.¹¹

Spectroscopic data¹¹ for **2** revealed the presence of the dicarbollide cage and triphenylphosphine group. The ¹¹B{¹H} NMR spectrum of **2** consists of ten resonances among which two signals at -14.41 and -15.37 ppm remain unchanged in the proton coupled ¹¹B NMR spectrum and thus can be

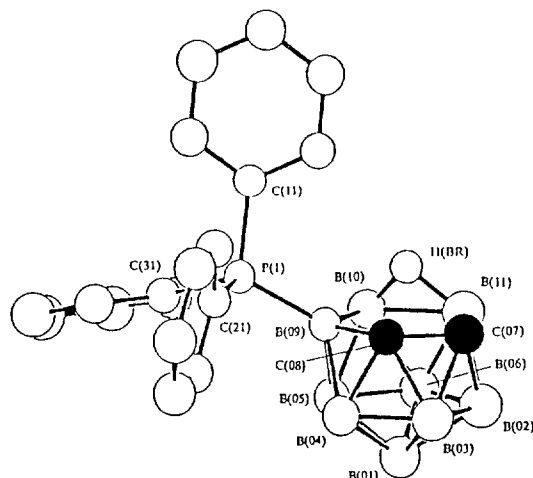


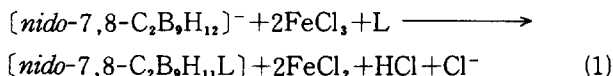
Figure 1. Structure of *nido*-9-P(C₆H₅)₃-7,8-C₂B₉H₁₁ showing the atom labeling scheme. All hydrogens except the *B-H-B* bridge have been omitted for clarity. Selected values of interatomic distances (Å). P(1)-B(09), 1.912(2); C(07)-C(08), 1.551(3); C(07)-B(11), 1.621(4); C(08)-B(09), 1.589(3); B(09)-B(10), 1.792(4); B(10)-B(11), 1.863(4).

ascribed to the B-P coupling with J = 155 Hz. The feature of the B-P coupling was further confirmed by 96.295 MHz ¹¹B NMR spectra. Although spectroscopic data for **2** could not lead to the positional assignment of the phosphorus-substituted boron atom, the number and the ratio of the resonances suggested that the formation of the B-P bond had occurred asymmetrically to make nine boron nuclei nonidentical.

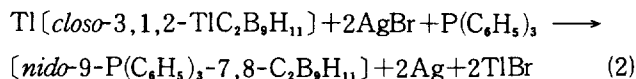
The C₁ molecular symmetric nature of **2** is illustrated in

Figure 1, from which the boron atom attached to the triphenylphosphine ligand is identified as the asymmetric one, B(09), in the pentagonal bonding face of the carborane cage. The geometrical feature of the C_2B_9 cage is not unusual and the B-P distance of 1.912(2)Å can be reasonably compared to those (1.938(8)Å and 1.917(12)Å) observed in phosphinonickelacarborane¹² and phosphinoplatinacarborane.¹³ The crystal structure of **2** consists of two enantiomers related by a center of symmetry to form the racemic mixture.

The class of charge-compensated *nido*-7,8- C_2B_9 cages which carry the Lewis base on one of the three boron atoms of the upper pentagonal C_2B_3 belt has been prepared via oxidative ligand substitution^{14,15} or ligand migration.^{12,16,17} In case of tetrahydrofuran, pyridine, diethyl sulfide, acetonitrile, triethylamine, methyl isonicotinate or other nitrogen-containing donors as a Lewis base, L, the former reaction afforded a charge-compensated carborane cage as outlined in eq. 1.^{14,15} With L = triphenylphosphine, the latter reaction



followed by degradation in hot glacial acetic acid led to the symmetric [*nido*-10-P(C_6H_5)₃-7,8- $C_2B_9H_{11}$].^{12,16} The formation¹⁸ of the asymmetric zwitterionic compound **2** using [$Tl_2C_2B_9H_{11}$]⁸ as a synthon provides a new synthetic route to the class of charge-compensated carboranes and is likely to occur according to eq. 2 which can also be designated as oxidative substitution. The reason for the regioselectivity of the foregoing reactions is, as yet,



unknown. In case of lighter congener of silver, it is interesting to note that the similar reaction condition of eq. 2 resulted in the formation of dinuclear *closo*-[*exo*-4,8-(μ -H)₂-Cu(P(C_6H_5)₃)₃-3-(P(C_6H_5)₃)₃-1,2-Cu $C_2B_9H_9$] which demonstrates a set of unusual structural features such as a Cu(I)-Cu(I) interaction, an icosahedral *closo*-Cu^I C_2B_9 cage and fluxional processes involving metal sites.^{19,3c} The further study of the reaction system of AgBr and dicarbollide anion as well as the chemistry of **2** are under investigation.

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- The formation of **2** seems to require an extremely anhydrous reaction condition since white crystalline solid which consists of monoanionic [*nido*-7,8- $C_2B_9H_{12}$]⁻ and unidentified cationic triphenylphosphinosilver species has often been isolated.
- (a) Suitable crystals of **2** were grown from dichloromethane/ether. Diffraction data were collected at 25 °C on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of the Department of Chemistry and Biochemistry, UCLA, using Mo K α radiation, to a maximum 2θ value of 54°. Data were corrected for Lorentz and polarization effects. Intensity data for 3433 reflections with $I > 3\sigma(I)$ were used for structure solution and refinement using MULTAN 80 and SHELX 76. (b) Crystallographic data for **2**: $a = 10.408(1)\text{Å}$, $b = 15.391(1)\text{Å}$, $c = 14.914(1)\text{Å}$, $\beta = 108.748(1)^\circ$, $V = 2260\text{Å}^3$, space group $P2_1/C$, $R(R_w) = 4.6(6.2)\%$.
- Spectroscopic data for **2**: ¹¹B{¹H}NMR (160.463 MHz, in dichloromethane, referenced to external BF₃·OEt₂ in C₆D₆, chemical shifts upfield of the reference are designated as negative): -2.97, -9.26, -14.89(d, J = 155 Hz), -16.37, -17.80, -23.46, -25.50, -26.89, -36.04 ppm. ¹H NMR (in CD₂Cl₂, referenced to TMS): 7.7 and 7.8 (C₆H₅), 2.3-2.4(br, carborane CH) ppm. IR spectrum (KBr): 3061(w), 2548(vs), 1483(m), 1437(s), 1186(w), 1103(s), 1025(m), 1000(w), 750(s), 716(s), 693(s), 515(s) cm⁻¹.
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