

Synthesis and Characterization of *o*-Carboranylmethylenephosphine. Crystal Structure of $(C_2B_{10}H_{11})CH_2PPh_2$ and $(C_2B_{10}H_{11})CH_2PMe_2$

Dae-Hyun Kim, Heung-Sae Lee, Jaejung Ko,* Kwonil Park,[†] Sung-Il Cho,[†] Jeong-In Shon,[‡] and Sang Ook Kang*

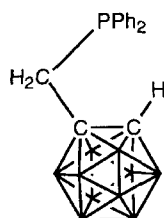
Department of Chemistry, Korea University, 208 Seochang, Chochiwon, Chung-nam 339-700, Korea

[†]*Department of Chemical Engineering, Junnong-dong 90, Seoul City University, Seoul 130-743, Korea*

[‡]*Department of Chemistry, Hanlim University, Chunchon 200-702, Korea*

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The preparation and coordination chemistry of intramolecular coordination complexes have been an area of great interest for a number of years.¹ Our interest has been in the development of a potential ligand system in which the *o*-carborane nucleus functions as a ligand backbone.^{2,3} The carborane moiety, because of its unusual geometry and stability, is being extensively explored both from the standpoint of its own chemical reactivity as well as its function as a substituent. In contrast to the large volume of work reported on chelating 1,2-diphosphino-*o*-carboranes,⁴ only a few one-armed monodentate 1-phosphino-*o*-carboranes have been studied. These one-armed monophosphino-*o*-carboranes are of interest since comparative studies can be made of the relative intramolecular-coordination influences of phosphorous in the C,P-chelates of the metal complexes. Previously, the synthesis of such an one-armed monophosphino *o*-carboranyl ligand system, 1-diphenylphosphinomethyl-1,2-dicarba-*closo*-dodecaborane(12), has been reported.⁵ However, the detailed preparation and characterization of such complexes have never been thoroughly studied.



1-diphenylphosphinomethyl-1,2-dicarba-*closo*-dodecaborane(12)

As an extension of our interest in obtaining a monofunctional *o*-carboranyl ligand system, we have recently reported the synthesis, X-ray structure, and spectroscopic properties the 1-aminomethyl-1,2-dicarba-*closo*-dodecaborane(12) and 1-diphenylphosphinomethyl-1,2-dicarba-*closo*-dodecaborane(12), as well as the molecular structure of each complex.⁶ In the present work, we have prepared and spectroscopically and analytically characterized a series of one-armed monophosphino-*o*-carboranes. Thus, in the present work, the synthesis of a series of complex 1-dialkylphosphinomethyl-1,2-dicarba-*closo*-dodecaboranes(12) **3** is now being studied in detail. Due to our interest in the formation of those complexes **3**, a single crystal X-ray diffraction determination of 1-dimethylphosphinomethyl-1,2-dicarba-*closo*-dodecaborane(12) **3a** and 1-ditertiarybutylphosphinomethyl-1,2-dicarba-*closo*-dode-

caborane(12) **3c** was carried out to elucidate the nature of the reaction.

Experimental Section

Materials and Instrumentation. Decaborane and propargylbromide were purchased from the Callery Chemical Co. and Aldrich, respectively, and used without purification. Chlorodialkylphosphines, PMe_2Cl , PPr^i_2Cl , and PBu^t_2Cl , were obtained from Strem Chemicals. All manipulations were carried out under an atmosphere of argon using Schlenk techniques. Tetrahydrofuran, toluene, and hexane were distilled under an atmosphere of nitrogen from sodium/benzophenone. Methylene chloride and chloroform- d_1 were distilled under nitrogen from P_2O_5 and stored in a Schlenk storage flask until needed. IR spectra and 1H and ^{11}B NMR spectra were recorded on a Biorad FTS-165 spectrophotometer and a Gemini 2000 spectrometer, respectively. High- and low-resolution mass spectra were obtained on a VG Micro-mass 7070H mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. $B_{10}H_{12}(SEt_2)_2$ ⁷ and 1-(bromomethyl)-*o*-carborane⁸ were prepared using the literature methods. All melting points were uncorrected.

X-ray Crystallography. Suitable crystals of **3a** and **3c** were obtained by the slow diffusion of hexane into a methylene chloride solution of the complexes at room temperature. They were then mounted on a glass fiber. Diffraction measurements were made on an Enraf CAD4 automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The unit cell was determined by using search, center, index and least-squares routines. The intensity data were corrected for Lorentz and polarization effects and for the anisotropic decay. Each structure was solved by the application of direct methods using the SHELXL-86 program^{9a} and least-squares refinement using SHELXL-93.^{9b}

Compound **3a** crystallized in the monoclinic crystal system. The space group $P2_1/c$ (No. 14) was uniquely identified from the systematic absences in the data. All hydrogen atoms, including those on the cage B-H group, were located and refined with isotropic thermal parameters. The final R value was 0.0563 with 2645 ($I > 2\sigma(I)$) observed reflections and 158 parameters. Compound **3c**·HBr crystallized in the monoclinic crystal system. The space group Cc (No. 9) was determined from the systematic absences in the intensity data. The unit cell of complex **3c** contains two independent molecules. The

asymmetric unit consists of a $(C_2B_{10}H_{11})CH_2PBU_2$ neutral molecule and HBr. All of the nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located and refined with isotropic thermal parameters. The final R value was 0.0529 with 4359 ($I > 2\sigma I$) observed reflections and 451 parameters.

$(C_2B_{10}H_{11})CH_2PMe_2$ (3a). A solution of 2.03 g (21.0 mmol) of chlorodimethylphosphine in 30 mL of dry ether was added dropwise to an ethereal solution of bromo(*o*-carboranylmethyl)magnesium which was obtained from 4.98 g (21.0 mmol) of 1-(bromomethyl)-*o*-carborane and 1.00 g of magnesium at 5 °C. The mixture was refluxed for 2 h and cooled, and water was then added. The ether layer was separated and dried over $CaCl_2$. After the removal of the ether by vacuum, the residue was recrystallized from hexane. A 2.60 g (11.9 mmol, 57%) sample of complex **3a** was obtained. ^{11}B NMR (64.2 MHz, ppm, C_6D_6); -3.2 (d, 1B, $J_{BH} = 140$ Hz), -6.3 (d, 1B, $J_{BH} = 130$ Hz), -10.0 (d, 2B, $J_{BH} = 130$ Hz), -11.2 (d, 2B, $J_{BH} = 130$ Hz), -13.6 (d, 4B, $J_{BH} = 140$ Hz); 1H NMR (200.13 MHz, ppm, C_6D_6) 3.88 (s, 1H, $CHCB_{10}H_{10}$), 2.31 (s, 2H, CH_2), 1.07 (d, 6H, CH_3 , $J_{PH} = 3.2$ Hz); exact mass calcd. for $^{11}B_{10}^{12}C_5^1H_{19}^{31}P$ 220.2155, found 220.2160; Anal. Calcd.: C, 27.51; H, 8.77. Found: C, 27.55; H, 8.82. Rf = 0.19 by silica gel TLC analysis (hexane); Mp = 68-69 °C; IR spectrum (KBr pellet, cm^{-1}) 2986 (w, C-H), 2960 (w, C-H), 2590 (s, B-H), 2570 (s, B-H), 1419 (m, P-C), 1290 (m), 1200 (w), 1130 (w), 1100 (m), 1050 (s), 1020 (w), 948 (w), 800 (w), 718 (m), 670 (w), 510 (w), 450 (w).

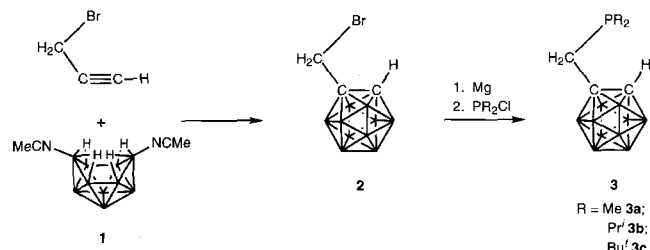
$(C_2B_{10}H_{11})CH_2PPR'_2$ (3b). A solution of 3.20 g (21.0 mmol) of chlorodiisopropylphosphine in 30 mL of dry ether was added dropwise to an ethereal solution of bromo(*o*-carboranylmethyl)magnesium which was obtained from 4.98 g (21.0 mmol) of 1-(bromomethyl)-*o*-carborane and 1.00 g of magnesium at 5 °C. The mixture was refluxed for 2 h and cooled, and water was then added. The ether layer was separated and dried over $CaCl_2$. After the removal of the ether by vacuum, the residue was recrystallized from hexane. A 2.42 g (8.82 mmol, 42%) sample of complex **3b** was obtained. ^{11}B NMR (64.2 MHz, ppm, C_6D_6); -2.5 (d, 1B, $J_{BH} = 160$ Hz), -5.8 (d, 1B, $J_{BH} = 140$ Hz), -10.0 (d, 2B, $J_{BH} = 120$ Hz), -11.6 (d, 2B, $J_{BH} = 140$ Hz), -13.5 (d, 4B, $J_{BH} = 135$ Hz); 1H NMR (200.13 MHz, ppm, C_6D_6) 3.90 (s, 1H, $CHCB_{10}H_{10}$), 2.47 (ds, 1H, $CH(CH_3)_2$), 1.56 (s, 2H, CH_2), 1.37 (dt, 6H, $CH(CH_3)_2$); exact mass calcd. for $^{11}B_{10}^{12}C_9^1H_{27}^{31}P$ 276.2781, found 276.2784; Anal. Calcd.: C, 39.4; H, 9.92. Found: C, 39.6; H, 9.88. Rf = 0.26 by silica gel TLC analysis (hexane); Mp = 70-72 °C; IR spectrum (KBr pellet, cm^{-1}) 3020 (s, C-H), 2984 (w, C-H), 2965 (w, C-H), 2904 (m, C-H), 2815 (w), 2646 (s, B-H), 2634 (w, B-H), 2592 (s, B-H), 2570 (s, B-H), 2547 (s, B-H), 1419 (m, P-C), 1297 (m), 1282 (w), 1218 (m), 1137 (w), 1113 (m), 1060 (s), 1019 (s), 944 (s), 916 (m), 883 (m), 805 (w), 720 (s), 673 (m), 516 (w), 458 (w).

$(C_2B_{10}H_{11})CH_2PBut_2$ (3c). A solution of 3.79 g (21.0 mmol) of chloroditertiarybutylphosphine in 30 mL of dry ether was added dropwise to an ethereal solution of bromo

(*o*-carboranylmethyl)magnesium which was obtained from 4.98 g (21.0 mmol) of 1-(bromomethyl)-*o*-carborane and 1.00 g of magnesium at 5 °C. The mixture was refluxed for 2 h and cooled, and water was then added. The ether layer was separated and dried over $CaCl_2$. After the removal of the ether by vacuum, the residue was recrystallized from hexane. A 2.48 g (8.19 mmol, 39%) sample of complex **3c** was obtained. ^{11}B NMR (64.2 MHz, ppm, C_6D_6); -1.8 (d, 1B, $J_{BH} = 145$ Hz), -5.6 (d, 1B, $J_{BH} = 135$ Hz), -9.9 (d, 2B, $J_{BH} = 125$ Hz), -11.0 (d, 2B, $J_{BH} = 125$ Hz), -13.0 (d, 4B, $J_{BH} = 140$ Hz); 1H NMR (200.13 MHz, ppm, C_6D_6) 3.92 (s, 1H, $CHCB_{10}H_{10}$), 2.37 (s, 2H, CH_2), 1.00 (d, 18H, $C(CH_3)_3$); exact mass calcd. for $^{11}B_{10}^{12}C_{11}^1H_{31}^{31}P$ 304.3094, found 304.3096; Anal. Calcd.: C, 43.68; H, 10.33. Found: C, 43.71; H, 10.30. Rf = 0.36 by silica gel TLC analysis (hexane); Mp = 84-85 °C; IR spectrum (KBr pellet, cm^{-1}) 2990 (w, C-H), 2970 (w, C-H), 2580 (s, br, B-H), 1422 (m, P-C), 1280 (m), 1205 (w), 1136 (w), 1108 (m), 1048 (s), 1000 (w), 950 (w), 860 (w), 720 (m), 640 (w), 500 (w), 470 (w).

Results and Discussion

The treatment of bromomethyl-*o*-carborane ($C_2B_{10}H_{11}$) CH_2Br (**2**) with magnesium, followed by the reaction with a suitable chlorodialkylphosphine for 12 h, afforded the soluble product $(C_2B_{10}H_{11})CH_2PR_2$ (**3**) in moderate yields. The composition of the new complex **3** was unequivocally established by elemental analysis and the EI mass spectrum which contain the molecular ion. The following reaction scheme illustrates this reaction and the conditions responsible for determining the final composition of $(C_2B_{10}H_{11})CH_2PR_2$ (**3**).



Furthermore, the spectroscopic data (1H and ^{11}B NMR) associated with complex **3** are also consistent with its assigned structure. The ^{11}B NMR spectra of **3** consist of a set of overlapping doublets of relative intensities 1 : 1 : 2 : 2 : 4. The plane of symmetry indicated by the NMR data for complex **3** can be consistent only with substitution on the carborane at C (1) and C (2). The assignment of these resonances to the B (9), B (12), B (8, 10), B (4, 5), and B (7, 11, 3, 6) borons, respectively, is consistent with the assignments previously made by Todd for the spectrum of *closo*-3-Ph-1,2- $C_2B_{10}H_{10}$.¹⁰ The 1H data are likewise in agreement with the proposed cage structure, thus confirming the presence of a cage C-H resonance (3.9-4.0 ppm) at the cage 2-position and one methylene (1.5-2.4 ppm) and two P-alkyl (1.0-1.4 ppm) resonances of the phosphine substituent at the cage 1-position.

The molecular structures of **3a** and **3c** were determined by

Table 1. X-ray crystallographic data and processing parameters for compounds **3a** and **3c**

	3a	3c · HBr
Formula:	B ₁₀ C ₅ H ₁₉ P	B ₁₀ C ₁₁ H ₃₂ PBr
Formula Weight:	218.27	383.35
Crystal Class:	monoclinic	monoclinic
Space group:	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>Cc</i> (No. 9)
Z:	4	4
Cell constants:		
a, Å	10.3143(8)	11.7128(16)
b, Å	9.5504(5)	29.014(3)
c, Å	13.9751(14)	13.7743(18)
V, Å ³	1348.73(18)	4238.6(9)
α, deg		
β, deg	101.553(6)	115.112(12)
γ, deg		
μ, cm ⁻¹	0.162	2.005
crystal size, mm	0.40×0.60×0.60	0.30×0.40×0.40
D _{calcd} , g/cm ³	1.075	1.198
F(000)	456	1576
Radiation:	Mo-Kα	Mo-Kα
	(λ = 0.7170 Å)	(λ = 0.7170 Å)
Θ range, deg	2.02-25.97	1.40-25.97
h, k, l collected	±12, +11, +17	±14, +35, +16
No. reflections		
measured:	2762	4443
No. unique reflections:	2645	4359
No. reflections		
used in refinement	2645	4359
[I > 2σ(I)]		
No. parameters	158	451
Data/Parameter Ratio	16.74	9.67
aR1:	0.0563	0.0529
bWR2:	0.1568	0.1284
GOF:	1.120	0.904

^aR1 = $\sum |F_o| - |F_c| / \sum |F_o|$ (based on reflections with $F_o^2 > 2\sigma F_o^2$). ^bWR2 = $[\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F_o^2$).

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **3a**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U _{eq}
P(1)	7056(1)	1428(1)	219(1)	41(1)
C(1)	7850(2)	-745(3)	1669(2)	33(1)
C(2)	6346(3)	-1400(3)	1430(2)	41(1)
C(3)	8293(3)	213(3)	923(2)	45(1)
C(4)	7385(4)	3034(4)	939(3)	72(1)
C(5)	7958(4)	1831(4)	-745(2)	56(1)
B(3)	7633(4)	-2484(4)	1345(2)	43(1)
B(4)	8913(3)	-1921(3)	2303(2)	37(1)
B(5)	8340(3)	-486(3)	2896(2)	39(1)
B(6)	6689(3)	-130(4)	2303(3)	41(1)
B(7)	6283(4)	-3046(4)	1859(3)	51(1)
B(8)	7938(4)	-3405(3)	2452(3)	46(1)
B(9)	8372(3)	-2182(4)	3411(2)	42(1)
B(10)	6994(3)	-1065(4)	3414(3)	43(1)
B(11)	5714(3)	-1605(4)	2449(3)	46(1)
B(12)	6743(3)	-2868(4)	3148(3)	42(1)

X-ray diffraction analysis. The compound exists as a discrete molecule in the unit cell with no unusually shorter inter- or intramolecular contacts. Table 1 lists the X-ray data collection and processing parameters, while Tables 2, 3, and 4 give the atomic coordinates and the selected distances and angles, respectively. The molecular structure and atom-labeling scheme for complexes **3a** and **3c** are shown in Figure 1 and Figure 2, respectively. Complexes **3a** and **3c** are structurally related. The overall structures of **3a** and **3c** contain an dialkylphosphinomethane fragment substituted at the 1-position of the *o*-carborane cage system. The drawings in Figures 1 and 2 illustrate how the dialkylphosphinomethane

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **3c · HBr**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U _{eq}
Br(1)	9458(1)	544(1)	8912(1)	50(1)
P(1)	9382(2)	-560(1)	7430(2)	31(1)
C(1)	11752(8)	-519(3)	7249(7)	30(2)
C(2)	12508(11)	-265(5)	8461(11)	60(3)
C(3)	10426(8)	-728(3)	6803(8)	31(2)
C(4)	9284(12)	-1026(4)	8311(9)	46(3)
C(5)	7893(9)	-354(4)	6361(8)	36(2)
C(6)	10665(13)	-1186(6)	9009(12)	88(5)
C(7)	8736(18)	-831(5)	9045(13)	90(5)
C(8)	8531(15)	-1428(4)	7678(12)	76(4)
C(9)	8224(11)	84(4)	5921(10)	51(3)
C(10)	6954(10)	-225(4)	6829(10)	54(3)
C(11)	7291(11)	-712(5)	5460(10)	59(3)
B(3)	13068(11)	-794(5)	8160(11)	47(3)
B(4)	12727(12)	-779(6)	6751(14)	60(4)
B(5)	12093(9)	-252(4)	6350(8)	29(2)
B(6)	11872(11)	75(4)	7282(10)	42(3)
B(7)	14130(11)	-346(5)	8807(12)	55(4)
B(8)	14276(13)	-667(5)	7729(14)	61(4)
B(9)	13620(13)	-311(7)	6573(13)	62(4)
B(10)	13118(14)	191(6)	6907(13)	62(4)
B(11)	13415(12)	188(5)	8283(12)	54(4)
B(12)	14500(13)	-57(5)	7817(11)	56(4)
Br(1')	10544(1)	1955(1)	11083(1)	50(1)
P(1')	11951(2)	3059(1)	12566(2)	31(1)
C(1')	14493(8)	3015(3)	12756(8)	30(2)
C(2')	14038(13)	2763(4)	11518(11)	62(3)
C(3')	13612(9)	3230(3)	13173(8)	32(2)
C(4')	11528(10)	2853(4)	13629(9)	40(3)
C(5')	10969(9)	3528(4)	11681(9)	41(3)
C(6')	12287(11)	2411(4)	14060(9)	48(3)
C(7')	11828(11)	3207(4)	14545(10)	53(3)
C(8')	10122(10)	2732(5)	13180(10)	55(3)
C(9')	10842(14)	3931(4)	12308(11)	70(4)
C(10')	9657(13)	3328(5)	10944(13)	96(6)
C(11')	11624(12)	3679(5)	10988(12)	78(4)
B(3')	14930(11)	3294(5)	11872(10)	43(3)
B(4')	15977(12)	3278(6)	13233(12)	56(4)
B(5')	15733(9)	2750(4)	13647(8)	33(3)
B(6')	14570(12)	2428(4)	12698(11)	45(3)
B(7')	15311(13)	2843(5)	11180(13)	56(4)
B(8')	16527(14)	3159(6)	12268(15)	64(4)
B(9')	17057(13)	2836(7)	13408(13)	64(5)
B(10')	16199(15)	2300(6)	13098(13)	65(4)
B(11')	15138(13)	2313(5)	11707(13)	54(4)
B(12')	16685(12)	2570(6)	12175(11)	59(4)

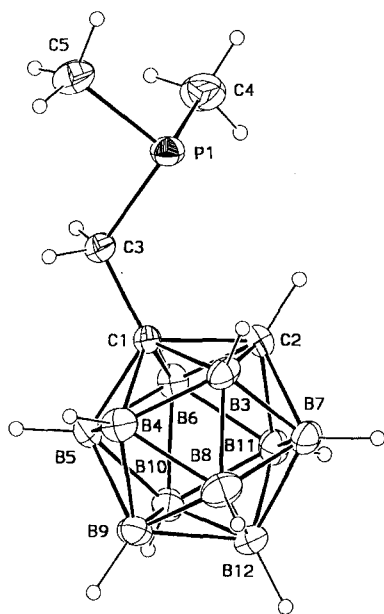


Figure 1. Molecular structure of **3a**. The thermal ellipsoids are drawn at the 30% probability level.

substituent effectively faces the large *o*-carborane from the side. The phosphorous atom P(1) is coplanar with a standard deviation of 0.009 Å for **3a** and 0.034 (Ave.) Å for **3c** and with the three atoms C(3), C(1), and C(2). The normal to this plane almost bisects the directions of the two orthogonal alkyl groups of the dialkylphosphine. The two carbon atoms of the two alkyl groups and one carbon atom of the methyl ene unit are bonded to a phosphorous atom in a pyramidal arrangement. The P-C bond lengths of 1.825(3)-1.855(3) Å and C-P-C angles of 97.19(14)-101.59(17)° for **3a** are similar to those in 1-PPh₂-2-Me-C₂B₁₀H₁₀.¹¹ The inter-cage boron-boron (1.763-1.790 Å) and boron-carbon (1.688-1.729 Å) distances are normal, and the carbon-carbon distance between the only adjacent carbons, C(1)-C(2), of 1.644(3) Å, is also in the range previously observed in other *o*-carborane cage systems.¹²

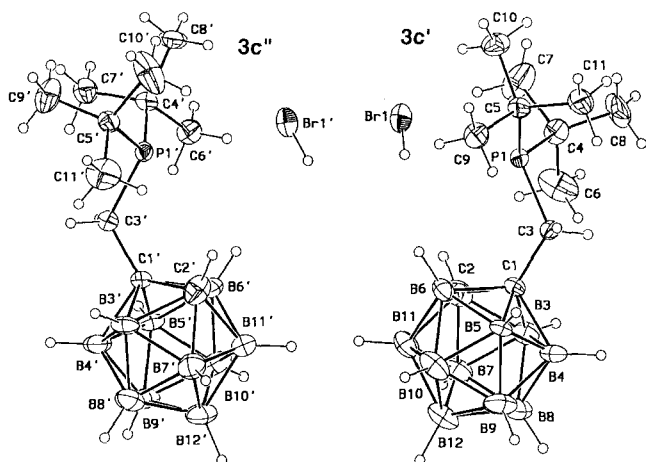


Figure 2. Molecular structure of **3c · HBr**. The thermal ellipsoids are drawn at the 30% probability level.

Table 4. Selected interatomic distances and angles in **3a** and **3c · HBr**

Bond Distances (Å) in 3a			
P(1)-C(5)	1.825(3)	P(1)-C(4)	1.829(4)
P(1)-C(3)	1.855(3)	C(1)-C(3)	1.524(4)
C(1)-C(2)	1.644(3)		
Bond Angles (°) in 3a			
C(5)-P(1)-C(4)	99.43(17)	C(5)-P(1)-C(3)	97.19(14)
C(4)-P(1)-C(3)	101.59(17)	C(3)-C(1)-C(2)	119.4(2)

Bond Distances (Å) in 3c · HBr			
Molecule 3c' · HBr		Molecule 3c'' · HBr	
P(1)-C(3)	1.836(10)	P(1')-C(3')	1.830(10)
P(1)-C(5)	1.841(10)	P(1')-C(4')	1.833(11)
P(1)-C(4)	1.853(10)	P(1')-C(5')	1.862(10)
C(1)-C(3)	1.532(12)	C(1')-C(3')	1.512(13)
C(1)-C(2)	1.691(16)	C(1')-C(2')	1.719(16)

Bond Angles (°) in 3c · HBr			
Molecule 3c' · HBr		Molecule 3c'' · HBr	
C(3)-P(1)-C(5)	107.7(5)	C(3')-P(1')-C(4')	108.6(5)
C(3)-P(1)-C(4)	110.7(5)	C(3')-P(1')-C(5')	110.0(5)
C(5)-P(1)-C(4)	117.4(5)	C(4')-P(1')-C(5')	117.4(5)
C(3)-C(1)-C(2)	125.8(8)	C(3')-C(1')-C(2')	125.3(8)

The (C₂B₁₀H₁₁)CH₂PBu'₂ **3c** complex crystallizes with two pairs of independent molecules (**3c'** and **3c''**) in the monoclinic unit cell. The molecular dimensions of **3c'** and **3c''** are similar (Table 4). The molecular structure of complex **3c** is very similar to that found for complex **3a**. Both molecules possess the one-armed *exo*-substituted *o*-carborane cage geometry (Figure 2). The P-C bond lengths [1.843 (av.) Å] and C-P-C angles [112.0 (av.) °] in **3c'/3c''** are similar to those found in compound **3a**. The remaining carbon-carbon distances (1.497-1.560 Å) on the tertiary butyl groups of the ditertiary butylphosphine appear normal.

In conclusion, this report provides the detailed synthesis of *o*-carboranymethylenephosphine (**3**). A combination of X-ray crystallographic and spectroscopic studies confirms the nature of this compound and reaction chemistry between bromomethyl-*o*-carborane (C₂B₁₀H₁₁)CH₂Br (**2**) and suitable dialkylchlorophosphines. Thus, we have prepared a series of stable one-armed monophosphino-*o*-carboranes containing CH₂PMe₂, CH₂PPr'₂, and CH₂PBu'₂ groups utilizing *o*-carborane as the backbone. These derivatives are remarkably stable to air and moisture.

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Supplementary Material Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms, and listings of observed and calculated structure factors. Supplementary materials are available from one of the authors (S. O. Kang, Fax: 0415-867-5396) upon request.

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