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## Key indicators

Single-crystal X-ray study

T = 160 K

Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$ 

H-atom completeness 98%

Disorder in main residue

R factor = 0.087

wR factor = 0.181

Data-to-parameter ratio = 14.8

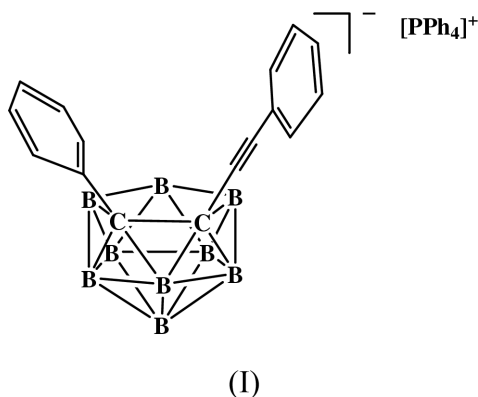
For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Tetraphenylphosphonium 7-phenylethynyl-8-phenyl-  
7,8-*nido*-dicarbadecahydroundecaborate(1-)

In the title compound,  $\text{C}_{24}\text{H}_{20}\text{P}^+\cdot\text{C}_{16}\text{H}_{20}\text{B}_9^-$ , the presence of the  $\text{C}_2$  spacer of the phenylethynyl group reduces the intramolecular crowding between the two phenyl groups of the carborane-cage anion. The position of the B atom connected to both cage C atoms is disordered.

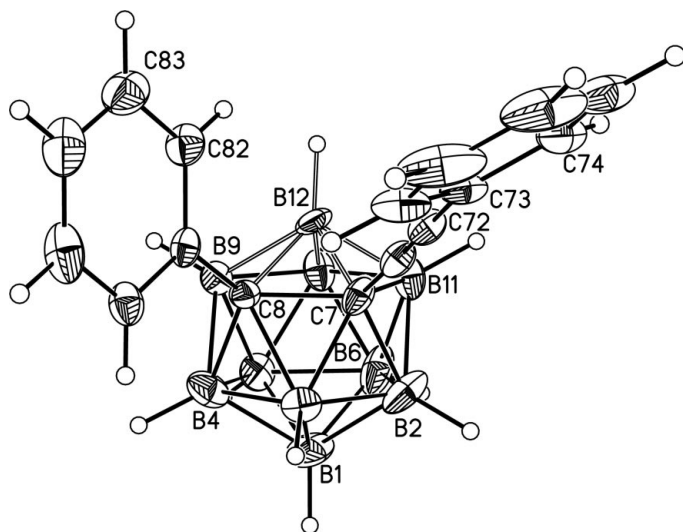
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## Comment

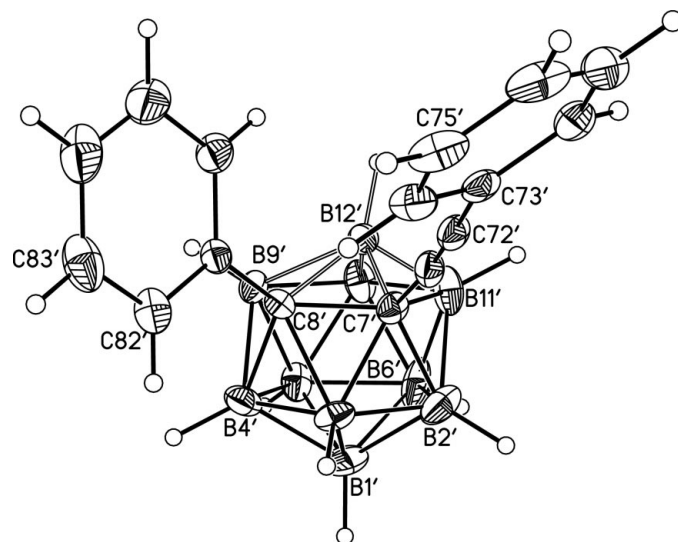
*nido*-Disubstituted carboranes have been synthesized with a variety of counter-ions to establish a pattern of inter- and intramolecular interactions. In the  $[\text{HNET}_3]^+$ ,  $[\text{Me}_3\text{NCH}_2\text{Ph}]^+$  (Cowie *et al.*, 1993) and  $[\text{Rh}(\text{dppe})_2]^+$  (Donohoe *et al.*, 2001) salts of  $[\text{7,8-Ph}_2\text{-7,8-}i\text{nido-C}_2\text{B}_9\text{H}_{10}]^-$ , the phenyl substituents lie roughly orthogonal to the open  $\text{C}_2\text{B}_3$  face of the cage. This conformation is quantified by the angle  $\theta$  defined as the modulus of the average  $\text{C}_{\text{cage}}-\text{C}_{\text{cage}}-\text{C}_{\text{Ph}}-\text{C}_{\text{Ph}}$  torsion angle (Cowie *et al.*, 1994). In the  $[\text{HNET}_3]^+$  and  $[\text{Rh}(\text{dppe})_2]^+$  salts, the phenyl-ring conformations are described by  $\theta$  values of  $5.6 (5)$ ,  $10.0 (6)$  and  $14.6 (5)$ ,  $20.6 (6)^\circ$ , respectively. Low  $\theta$  values in this anion are necessary to avoid phenyl...phenyl crowding. However, in the title compound, (I) (two crystallographically independent molecules, data for primed molecule in square brackets; Figs. 1 and 2), whilst the cage-bound phenyl group has a relatively low  $\theta$  value of  $15.8 (7)^\circ$  [ $15.1 (7)^\circ$ ], the phenyl group of the phenylethynyl substituent subtends a  $\theta$  value of  $57.6 (7)^\circ$  [ $52.2 (7)^\circ$ ]. Evidently, the presence of the  $\text{C}_2$  spacer between C7 and the C73-C78 ring reduces the intramolecular crowding between the two phenyl groups of any one anion and allows the resultant conformations.



In (I) the two crystallographically independent cages are disordered in that the B3, B12, B3' and B12' positions are partially occupied (60, 40, 70 and 30%, respectively, based on  $U_{\text{iso}}$  values). Such positional disorder may be fostered by the approximately spherical shape of the  $[\text{PPh}_4]^+$  cation.



**Figure 1**  
The molecular structure of cage *A* of (I) showing 50% probability displacement ellipsoids.



**Figure 2**  
The molecular structure of cage *B* of (I) showing 50% probability displacement ellipsoids.

## Experimental

A 5 ml solution of  $\text{PPh}_4\text{Br}$  (60.12 mg, 143.38  $\mu\text{mol}$ ) in water was added slowly to  $\text{K}[7\text{-CCPh-8-Ph-7,8-C}_2\text{B}_9\text{H}_{10}]$  (50 mg, 143.38  $\mu\text{mol}$ ) dissolved in 10 ml water, producing a white precipitate. After filtration and washing with water, the white solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and dried over  $\text{MgSO}_4$ . Recrystallization from 333–353 K light petroleum/ $\text{CH}_2\text{Cl}_2$  gave 48.8 mg (51.6%) of (I) as colourless crystals.  $^{11}\text{B}$   $\{^1\text{H}\}$  FT-NMR data for (I): (128.4 MHz,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  in  $\text{CDCl}_3$ ):  $\delta/\text{p.p.m.} = -32.5$  (1B),  $-30.0$  (1B),  $-17.4$  (1B),  $-16.4$  (1B),  $-14.4$  (1B),  $-13.5$  (1B),  $-8.6$  (1B),  $-4.8$  (2B). NMR spectra were recorded on a Bruker DPX400 spectrometer at 293 K.

### Crystal data

$\text{C}_{24}\text{H}_{20}\text{P}^+\cdot\text{C}_{16}\text{H}_{20}\text{B}_9^-$	$Z = 4$
$M_r = 648.98$	$D_x = 1.179 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.063$ (2) $\text{\AA}$	Cell parameters from 37 reflections
$b = 19.007$ (4) $\text{\AA}$	$\theta = 2.2\text{--}10.7^\circ$
$c = 20.344$ (4) $\text{\AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\alpha = 71.469$ (14) $^\circ$	$T = 160$ (2) K
$\beta = 83.522$ (16) $^\circ$	Plate, colourless
$\gamma = 84.235$ (16) $^\circ$	$0.90 \times 0.30 \times 0.10 \text{ mm}$
$V = 3657.1$ (13) $\text{\AA}^3$	

### Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.092$
$\omega$ scans	$\theta_{\text{max}} = 24.9^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 11$
$T_{\text{min}} = 0.925$ , $T_{\text{max}} = 0.990$	$k = -21 \rightarrow 20$
14 197 measured reflections	$l = -23 \rightarrow 23$
11 336 independent reflections	3 standard reflections
4545 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: none

### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2]$
$wR(F^2) = 0.181$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} < 0.001$
11336 reflections	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
764 parameters	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

B1–B2	1.769 (11)	B1'–B2'	1.762 (11)
B1–B3	1.655 (13)	B1'–B3'	1.701 (11)
B1–B4	1.771 (11)	B1'–B4'	1.753 (10)
B1–B5	1.776 (11)	B1'–B5'	1.761 (10)
B1–B6	1.802 (12)	B1'–B6'	1.784 (11)
B2–B3	1.663 (14)	B2'–B3'	1.681 (12)
B2–B6	1.750 (11)	B2'–B6'	1.764 (10)
B2–C7	1.681 (9)	B2'–C7'	1.687 (9)
B2–B11	1.799 (11)	B2'–B11'	1.773 (11)
B3–B4	1.707 (13)	B3'–B4'	1.729 (11)
B3–C7	1.713 (13)	B3'–C7'	1.697 (11)
B3–C8	1.750 (13)	B3'–C8'	1.754 (10)
B4–B5	1.743 (11)	B4'–B5'	1.757 (10)
B4–C8	1.685 (9)	B4'–C8'	1.695 (8)
B4–B9	1.777 (10)	B4'–B9'	1.802 (9)
B5–B6	1.805 (10)	B5'–B6'	1.791 (10)
B5–B9	1.742 (10)	B5'–B9'	1.752 (9)
B5–B10	1.795 (10)	B5'–B10'	1.783 (10)
B6–B10	1.756 (11)	B6'–B10'	1.751 (11)
B6–B11	1.729 (10)	B6'–B11'	1.754 (10)
C7–C8	1.600 (7)	C7'–C8'	1.582 (7)
C7–B11	1.659 (8)	C7'–B11'	1.652 (8)
C7–B12	1.721 (18)	C7'–B12'	1.610 (6)
C8–B9	1.651 (8)	C8'–B9'	1.644 (8)
C8–B12	1.76 (2)	C8'–B12'	1.784 (6)
B9–B10	1.787 (10)	B9'–B10'	1.802 (9)
B9–B12	1.732 (18)	B9'–B12'	1.831 (7)
B10–B11	1.812 (10)	B10'–B11'	1.822 (9)
B10–B12	1.655 (19)	B10'–B12'	1.609 (8)
B11–B12	1.638 (18)	B11'–B12'	1.449 (8)
C7–C8–C81–C82	74.7 (7)	C7'–C8'–C81'–C82'	−106.5 (6)
C7–C8–C81–C86	−106.0 (6)	C7'–C8'–C81'–C86'	76.2 (7)

The *exo*-cage H atoms were constrained to idealized positions (B–H 1.12  $\text{\AA}$ ) as were the phenyl H atoms (C–H 0.95  $\text{\AA}$ ). The *endo*-cage H atoms were not found in the difference map and not introduced, since their positions were masked by the disordered boron atoms B12 and B12'. The displacement parameter for B12' was refined isotropically to avoid a non-positive definite value. The  $U_{\text{iso}}$  parameters of the H atoms were defined as  $1.2U_{\text{iso}}$  of the parent atoms. The phenyl rings were constrained to idealized hexagons

(C—C 1.390 Å and C—C—C 120°) in the [PPh<sub>4</sub>]<sup>+</sup> cation and the cage-bound phenyl groups.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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