

Synthesis and Reactivity of 10-Vertex *arachno*-Platinacarboranes

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Reaction of $[\text{Pt}_3(\text{CNR})_6]$ with *arachno*-4- R' -4- CB_8H_{13} in THF (tetrahydrofuran) gives the platinum-monocarborane species $[\text{9,9}-(\text{CNR})_2\text{-6-}R'\text{-}i\text{arachno-9,6-PtCB}_8\text{H}_{11}]$ ($R = \text{Bu}^t$, $R' = \text{H}$ (**1**); $R = \text{Xyl}$ ($\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$), $R' = \text{H}$ (**2**); $R = \text{Bu}^t$, $R' = \text{Ph}$ (**3**)). The related compound $[\text{9,9}-(\text{PMe}_2\text{Ph})_2\text{-}i\text{arachno-9,6-PtCB}_8\text{H}_{12}]$ (**5**) can be synthesized by treating *arachno*-4- CB_8H_{14} with $[\text{PtMe}_2(\text{PMe}_2\text{Ph})_2]$ in CH_2Cl_2 . Compounds **1–3** and **5** are all formed in high yields (>80%), enabling reactivity studies to be carried out. A single isocyanide ligand in **1** can be easily exchanged for a phosphine, as is the case with $[\text{9-CNBU}^t\text{-9-PPh}_3\text{-}i\text{arachno-9,6-PtCB}_8\text{H}_{12}]$ (**6**), or, by using bidentate dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), both isocyanide groups are replaced, giving $[\text{9,9-dppe-}i\text{arachno-9,6-PtCB}_8\text{H}_{12}]$ (**7**). Treatment with $[\text{NET}_4][\text{CN}]$ allows the isocyanides in **1** to be replaced by cyanide ligands, giving the dianionic complex $[\text{NET}_4]_2[\text{9,9}-(\text{CN})_2\text{-}i\text{arachno-9,6-PtCB}_8\text{H}_{12}]$ (**8**) or the monoanionic species $[\text{NET}_4][\text{9-CNBU}^t\text{-9-CN-}i\text{arachno-9,6-PtCB}_8\text{H}_{12}]$ (**9**) depending on the stoichiometry of the reaction. Reaction of **1** or **3** with I_2 yields the platinum(IV) complexes $[\text{9,9}-(\text{CNBU}^t)_2\text{-9,9-I}_2\text{-6-}R'\text{-}i\text{arachno-9,6-PtCB}_8\text{H}_{11}]$ ($R' = \text{H}$ (**10**), Ph (**11**)), respectively, by an oxidative addition reaction. Using the same reagent, compound **7** forms solvent-dependent, boron-substituted products: $[\text{9,9-dppe-4,8-I}_2\text{-}i\text{arachno-9,6-PtCB}_8\text{H}_{10}]$ (**12**) is obtained in CH_2Cl_2 , whereas $[\text{9,9-dppe-4-O}(\text{CH}_2)_4\text{I}]$ -8- I -*arachno*-9,6- $\text{PtCB}_8\text{H}_{10}$ (**13**) results when THF is used as solvent.

Introduction

Our research has concentrated on the synthesis and reactivity of metallamonocarboranes, still a relatively unexplored area when compared with that of their dicarborane counterparts.¹ The original work was limited to icosahedral metal–monocarbollide complexes $\{\text{MCB}_{10}\}$,^{2,3} but since the discovery of the “Brellocks reaction”⁴ and the resulting availability of a range of intermediate-sized monocarboranes, we have been able to expand our studies to smaller, subicosahedral metallamonocarborane species. This reaction initially provides a facile route from commercially available decaborane ($\text{B}_{10}\text{H}_{14}$) to *nido*- and *arachno*- $\{\text{CB}_9\}$ species, which can then be further manipulated to form monocarboranes with fewer than 10 vertices.⁵ To date the majority of metallamonocarboranes formed using these monocarborane ligands have had a *closo* configuration. The reaction of suitable metal carbonyl precursors with 10-vertex monocarborane clusters yields 11- and 12-vertex $\{\text{closo-M}_n\text{CB}_9\}$ clusters

($M = \text{Re},^6 \text{Mn},^7 \text{Mo},^8 n = 1$; $M = \text{Co},^9 n = 2$), whereas 9- and 10-vertex $\{\text{closo-M}_n\text{CB}_7\}$ ($M = \text{Fe},^{10} n = 1$; $M = \text{Fe},^{10} \text{Co},^9 n = 2$) and 10- and 12-vertex $\{\text{closo-M}_n\text{CB}_8\}$ species ($M = \text{Fe},^{11} \text{Co},^9 \text{Re},^{12} n = 1$; $M = \text{Ru},^{13} n = 3$) are formed via oxidative insertion when the anions $[\text{closo-CB}_n\text{H}_{n+1}]^-$ ($n = 7, 8$) are treated with appropriate M^0 fragments.

Examples of open cluster *nido*- and *arachno*-metallamonocarboranes are much more limited. Some 10-vertex $\{\text{nido-MCB}_8\}$ ($M = \text{Ru}, \text{Os}^{14}$) and $\{\text{arachno-MCB}_8\}$ ($M = \text{Fe},^{11} \text{Ru},^{14} \text{Ir},^{15} \text{Pt}^{16,17}$) compounds have been identified, along with a single $\{\text{nido-PtCB}_9\}$ species.¹⁷ However, the yields of these compounds are generally low, and studies of further reactions have therefore been restricted to the anion $[\text{4,9-}\{\text{Fe}(\text{CO})_4\}\text{-9,9,9-(CO)}_3\text{-}i\text{arachno-9,6-FeCB}_8\text{H}_{11}]^-$.¹¹

To add to this relatively small portfolio of open metallamonocarboranes and further extend our knowledge of their chemistry, we herein present the high-yield synthesis of several

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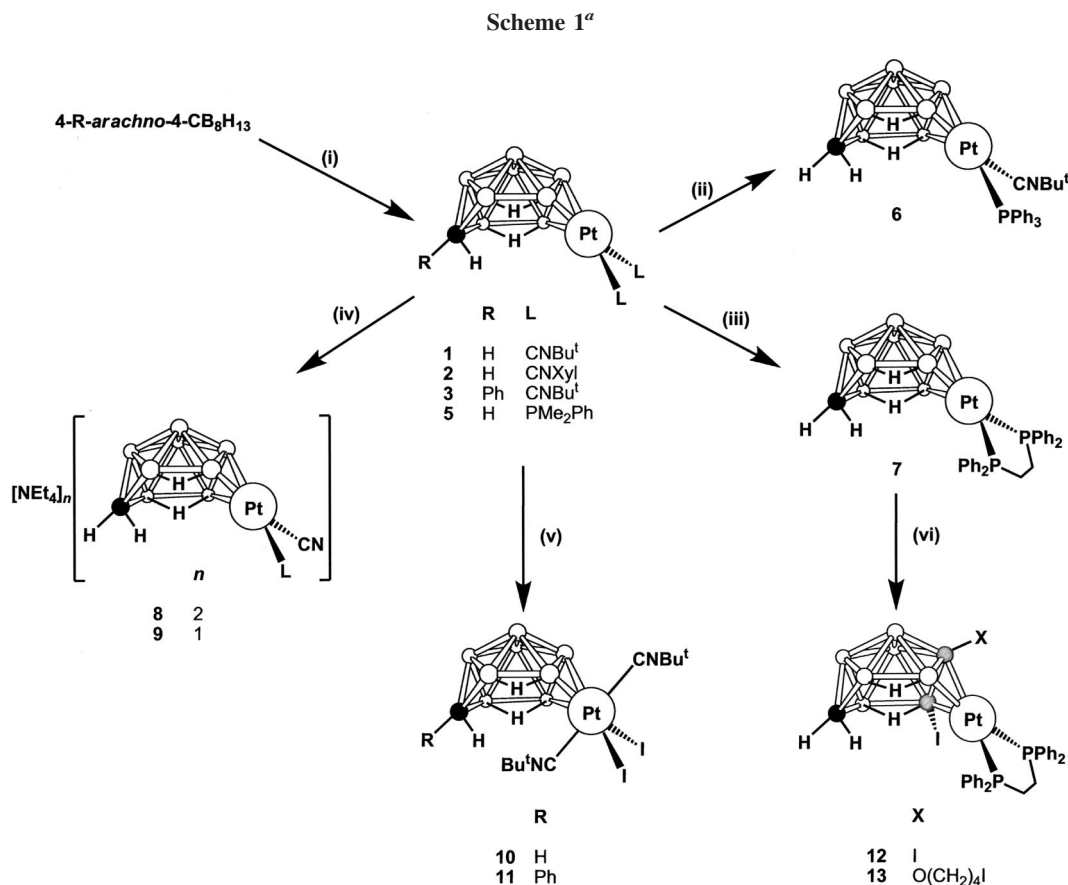
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^a Reagents and conditions: (i) [Pt₃(CNR)₆] in THF (**1**, **2**, and **3**), or [PtMe₂(PMe₂Ph)₂] in CH₂Cl₂ (**5**); (ii) **1** with PPh₃ in CH₂Cl₂; (iii) **1** with dppe in CH₂Cl₂; (iv) **1** with *n* molar equivalents of [NEt₄][CN] in CH₂Cl₂; (v) **1** or **3** with I₂ in CH₂Cl₂; (vi) **7** with I₂ in CH₂Cl₂ (**12**) or in THF (**12** + **13**). Key: ● = C, ○ = BH, gray ○ = B.

Table 1. Analytical and Physical Data

compd	$\nu_{\max}(\text{CN})^a/\text{cm}^{-1}$	yield (%)	Anal./% ^b			
			C	H	N	
1	[9,9-(CNBu ^t) ₂ -arachno-9,6-PtCB ₈ H ₁₂]	2201 s, 2179 s	91	28.1 (28.0)	6.5 (6.4)	5.9 (5.7)
2	[9,9-(CNXyl) ₂ -arachno-9,6-PtCB ₈ H ₁₂]	2181 s, 2155 s	85	40.4 (40.2)	5.3 (5.3)	5.1 (4.9)
3	[9,9-(CNBu ^t) ₂ -6-Ph-arachno-9,6-PtCB ₈ H ₁₁]	2203 s, 2181 s	81	37.4 (37.3)	6.3 (6.3)	5.2 (5.1)
4	[9,9-(CNBu ^t) ₂ -6-Ph-8-CNBu ^t -arachno-9,6-PtCB ₈ H ₉]	2216 s, 2186 s, 2162 m	2	42.3 (42.0)	6.6 (6.6)	6.8 (6.7)
5	[9,9-(PMe ₂ Ph) ₂ -arachno-9,6-PtCB ₈ H ₁₂]	2216 s, 2186 s, 2162 m	92	35.3 (35.2)	6.0 (5.7)	
6	[9-(CNBu ^t -9-PPh ₃ -arachno-9,6-PtCB ₈ H ₁₂)]	2184 s	94	44.2 (44.3)	5.7 (5.6)	2.0 (2.2)
7	[9,9-dppe-arachno-9,6-PtCB ₈ H ₁₂]	2184 s	95	45.9 (46.1)	5.2 (5.2)	
8	[NEt ₄] ₂ [9,9-(CN) ₂ -arachno-9,6-PtCB ₈ H ₁₂]	2106 m, 2096 m	98	38.6 (38.8) ^c	8.7 (8.7)	9.4 (9.6)
9	[NEt ₄][9-(CNBu ^t -9-CN)-arachno-9,6-PtCB ₈ H ₁₂]	2176 s, 2112 m	94	33.0 (33.1)	7.4 (7.6)	7.5 (7.7)
10	[9,9-(CNBu ^t) ₂ -9,9-I ₂ -arachno-9,6-PtCB ₈ H ₁₂]	2260 m, 2225 s	74	18.4 (18.2)	4.3 (4.2)	3.9 (3.9)
11	[9,9-(CNBu ^t) ₂ -9,9-I ₂ -6-Ph-arachno-9,6-PtCB ₈ H ₁₁]	2260 m, 2216 s	72	25.5 (25.5)	4.4 (4.3)	3.5 (3.5)
12	[9,9-dppe-4,8-I ₂ -arachno-9,6-PtCB ₈ H ₁₀]	2260 m, 2216 s	82	33.7 (33.9)	3.6 (3.6)	
13	[9,9-dppe-4-{O(CH ₂) ₄ I}-8-I-arachno-9,6-PtCB ₈ H ₁₀]	2260 m, 2216 s	63	36.3 (36.2)	4.1 (4.1)	

^a Measured in CH₂Cl₂; a broad, medium-intensity band observed at ca. 2500–2550 cm⁻¹ in the spectra of all compounds is due to B–H absorptions.

^b Calculated values are given in parentheses. ^c Solid contains 0.25 molar equiv of [NEt₄][CN].

arachno-platinamonocarboranes and report the results of preliminary reactivity studies carried out on these compounds.

Results and Discussion

The *arachno* 10-vertex platinum complex [9,9-(CNBu^t)₂-arachno-9,6-PtCB₈H₁₂] (**1**) was readily obtained by the reaction (18 h) of *arachno*-4-CB₈H₁₄ with [Pt₃(CNBu^t)₆],¹⁸ at ambient

temperature in tetrahydrofuran (THF). Analogous complexes [9,9-(CNXyl)₂-arachno-9,6-PtCB₈H₁₂] (**2**; Xyl = C₆H₃Me₂-2,6) and [9,9-(CNBu^t)₂-6-Ph-arachno-9,6-PtCB₈H₁₁] (**3**) were obtained in a similar manner using [Pt₃(CNXyl)₆] or *arachno*-4-Ph-4-CB₈H₁₃, respectively (Scheme 1). Compounds **1**–**3** were all obtained in high yields. Physical and spectroscopic data for all reported species (**1**–**13**) are detailed in Tables 1 and 2.

The solid-state structure of **1** was unequivocally established by an X-ray diffraction study, the results of which are illustrated in Figure 1. The *arachno* configuration of **1** was confirmed by

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Table 2. ^1H , ^{13}C , ^{11}B , and ^{31}P NMR Data^a

compound	$^1\text{H}/\delta^b$	$^{13}\text{C}/\delta^c$	$^{11}\text{B}/\delta^d$	$^{31}\text{P}/\delta^e$
1	1.55 (s, 18H, CH ₃), 0.83 (br s, 1H, cage CH), 0.10 (br s, 1H, cage CH), -3.17 (br, 2H, B-H-B)	137.8 [J(PtC) = 1255, (C≡N)], 58.3 (CMe ₃), 53.4 (br, cage C), 29.9 (CH ₃)	25.6 [J(PtB) = 314, B(4)], 3.0 [B(2)], -8.5 (2B), -15.9 [br, 2B, B(8), B(10)], -30.9 (2B)	
2	7.31 (t, $^3J(\text{HH}) = 7$, 4H, C ₆ H ₅), 7.18 (d, $^3J(\text{HH}) = 7$, 2H, C ₆ H ₅), 2.50 (s, 12H, CH ₃), 0.96 (br s, 1H, cage CH), 0.31 (br s, 1H, cage CH), -2.91 (br, 2H, B-H-B)	142.8 (Ph), 137.8 [J(PtC) = 1263, (C≡N)], 129.4, 127.9, 126.0 (Ph), 58.8 (CMe ₃), 53.4 (br, cage C), 30.1 (CH ₃)	25.4 [br, B(4)], 5.0 [B(2)], -4.5 (2B), -15.4 [br, 2B, B(8), B(10)], -30.1 (2B)	
3	7.17-6.99 (m, 5H, Ph), 1.57 (s, 27H, CH ₃), 1.25 (br s, 1H, cage CH), -2.20 (br, 1H, B-H-B)	146.1, 129.4, 127.7, 124.6 (Ph), 58.3, 58.1 (CMe ₃), 53.4 (br, cage C), 30.4, 30.3 (CH ₃)	13.2 [br, B(4)], 2.3, -5.9, -9.9, -20.4, -21.4, -24.0 [B(10)], -38.3	
4	7.36-7.26 (m, 10H, Ph), 1.72 (br, 12H, CH ₃), 0.76 (br s, 1H, cage CH), 0.02 (br s, 1H, cage CH), -2.89 (br, 2H, B-H-B)	138.2-128.9 (Ph), 53.3 (br, cage C), 18.4 (br, CH ₃)	27.5 [br, B(4)], 2.7 [B(2)], -7.8 (2B), -11.5 [br, 2B, B(8), B(10)], -29.0 (2B)	-5.3 [br, J(PtP) = 2684]
5	7.47-7.39 (m, 15H, Ph), 1.29 (s, 9H, CH ₃), 0.68 (br s, 1H, cage CH), -0.15 (br s, 1H, cage CH), -2.75 (br s, 1H, B-H-B), -3.76 (br, 1H, B-H-B)	141.4 (br, C≡N), 134.1-128.8 (Ph), 58.4 (CMe ₃), 53.4 (br, cage C), 29.9 (CH ₃)	26.9 [br, B(4)], 3.6 [B(2)], -8.2 (2B), -11.9, -12.9, -29.8 (2B)	28.8 [br, J(PtP) = 2687]
6	7.72-7.38 (m, 20H, Ph), 2.56-2.33 (m, 4H, CH ₂), 0.48 (br s, 1H, cage CH), -0.82 (br s, 1H, cage CH), -3.27 (br, 2H, B-H-B)	134.6-129.2 (Ph), 53.4 (br, cage C), 30.7 (br, CH ₂)	26.9 [br, B(4)], 1.6 [B(2)], -7.9 (2B), -12.4 [br, 2B, B(8), B(10)], -29.8 (2B)	57.2 [br, J(PtP) = 2596]
7	3.30 (q, 16H, CH ₂), 1.31 (t, 24H, CH ₃), 0.32 (br s, 1H, cage CH), -0.40 (br s, 1H, cage CH), -3.43 (br, 2H, B-H-B)	139.3 [J(PtC) = 1046, (C≡N)], 53.4 (br, cage C), 53.0 (CH ₂), 7.9 (CH ₃)	21.7 [J(PtB) = 310, B(4)], -1.6 [B(2)], -10.1 (2B), -20.7 [br, 2B, B(8), B(10)], -33.2 (2B)	
8	3.24 (q, 8H, CH ₂), 1.52 (s, 3H, NCH ₃), 1.31 (t, 12H, CH ₂ CH ₃), 0.56 (br s, 1H, cage CH), -0.13 (br s, 1H, cage CH), -3.29 (br, 2H, B-H-B)	140.3 (C≡N), 137.2 (C≡NBU ^l), 57.8 (CMe ₃), 53.4 (br, cage C), 53.1 (CH ₂), 30.3 (CMe ₃), 7.8 (CH ₂ CH ₃)	23.6 [J(PtB) = 315, B(4)], 0.8 [B(2)], -9.1 (2B), -18.0 [br, 2B, B(8), B(10)], -30.9, -32.9	
9	1.60 (s, 9H, CH ₃), 1.55 (s, 9H, CH ₃), 1.47 (br s, 1H, cage CH), 1.29 (br s, 1H, cage CH), -2.01 (br, 2H, B-H-B)	116.7, 116.2 (br, C≡N), 59.0 (CMe ₃), 53.4 (br, cage C), 30.0 (CH ₃)	17.2 [br, B(4)], 15.3 [B(2)], -3.0 [br, 2B, B(8), B(10)], -10.7 (2B), -28.5 (2B)	
10	7.42-7.24 (m, 5H, Ph), 1.56 (s, 9H, CH ₃), 1.41 (s, 9H, CH ₃), 1.29 (br s, 1H, cage CH), -1.57 (br, 2H, B-H-B)	140.3, 129.5, 128.8, 127.6 (Ph), 123.5 (br, C≡N), 61.0 (CMe ₃), 53.4 (br, cage C), 29.5 (CH ₃)	17.4 [br, B(4)], 16.3 [B(2)], -3.1 [br, 2B, B(8), B(10)], -7.9 (2B), -28.1 (2B)	
11	7.99-7.33 (m, 20H, Ph), 2.85-2.44 (m, 4H, CH ₂), 0.56 (br s, 1H, cage CH), -0.94 (br s, 1H, cage CH), -3.21 (br, 2H, B-H-B)	136.5-124.2 (Ph), 53.4 (br, cage C), 34.5 [J(PC) = 36, $^2J(\text{PC}) = 14$, PCH ₂], 30.9 [J(PC) = 34, $^2J(\text{PC}) = 13$, PCH ₂]	14.4 [B(4)], 2.0, -6.3, -8.7, -11.5, -23.7 (2B), -29.2	50.7 [br, J(PtP) = 2488]
12	7.81-7.35 (m, 20H, Ph), 3.36 (t, 2H, BOCH ₂), 2.78-2.29 (m, 4H, PCH ₂), 2.12 (t, 2H, CH ₂), 1.83 (m, 2H, CH ₂ CH ₂), 1.28 (m, 2H, BOCH ₂ CH ₂), 0.36 (br s, 1H, cage CH), -0.80 (br s, 1H, cage CH), -2.61 (br, 2H, B-H-B)	136.7-126.5 (Ph), 67.8 [$^3J(\text{PtC}) = 38$, BOCH ₂], 53.5 (br, cage C), 34.7 [J(PC) = 35, $^2J(\text{PC}) = 15$, PCH ₂], 33.6 (BOCH ₂ CH ₂), 30.5 [J(PC) = 35, $^2J(\text{PC}) = 14$, PCH ₂], 20.8 (CH ₂ CH ₂), 14.4 (CH ₂ I)	39.6 [J(PtB) = 334, B(4)], -0.5, -10.2, -13.3 (2B), -23.7, -26.7 [B(8)], -32.3	51.8 [br, J(PtP) = 2327]

^a Chemical shifts (δ) in ppm, coupling constants (J) in hertz, measurements at ambient temperatures in CD₂Cl₂. ^b Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. -1 to +4. ^c H-decoupled chemical shifts are positive to high frequency of SiMe₄. ^d H-decoupled chemical shifts are positive to high frequency of BF₃·Et₂O (external); resonances have singlet multiplicity and are of unit integral, except where indicated. ^e H-decoupled chemical shifts are positive to high frequency of 85% H₃PO₄(external).

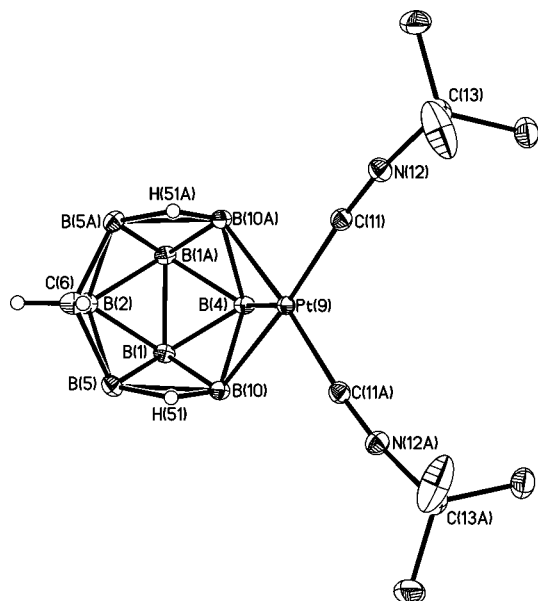
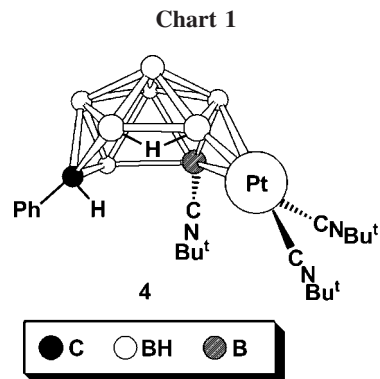


Figure 1. Structure of a whole molecule of compound **1** showing the crystallographic labeling scheme. Selected distances (Å): Pt(9)–B(4) 2.157(4), Pt(9)–B(10) 2.219(3), Pt(9)–C(11) 1.984(2), C(11)–N(12) 1.149(3), N(12)–C(13) 1.465(3). The C(11)–Pt(9)–C(11)^a angle is 91.65(13)°. In this and subsequent figures, thermal ellipsoids are drawn with 40% probability, and for clarity only chemically significant hydrogen atoms are shown. Symmetry code (a): + x, ½ – y, + z.

the presence of two hydrogen atoms bridging the “gunwale” boron vertices on the open face, analogous to [arachno-B₁₀H₁₄]²⁻. The cage carbon atom resides in the three-connected 6-position, and the platinum center is in the 9-position ligated by three boron atoms. A molecular plane of symmetry bisects these atoms and the boron atoms in positions 2 and 4 and coincides with a crystallographic mirror plane. Interatomic distances involving the platinum center are Pt(9)–B(4) = 2.157(4) Å, Pt(9)–B(10) = 2.219(3) Å, and Pt(9)–C(11) = 1.984(2) Å.

The IR spectrum of **1** shows two strong CN stretching bands at 2201 and 2179 cm⁻¹, and its ¹¹B{¹H} NMR spectrum shows a 1:1:2:2 set of resonances, consistent with the symmetric structure determined by X-ray crystallography. Platinum satellites are observed for the resonance at δ 25.6 [J(PtB) = 314 Hz], allowing this to be assigned to B(4); unresolved coupling to the platinum nucleus is also apparent for the peak at δ -15.9, and this peak is therefore tentatively allocated to B(8) and B(10). The ¹H NMR spectrum shows a diagnostic broad resonance at δ -3.17 corresponding to the B–H–B bridges.¹⁹ In the ¹³C{¹H} NMR spectrum coupling to the platinum nucleus is observed for the C≡N resonance at δ 137.8 [J(PtC) = 1255 Hz], while a broad resonance is observed at δ 53.4 that corresponds to the cage carbon atom. The IR and NMR spectra for compounds **2** and **3** are similar to those of **1** and therefore merit little further comment.

A second species was obtained during the synthesis of **3**. It was separated in low yield by column chromatography and initially identified as [9,9-(CNBu^t)₂-6-Ph-8-CN Bu^t-arachno-9,6-PtCB₈H₉] (**4**; see Chart 1) by an X-ray diffraction study (Figure 2). Compound **4** is closely related to **3**, except that the {BH₂} unit at position 8 in compound **3** has been replaced by the



isobal {B←:CNBu^t} moiety. Thus, although there is no overall change in cluster architecture upon substitution, the μ-H atom that formerly bridged the B(7)–B(8) connectivity is no longer present. All three CNBu^t groups in **4** therefore behave as two-electron donors with, correspondingly, very similar geometric parameters within each ligand. Attempts to synthesize **4** from **3** by direct reaction with CNBu^t were unsuccessful, and given the low yield of **4**, it is unwise to speculate upon its precise mechanism of formation. We note, however, that similar B–CNBu^t substitution has been reported in the synthesis of bis(isocyanide) derivatives of {NiCB₁₀} clusters using {Ni⁰(CNBu^t)₂} synthons.²⁰

The ¹¹B{¹H} NMR spectrum for **4** shows a separate resonance for each of the eight boron atoms. Unresolved coupling to the platinum nucleus allows the peak at δ 13.2 to be assigned to B(4), and the resonance at δ -24.0 can be assigned to the isocyanide-substituted boron atom, B(8), as no coupling to a hydrogen nucleus is apparent for this peak in the proton-coupled ¹¹B NMR spectrum. The ¹H NMR spectrum shows a diagnostic broad peak at δ -2.20 corresponding to the single B–H–B bridge, and the IR spectrum reveals three strong CN stretching bands at 2216, 2186, and 2162 cm⁻¹; the latter can be tentatively assigned to B–CN due to its smaller intensity and broader nature.

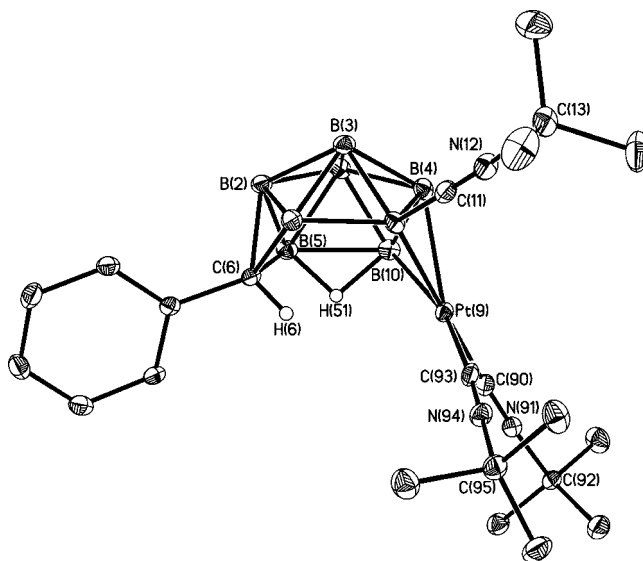


Figure 2. Structure of compound **4** showing the crystallographic labeling scheme. Selected distances (Å): Pt(9)–B(4) 2.233(3), Pt(9)–B(8) 2.245(3), Pt(9)–B(10) 2.157(3), Pt(9)–C(90) 1.987(3), C(90)–N(91) 1.151(4), N(91)–C(92) 1.459(4), Pt(9)–C(93) 1.966(3), C(93)–N(94) 1.148(4), N(94)–C(95) 1.469(4), B(10)–C(11) 1.543(4), C(11)–N(12) 1.144(4), N(12)–C(13) 1.464(4). The C(90)–Pt(9)–C(93) angle is 95.52(12)°.

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Phosphine-substituted 10-vertex *arachno*-platinacarborane species similar to **1–3** have been identified previously,^{16,17} and these are now found to be accessible in good yield from the reaction of *arachno*-4-CB₈H₁₄ with complexes such as [PtMe₂(PMe₂Ph)₂]. Addition of [PtMe₂(PMe₂Ph)₂] to a stirred CH₂Cl₂ solution of *arachno*-4-CB₈H₁₄ yielded [9,9-(PMe₂Ph)₂-*arachno*-9,6-PtCB₈H₁₂] (**5**), in near quantitative yield (see Scheme 1). Compound **5** has been previously isolated in low yields (<3%) as a byproduct in a reaction between [*arachno*-6-CB₉H₁₄][−] and [PtCl₂(PMe₂Ph)₂].¹⁷

The open nature of these *arachno* 10-vertex platinacarboranes (**1–5**) suggested that it may be possible to add further metal centers to these compounds and thus engender larger mixed-metal clusters. However, all reactions attempted in this area have thus far proved fruitless. Oxidative addition of neutral M⁰ fragments, as well as deprotonation (NaH) and subsequent addition of cationic metal fragments, resulted in either recovery of the starting material or simple ligand exchange between metal centers. The complex [9-CNBU¹-9-PPh₃-*arachno*-9,6-PtCB₈H₁₂] (**6**) was first identified from such a ligand exchange reaction when attempts were made to add an iridium center to **1** using [IrCl(CO)(PPh₃)₂]. Compound **6** (see Scheme 1) can more readily be obtained by simply stirring a CH₂Cl₂ solution of **1** with PPh₃. The ¹¹B{¹H} NMR spectrum of **6** shows a 1:1:2:1:1:2 set of resonances; unresolved coupling to the platinum nucleus is again observed for the lowest field peak at δ 26.8, which is assigned to B(4). Two broad resonances in the ¹H NMR spectrum at δ −2.75 and −3.76 are assigned to the two B–H–B bridges, and a broad unresolved peak in the ¹³C{¹H} NMR at δ 141.4 is assigned to the cyano carbon atom. The ³¹P{¹H} NMR spectrum shows a single resonance with ¹⁹⁵Pt satellites at δ 28.8 [*J*(PtP) = 2687 Hz], and the IR spectrum shows one strong CN stretching band at 2184 cm^{−1}.

It is notable that even with an excess of PPh₃ only one CNBU¹ ligand in **1** can be replaced, forming compound **6**. Nevertheless, both isocyanides can be replaced by using the bidentate ligand, dppe (Ph₂PCH₂CH₂PPh₂), giving [9,9-dppe-*arachno*-9,6-PtCB₈H₁₂] (**7**) in a similar manner to **6**. The ¹¹B{¹H} NMR spectrum of **7** shows a 1:1:2:2:2 set of resonances akin to that of compounds **1–3** and **5**, and the ³¹P{¹H} NMR spectrum shows a single resonance at δ 57.2 [*J*(PtP) = 2596 Hz].

Treatment of **1** with 2 equiv of [NEt₄][CN] yields quantitatively the dianionic species [NEt₄]₂[9,9-(CN)₂-*arachno*-9,6-PtCB₈H₁₂] (**8**; see Scheme 1). Its ¹¹B{¹H} NMR spectrum again shows a 1:1:2:2:2 set of resonances consistent with molecular symmetry. The ¹³C{¹H} NMR spectrum shows a C≡N resonance at δ 139.3 with ¹⁹⁵Pt satellites [*J*(PtC) = 1046 Hz] and the IR spectrum for **8** shows two CN stretching bands at 2106 and 2096 cm^{−1}. The solid-state structure of **8** was confirmed via an X-ray diffraction study and is illustrated in Figure 3. Compound **8** can also be formed when the phosphine derivatives (**5–7**) are treated with a slight excess of [NEt₄][CN]. Careful treatment of **1** with 1 equiv of [NEt₄][CN] gives the monoanionic species [NEt₄][9-CNBU¹-9-CN-*arachno*-9,6-PtCB₈H₁₂] (**9**; see Scheme 1). The different ligands coordinated to the platinum center in **9** account for the 1:1:2:2:1:1 set of resonances seen in its ¹¹B{¹H} NMR spectrum. Two C≡N stretching bands at 2176 and 2112 cm^{−1} in the IR spectrum of **9** can be assigned to the isocyanide and cyanide ligands, respectively.

Attempts were made to form *closo* 10-vertex platinacarboranes from species **1–3** and **5–7**. Heating to elevated temperatures had recently been found to facilitate cage closure in [4,9-

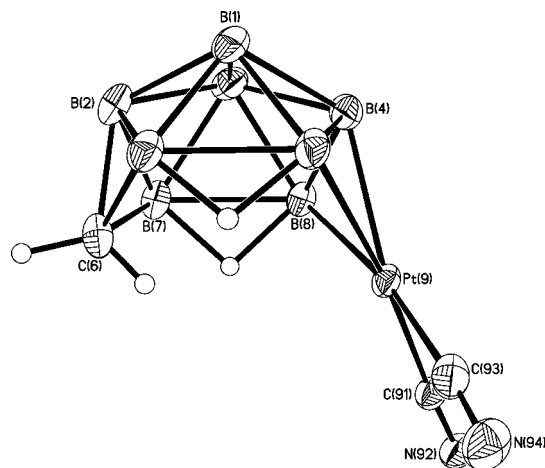


Figure 3. Structure of the dianion of compound **8** showing the crystallographic labeling scheme. Selected distances (Å): Pt(9)–B(4) 2.145(4), Pt(9)–B(8) 2.211(4), Pt(9)–B(10) 2.213(4), Pt(9)–C(91) 2.019(4), C(91)–N(92) 1.143(4), Pt(9)–C(93) 2.004(4), C(93)–N(94) 1.157(5). The C(91)–Pt(9)–C(93) angle is 90.62(15)°.

{Fe(CO)₄}-9,9,9-(CO)₃-*arachno*-9,6-FeCB₈H₁₁][−], forming the monoiron species [2,2,2-(CO)₃-*closo*-2,1-FeCB₈H₉][−].¹¹ Unfortunately, no such reaction occurs with the *arachno*-platinacarboranes described here, and they are recovered unchanged after heating toluene or xylene solutions to reflux temperatures for 24 h.

Addition of I₂ in the presence of a base such as Et₃N has been used successfully to oxidatively close *arachno*-monocarboranes to their *nido* or *closo* counterparts.⁵ This methodology was also applied to the present *arachno*-platinamonocarboranes. Although it was not possible to synthesize *nido* or *closo* species, some of the *arachno* clusters did react to yield further novel *arachno* species. Thus, treatment of **1** with I₂ at −78 °C led to the formation of [9,9-(CNBU¹)₂-9,9-I₂-*arachno*-9,6-PtCB₈H₁₂] (**10**). Instead of the whole cluster being oxidized and closing, oxidation is confined to the platinum center: the formal oxidation state of the now octahedral platinum center in **10** is +4 with two iodides taking up the extra coordination sites (see Scheme 1). The ¹¹B{¹H} NMR spectrum of **10** again shows a 1:1:2:2:2 set of resonances, albeit over a narrower field range. The resonance corresponding to B(4) at δ 17.2, identified by unresolved coupling to the platinum nucleus, is shifted upfield compared to the analogous peak (δ 25.6) for its precursor **1**. Two broad resonances are visible in the ¹³C{¹H} NMR spectrum at δ 116.7 and 116.2 for the two chemically different (*exo* and *endo*) cyano carbon atoms, as is a broad peak at δ 53.4 that corresponds to the cage carbon. The ¹H NMR spectrum shows the characteristic broad resonance corresponding to the two B–H–B bridges at δ −2.01.

It proved difficult to obtain single crystals of **10** suitable for X-ray diffraction analysis, but good quality single crystals were obtained for its phenylated counterpart, [9,9-(CNBU¹)₂-9,9-I₂-6-Ph-*arachno*-9,6-PtCB₈H₁₁] (**11**), obtained from **3** and I₂. The solid-state structure of **11** is illustrated in Figure 4, and its spectroscopic data are similar to those of **10**. Both compounds, although stable for prolonged periods of time in their solid form, decompose in solution relatively quickly. Decomposition apparently leads to a mixture of Pt(II) species including the precursors **1** and **3**, species with iodide substitution at boron vertices, and [PtI₂(dppe)]. These were partially characterized by NMR spectroscopy or preliminary X-ray diffraction studies, but they could not be isolated in sufficient amounts to permit full characterization.

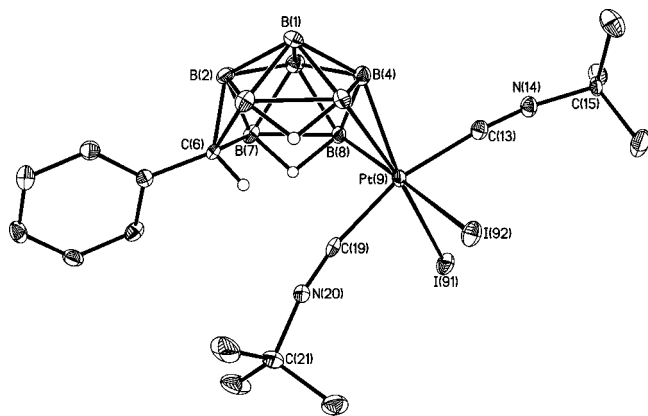


Figure 4. Structure of compound **11** showing the crystallographic labeling scheme. Selected distances (Å) and angles (deg): Pt(9)–I(91) 2.7325(3), Pt(9)–I(92) 2.7481(3), Pt(9)–B(4) 2.275(4), Pt(9)–B(8) 2.294(5), Pt(9)–B(10) 2.324(4), Pt(9)–C(13) 1.956(4), C(13)–N(14) 1.149(4), N(14)–C(15) 1.469(4), Pt(9)–C(19) 1.973(4), C(19)–N(20) 1.152(4), N(20)–C(21) 1.468(4). Selected angles are: I(91)–Pt(9)–I(92) 93.129(10), I(91)–Pt(9)–C(13) 85.57(11), I(91)–Pt(9)–C(19) 84.95(10), I(92)–Pt(9)–C(13) 85.13(11), I(92)–Pt(9)–C(19) 83.52(10), C(13)–Pt(9)–C(19) 164.77(14).

A different reaction takes place when compound **7** is similarly treated with I_2 . Now, rather than oxidative addition of iodine to the platinum center, substitution at boron vertices occurs (see Scheme 1), with [9,9-dppe-4,8- I_2 -*arachno*-9,6-PtCB₈H₁₀] (**12**) being isolated from the reaction of I_2 with **7** in CH_2Cl_2 . Here, two iodine atoms have replaced the terminal hydrogen atoms at positions 4 and 8. The $^{11}B\{^1H\}$ NMR spectrum of **12** shows a 1:1:1:1:2:1 set of resonances, with unresolved coupling to the platinum nucleus observed for the peak at δ 14.4, so that this resonance can be assigned to B(4); this resonance also remains a singlet in the 1H -coupled ^{11}B NMR spectrum, confirming that an iodine atom is attached to B(4). The $^{31}P\{^1H\}$ NMR spectrum shows a single, broad resonance with ^{195}Pt satellites at δ 50.7 [$J(PtP) = 2488$ Hz].

When the reaction that formed **12** is carried out with THF as solvent, [9,9-dppe-4- $\{O(CH_2)_4I\}$ -8-*arachno*-9,6-PtCB₈H₁₀] (**13**) is instead produced as the major product, with compound **12** formed in lesser yield. The $\{O(CH_2)_4I\}$ moiety attached to the cage in **13** is assumed to result from a boron-bound THF substituent that initially is introduced via iodine-promoted oxidative substitution,²¹ and which subsequently undergoes nucleophilic attack by I^- at its three-coordinate oxygen atom to give a neutral species. Several examples of cluster-bound THF substituents being opened by halide ions in this manner have been reported previously.²²

The $^{11}B\{^1H\}$ NMR spectrum of **13** shows a 1:1:1:2:1:1:1 set of resonances, with platinum satellites observed for the resonance at δ 39.6 [$J(PtB) = 334$ Hz], allowing the latter to be assigned to B(4). Its chemical shift is considerably downfield when compared with similar resonances discussed above, due to its oxygen substituent, while the resonance at δ -26.7 shows

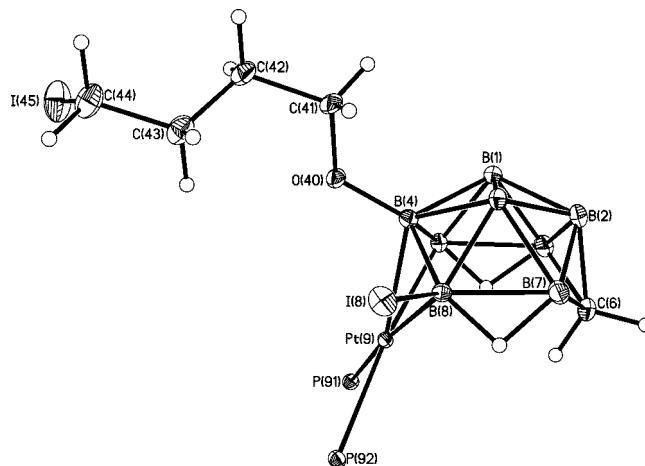


Figure 5. Structure of compound **13** showing the crystallographic labeling scheme. Selected distances (Å): Pt(9)–B(4) 2.190(4), Pt(9)–B(8) 2.195(4), Pt(9)–B(10) 2.240(4), Pt(9)–P(91) 2.2932(10), Pt(9)–P(92) 2.2857(12), B(4)–O(40) 1.408(5), O(40)–C(41) 1.429(4), C(44)–I(45) 2.162(4). The P(91)–Pt(9)–P(92) angle is 84.24(4)°.

no additional coupling in a 1H -coupled ^{11}B NMR spectrum, indicating that the corresponding boron atom has been substituted. The $^{31}P\{^1H\}$ NMR spectrum shows a single, broad resonance with ^{195}Pt satellites at δ 51.8 [$J(PtP) = 2327$ Hz]. In the $^{13}C\{^1H\}$ NMR spectrum, notably, the resonance corresponding to the carbon nucleus adjacent to the oxygen (δ 67.8) shows coupling to the platinum nucleus [$^3J(PtC) = 38$ Hz]. The solid-state structure of **13** was unequivocally determined via an X-ray diffraction study, of which the result is presented in Figure 5: this is entirely consistent with the spectral data.

Conclusions

The reaction of *arachno*-4-CB₈H₁₄, and its phenylated cousin 4-Ph-*arachno*-4-CB₈H₁₃, with platinum–isocyanide complexes provides a facile, high-yielding route to new *arachno*-platinum-monocarborane species, adding to the relatively sparsely studied class of open metallamonocarboranes. The synthesis of these complexes in such high yields has allowed preliminary investigation of their reaction chemistry. Their $\{PtCB_8\}$ cores, however, have thus far proven to be unusually stable for such open metallacarborane clusters, withstanding various attempted cage-closure reactions and the addition of further metal centers.

Oxidative addition of I_2 to the platinum center, as in the formation of **10** and **11**, or iodine-promoted cage substitution, as occurred in the synthesis of **12** and **13**, show an insight into the type of reaction chemistry that may be possible for these species. These various products highlight how subtle changes in the precursors or conditions can have a significant effect upon reactivity. It is anticipated that the high-yielding synthesis of all these *arachno*-platinum-monocarboranes can ultimately be exploited to reveal further interesting reaction chemistry in the future.

Experimental Section

General Considerations. Reactions were carried out under an atmosphere of dry nitrogen using Schlenk line techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40–60 °C. Chromatography columns (ca. 20 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60–200 mesh).

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Table 3. Data for Crystal Structure Analyses of Compounds 1, 4, 8, 11, and 13

	1	4	8	11	13
formula	C ₁₁ H ₃₀ B ₈ N ₂ Pt	C ₂₂ H ₄₁ B ₈ N ₃ Pt	C ₁₉ H ₅₂ B ₈ N ₄ Pt	C ₁₇ H ₃₄ B ₈ I ₂ N ₂ Pt	C ₃₁ H ₄₂ B ₈ I ₂ OP ₂ Pt
fw	471.94	629.15	618.22	801.83	1027.96
space group	<i>Pnma</i>	<i>P1</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>P1</i>
<i>a</i> , Å	11.6161 (8)	11.4393 (3)	31.728 (8)	14.3012 (11)	10.086 (2)
<i>b</i> , Å	17.7030 (12)	11.5230 (3)	11.472 (3)	10.3809 (7)	11.493 (2)
<i>c</i> , Å	9.5129 (6)	12.9427 (3)	17.010 (5)	22.6397 (14)	17.784 (4)
α , deg	90	80.784 (1)	90	90	77.85 (3)
β , deg	90	81.299 (2)	109.609 (13)	125.297 (4)	74.33 (3)
γ , deg	90	61.667 (1)	90	90	71.97 (3)
<i>V</i> , Å ³	1956.2 (2)	1476.71 (6)	5833 (2)	2743.2 (3)	1869.2 (6)
<i>Z</i>	4	2	8	4	2
μ (Mo K α), cm ⁻¹	0.7164	0.1415	0.4826	0.7374	0.5516
no. of reflns measd	47 288	31 116	36 026	42 894	35 441
no. of indep reflns	3064	8447	7221	7509	9086
<i>R</i> _{int}	0.0429	0.0347	0.044	0.0538	0.0491
wR2, <i>R</i> ₁ (all data) ^a	0.0498, 0.0222	0.0612, 0.0375	0.0667, 0.0393	0.0529, 0.0511	0.0688, 0.0335

$$^a wR_2 = [\sum\{w(F_o - F_c)^2\} / \sum w(F_o)^2]^{1/2}; R_1 = \sum||F_o| - |F_c|| / \sum|F_o|.$$

Preparative thin-layer chromatography (TLC) was performed on 20 × 20 cm glass plates (Analtech, silica gel GF₂₅₄). NMR spectra were recorded at the following frequencies: ¹H 360.13, ¹³C 90.56, ³¹P 145.78, and ¹¹B 115.5 MHz. The compounds *arachno*-4-CB₈H₁₄,^{5a} 4-Ph-*arachno*-4-CB₈H₁₃,^{5c} [Pt(bicyclo[2.2.1]heptene)₃]₂,²³ and [PtMe₂(PMe₂Ph)₂]₂²⁴ were prepared according to the literature; all other materials were used as received.

Synthesis of [9,9-(CNBu)^t]₂-*arachno*-9,6-PtCB₈H₁₂] and [9,9-(CNXyl)₂-*arachno*-9,6-PtCB₈H₁₂]. Stoichiometric amounts of [Pt(bicyclo[2.2.1]heptene)₃] (1.270 g, 2.66 mmol) and CNBu^t (0.65 mL, 5.71 mmol) were mixed in THF (30 mL), affording [Pt₃(CNBu^t)₆] in situ. Solid *arachno*-4-CB₈H₁₄ (0.300 g, 2.66 mmol) was immediately added to this orange solution, and the resulting mixture was stirred at ambient temperature for 14 h. Volatiles were removed in vacuo, and the residue was dissolved in CH₂Cl₂ (ca. 5 mL) and transferred to the top of a chromatography column. Elution with CH₂Cl₂-petroleum ether (4:1) afforded a colorless eluate that was collected and, after evaporation of solvent in vacuo, gave [9,9-(CNBu^t)₂-*arachno*-9,6-PtCB₈H₁₂] as a white powder (**1**; 1.142 g, 91%). [9,9-(CNXyl)₂-*arachno*-9,6-PtCB₈H₁₂] (**2**; 0.860 g, 85%) was synthesized analogously from *arachno*-4-CB₈H₁₄ (0.200 g, 1.78 mmol) using CNXyl in the place of CNBu^t.

Synthesis of [9,9-(CNBu)^t]₂-6-Ph-*arachno*-9,6-PtCB₈H₁₁] and [9,9-(CNBu)^t]₂-6-Ph-8-CNBU^t-*arachno*-9,6-PtCB₈H₉]. By a similar procedure to that described above for **1**, [Pt₃(CNBu^t)₆] was synthesized by mixing [Pt(bicyclo[2.2.1]heptene)₃] (0.506 g, 1.06 mmol) and CNBu^t (0.30 mL, 2.63 mmol) in THF (20 mL), followed by addition of 4-Ph-*arachno*-4-CB₈H₁₃ (0.200 g, 1.06 mmol) to this solution. After stirring at ambient temperature for 14 h the volatiles were removed in vacuo, and the residue was dissolved in CH₂Cl₂ (ca. 3 mL) and added to the top of a chromatography column. Elution using CH₂Cl₂-petroleum ether (4:1) afforded two fractions. The first, colorless fraction, after evaporation of solvent in vacuo, yielded [9,9-(CNBu^t)₂-6-Ph-*arachno*-9,6-PtCB₈H₁₁] (**3**; 0.470 g, 81%) as a white powder. The second, slower moving, pale yellow fraction was collected and further purified by preparative TLC using CH₂Cl₂-petroleum ether (3:2) as the liquid phase. A single band (*R_f* = 0.32) was removed, which after evaporation of solvent in vacuo gave [9,9-(CNBu^t)₂-6-Ph-8-CNBU^t-*arachno*-9,6-PtCB₈H₉] (**4**; 0.013 g, 2%) as a pale yellow powder.

Synthesis of [9,9-(PMe₂Ph)₂-*arachno*-9,6-PtCB₈H₁₂]. Solid [PtMe₂(PMe₂Ph)₂] (0.135 g, 0.27 mmol) was added to a CH₂Cl₂ (10 mL) solution of *arachno*-4-CB₈H₁₄ (0.030 g, 0.27 mmol). After

stirring at ambient temperature for 10 h the volatiles were removed in vacuo and the resulting residue was added to a chromatography column. Using CH₂Cl₂ as eluent, a colorless solution was collected, which, after evaporation of solvent in vacuo, gave [9,9-(PMe₂Ph)₂-*arachno*-9,6-PtCB₈H₁₂] (**5**; 0.144 g, 92%) as a white, microcrystalline solid.

Synthesis of [9-CNBU^t-9-PPh₃-*arachno*-9,6-PtCB₈H₁₂]. Compound **1** (0.100 g, 0.21 mmol) was dissolved in CH₂Cl₂ (15 mL), and PPh₃ (0.060 g, 0.23 mmol) was added. After 16 h at ambient temperature, volatiles were removed in vacuo and the residue was redissolved in CH₂Cl₂ (ca. 2 mL) and transferred to the top of a chromatography column. Elution with CH₂Cl₂-petroleum ether (4:1) gave a colorless solution, which was collected and, after evaporation of solvent in vacuo, gave [9-CNBU^t-9-PPh₃-*arachno*-9,6-PtCB₈H₁₂] (**6**; 0.128 g, 94%) as a white, crystalline solid.

Synthesis of [9,9-dppe-*arachno*-9,6-PtCB₈H₁₂]. Compound **1** (0.300 g, 0.64 mmol) was dissolved in CH₂Cl₂ (25 mL), and dppe (0.260 g, 0.65 mmol) was added. After 16 h at ambient temperature, volatiles were removed in vacuo, the sample washed with petroleum ether (3 × 30 mL), and the residue was redissolved in a minimum amount of CH₂Cl₂ (ca. 5 mL). Petroleum ether (ca. 50 mL) was then layered above this solution, and the sample was kept at -30 °C for 72 h. The clear, colorless crystals of [9,9-dppe-*arachno*-9,6-PtCB₈H₁₂] (**7**; 0.428 g, 95%) that resulted were collected by filtration and dried in vacuo.

Synthesis of [NEt₄]₂[9,9-(CN)₂-*arachno*-9,6-PtCB₈H₁₂] and [NEt₄][9-CNBU^t-9-CN-*arachno*-9,6-PtCB₈H₁₂]. Compound **1** (0.100 g, 0.21 mmol) was dissolved in CH₂Cl₂ (15 mL), and [NEt₄][CN] (0.066 g, 0.42 mmol) was added. After 4 h at ambient temperature, volatiles were removed in vacuo, and the residue was washed with petroleum ether (3 × 30 mL). The white powder that resulted was dried in vacuo and identified as [NEt₄]₂[9,9-(CN)₂-*arachno*-9,6-PtCB₈H₁₂] (**8**; 0.128 g, 98%). [NEt₄][9-CNBU^t-9-CN-*arachno*-9,6-PtCB₈H₁₂] (**9**; 0.108 g, 94%) was synthesized in a similar manner by using just 1 equiv of [NEt₄][CN].

Synthesis of [9,9-(CNBU^t)₂-9,9-I₂-*arachno*-9,6-PtCB₈H₁₂] and [9,9-(CNBU^t)₂-9,9-I₂-6-Ph-*arachno*-9,6-PtCB₈H₁₁]. Compound **1** (0.100 g, 0.21 mmol) was dissolved in CH₂Cl₂ (10 mL), and the solution was cooled to -78 °C. A CH₂Cl₂ solution (10 mL) of I₂ (0.110 g, 0.43 mmol) was slowly added over a period of 1 h. Solid Na₂S₂O₃ (0.100 g, 0.63 mmol) and water (20 mL) were added, and the mixture was shaken before separating the yellow CH₂Cl₂ layer. The aqueous phase was extracted with further CH₂Cl₂ (20 mL), and the combined extracts were dried with MgSO₄ before removal of volatiles in vacuo. The residue was redissolved in the minimum amount of CH₂Cl₂ (ca. 2 mL), layered with petroleum ether, and kept at -30 °C for 72 h. This afforded orange crystals of [9,9-(CNBU^t)₂-9,9-I₂-*arachno*-9,6-PtCB₈H₁₂] (**10**; 0.113 g, 74%), which

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were collected and dried in vacuo. In a similar manner [9,9-(CNBu^t)₂-9,9-I₂-6-Ph-*arachno*-9,6-PtCB₈H₁₁] was synthesized from compound **3** (0.100 g, 0.18 mmol) and isolated as an orange, crystalline solid (**11**; 0.104 g, 72%).

Synthesis of [9,9-dppe-4,8-I₂-*arachno*-9,6-PtCB₈H₁₀] and [9,9-dppe-4-{O(CH₂)₄I}-8-I-*arachno*-9,6-PtCB₈H₁₀]. Compound **7** (0.100 g, 0.14 mmol) was dissolved in CH₂Cl₂ (10 mL) and cooled to -78 °C. A CH₂Cl₂ (10 mL) solution of I₂ (0.100 g, 0.28 mmol) was slowly added over a period of 1 h. When addition was complete, the solution was allowed to warm to ambient temperature and then water (20 mL) and Na₂S₂O₃ (0.100 g, 0.63 mmol) were added. The mixture was shaken and the CH₂Cl₂ layer separated. Two further extractions with CH₂Cl₂ (2 × 20 mL) were performed, and the combined extracts were dried over MgSO₄ and then evaporated to dryness in vacuo. The resulting residue was redissolved in CH₂Cl₂ (ca. 5 mL) and added to a chromatography column, eluting with CH₂Cl₂-petroleum ether (3:2). A colorless solution was collected and evaporated in vacuo to give [9,9-dppe-4,8-I₂-*arachno*-9,6-PtCB₈H₁₀] as a white powder (**12**; 0.110 g, 82%). In an analogous reaction using THF as the solvent, the major product of the reaction was [9,9-dppe-4{O(CH₂)₄I}-8-I-*arachno*-9,6-PtCB₈H₁₀] (**13**; 0.091 g, 63%), along with compound **12** (0.032 g, 24%), which eluted from the column before compound **13**.

Structure Determinations. Experimental data for compounds **1**, **4**, **8**, **11**, and **13** are listed in Table 3. The solid-state structures of compounds **5-7**, **9**, and **12** were also determined by X-ray diffraction studies; experimental data for these compounds can be found in the crystallographic information file (CIF) in the Supporting Information. Data were collected at 110(2) K on a Bruker-Nonius X8 APEX CCD area-detector diffractometer using Mo K α X-radiation ($\lambda = 0.71073$ Å). Several sets of narrow data "frames" were collected at different values of θ , for various initial values of φ and ω , and using 0.5° increments of φ or ω . The data frames

were integrated using SAINT;²⁵ the substantial redundancy in data allowed an empirical absorption correction (SADABS)²⁵ to be applied, based on multiple measurements of equivalent reflections.

Structures were solved by direct methods using SHELXS-97²⁶ and refined with full-matrix least-squares on F^2 using SHELXL-97.²⁷ All non-hydrogen atoms were assigned anisotropic displacement parameters. The locations of cage carbon atoms were verified by examination of their isotropic thermal parameters, in conjunction with comparisons of B-B and C-B internuclear distances. All hydrogen atoms in organic functions plus terminal B-H hydrogen atoms were set riding on their parent atoms in calculated positions; all other hydrogen atoms were located in difference maps and allowed positional refinement. All hydrogen atoms were assigned calculated isotropic thermal parameters defined as $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{iso}}(\text{parent})$ or $U_{\text{iso}}(\text{H}) = 1.5 \times U_{\text{iso}}(\text{parent})$ for methyl groups.

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Supporting Information Available: Full details of the crystal structure analyses in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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