Icosahedral palladium metallocarboranes with thiophene substituents: unexpected cage substitution products from the reaction of Pd(PMe$_2$Ph)$_2$Cl$_2$ with Tl$_2$[7-(RC$_4$H$_2$S)-7,8-*nido*-C$_2$B$_9$H$_{10}$] (R = Me or H) [1]

Despo M. Michaelidou, D. Michael P. Mingos *, David J. Williams, Andrew J.P. White

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

Abstract

Pd(PMe$_2$Ph)$_2$Cl$_2$ with Tl$_2$[7-(C$_4$H$_2$RS)-7,8-*nido*-C$_2$B$_9$H$_{10}$] (R = H or Me) gives 1-C$_4$H$_2$RS-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd-C$_2$B$_9$H$_{10}$ as the major and [1-C$_4$H$_2$RS-3,3-(PMe$_2$Ph)$_2$-8-(PMe$_2$Ph)-3,1,2-Pd-C$_2$B$_9$H$_9$][C$_4$H$_2$RS-C$_2$B$_9$H$_{12}$] as the minor product. The crystal structures of the major (R = Me) and minor products (R = H) show that both have icosahedral metallocarborane cages, but that the latter has one of the hydrogen atoms on the pentagonal face of the ligand adjacent to the metal replaced by PMe$_2$Ph.

Keywords: Metalloboranes; Palladium metalloboranes; Carboranes; Thiophene substituted metalloboranes

1. Introduction

As part of a more general study of the effect of bulky substituents on the rearrangements of metallocarboranes, some thiophene-substituted metallocarboranes of palladium and platinum were synthesised and characterised. Phenyl-substituted platinacarbaboranes, for example 1-Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pt(C$_2$B$_9$H$_{10}$) and the disubstituted compound 1,11-Ph$_2$-3,3-(PMe$_2$Ph)$_2$-3,1,11-Pt(C$_2$B$_9$H$_9$) [1], have been previously synthesised and their skeletal rearrangements investigated. The related palladium compounds 1-Ph-3-(cod)-3,1,2-Pd(C$_2$B$_9$H$_{10}$) and Pd(cod)-η^5-7,8-Me$_2$-7,8-C$_2$B$_9$H$_9$ have also been reported by other workers [2,3]. These studies established that steric effects play an important role in influencing the rearrangement barriers in these metallocarboranes. This paper describes the products from the reaction of Pd(PMe$_2$Ph)$_2$Cl$_2$ with Tl$_2$[7-(RC$_4$H$_2$S)-7,8-*nido*-C$_2$B$_9$H$_{10}$] (R = Me or H).

2. Experimental details

2.1. Synthesis and characterisation

Reactions were generally performed under N$_2$ by use of standard Schlenk techniques, although some subsequent manipulations were carried out in the open laboratory. All solvents were dried and distilled under N$_2$ prior to use. The NMR spectra were recorded on a Jeol JNM-EX270 FT spectrometer. ^{1}H, ^{11}B{^{1}H} and ^{31}P{^{1}H} chemical shifts were referenced to tetramethylsilane, BF$_3$·OEt$_2$ and H$_3$PO$_4$ respectively. Electron impact (EI) mass spectra were recorded on a VG Micromass 7070B and fast atom bombardment (FAB) mass spectra were recorded on a VG AutoSpecQ mass spectrometer using 3-nitrobenzyl alcohol matrix.

Microanalyses were performed by the departmental service. Preparative thin layer chromatography was performed using silica-coated (thickness 0.2 mm) 20 × 20 cm^2 glass plates (Merck).

2.1.1. [1-(MeC$_4$H$_2$S)-closo-1,2-C$_2$B$_{10}$H$_{11}$] 1

A solution of B$_{10}$H$_{14}$ (1.92 g, 16.0 mmol) in a mixture of acetonitrile (3 ml) and toluene (15 ml) was refluxed for 2 h. A solution of freshly-prepared 2-ethynyl-5-methylthiophene (2 g, 16.3 mmol) [4] in toluene (5 ml)

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was then added dropwise to the refluxing mixture. The resulting orange-brown mixture was refluxed for a further 21 h, after which time the solvents were removed under reduced pressure at room temperature. To the solid, MeOH (20 ml) was added and this was removed after stirring for a brief period. To the resulting brown tar, hexane was added (150 ml) and the extract was collected. The extraction was repeated twice with hexane (50 ml). The extracts were combined and the solvent was removed under reduced pressure. The crude product was sublimed at 140 °C under vacuum (1 mm Hg) to yield [1-(MeC$_4$H$_2$S)-closo-1,2-C$_2$B$_{10}$H$_{11}$] 1, as a pure white powder. Yield 1.3 g, 34%. Calculated for C$_7$H$_{16}$B$_{10}$S: 35.0% C, 6.7% H. Found for 1: 34.9% C, 6.4% H.

NMR. ^{1}H (CDCl$_3$): 6.97 (d, 1 H, MeC$_4$H$_2$S), 6.54 (d, 1 H, MeC$_4$H$_2$S), 3.78 (s, 1 H, cage C–H), 2.40 [s, 3 H, MeC$_4$H$_2$S]. ^{11}B{^{1}H}(CDCl$_3$): −1.8 (1 B), −5.2(1 B), −9.9 (4 B), −11.6 (2 B), −12.9 (2 B). Mass spectrum (EI): m/z 240 M$^+$.

2.1.2. [7-(MeC$_4$H$_2$S)-nido-7,8-C$_2$B$_9$H$_{11}$][Me$_3$NH] 2

A solution of KOH (1.06 g, 30 mmol) in dried methanol (20 ml) was added under N$_2$ to a flask containing [1-(MeC$_4$H$_2$S)-closo-1,2-C$_2$B$_{10}$H$_{11}$] (1.22 g, 5.1 mmol). The resultant solution was refluxed under N$_2$ at 80 °C for 23 h. The solvent was removed under reduced pressure, the residue was redissolved in ethanol (70 ml) and a stream of CO$_2$ (from 50 g of dry ice) was passed through the solution. The precipitated K$_2$CO$_3$ was filtered off and washed with ice-cold ethanol. The combined filtrate and washings were evaporated to dryness under reduced pressure and the residue was dissolved in distilled water, filtered through Celite (1 cm) and was then treated with an aqueous solution of [Me$_3$NH]Cl (1.5 g, 15.7 mmol). The mixture was cooled to 0 °C when a white-cream precipitate was formed which was isolated by filtration and dried in vacuum. This was shown to be [7-(MeC$_4$H$_2$S)-nido-7,8-C$_2$B$_9$H$_{11}$][Me$_3$NH] by NMR spectroscopy and mass spectrometry. Yield 1.0 g, 64%. Calculated for C$_{10}$H$_{26}$B$_9$NS: 41.5% C, 9.0% H, 4.8% N. Found for 2: 41.5% C, 8.8% H, 4.8% N.

NMR. ^{11}B{^{1}H}(CD$_3$COCD$_3$): −8.5 (1 B), −9.7 (1 B), −12.7 (1 B), −17.4 (3 B), −22.4 (1 B), −32.2 (1 B), −35.1 (1 B). Mass spectrum (negative FAB): m/z 229 M$^-$.

2.1.3. Tl$_2$[7-(MeC$_4$H$_2$S)-nido-7,8-C$_2$B$_9$H$_{10}$] 3

[7-(MeC$_4$H$_2$S)-nido-7,8-C$_2$B$_{10}$H$_{11}$][Me$_3$NH] (0.993 g, 3.43 mmol) was dissolved in a solution of KOH (0.385 g, 6.87 mmol) in H$_2$O (12 ml). An aqueous solution of thallium(I) acetate (1.81 g, 6.87 mmol in 10 ml of H$_2$O) was added dropwise under N$_2$ causing immediate formation of a yellow precipitate. The solid was isolated by filtration, washed with water, ethanol

and hexane and dried under vacuum. It was shown to be Tl$_2$[7-(MeC$_4$H$_2$S)-nido-7,8-C$_2$B$_9$H$_{10}$] by elemental analysis. Yield 2.2 g, 99%. Calculated for C$_7$H$_{15}$B$_9$STl$_2$: 13.2 C%, 2.35 H%. Found for 3: 13.1 C%, 2.1 H%.

2.1.4. Tl$_2$[7-(C$_4$H$_3$S)-nido-7,8-C$_2$B$_9$H$_{10}$] 4

[7-(C$_4$H$_3$S)-nido-7,8-C$_2$B$_9$H$_{11}$][Me$_3$NH] (1.19 g, 4.3 mmol) [5] was dissolved in a solution of KOH (0.48 g, 8.67 mmol) in H$_2$O (12 ml). An aqueous solution of thallium(I) acetate (2.28 g, 8.6 mmol in 10 ml of H$_2$O) was added dropwise under N$_2$, causing immediate formation of a yellow precipitate. The solid was isolated by filtration, washed with water, ethanol and hexane and dried under vacuum. It was shown to be Tl$_2$[7-(C$_4$H$_3$S)-nido-7,8-C$_2$B$_9$H$_{10}$] by elemental analysis. Yield 2.7 g, 99%. Calculated for C$_7$H$_{15}$B$_9$STl$_2$: 11.6 C%, 2.1 H%. Found for 4: 12.0 C%, 1.8 H%.

2.1.5. 1-C$_4$H$_3$S-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$ 5 and [1-C$_4$H$_3$S-8-PMe$_2$Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_9$] [7-C$_4$H$_3$S-nido-7,8-C$_2$B$_9$H$_{11}$] 6

To a dry mixture of Tl$_2$[7-C$_4$H$_3$S-nido-7,8-C$_2$B$_9$H$_{10}$] (0.360 g, 0.57 mmol) and [PdCl$_2$(PMe$_2$Ph)$_2$] (0.262 g, 0.57 mmol) thf (30 ml) was added at −78 °C. The reaction mixture was allowed to warm up to room temperature and was further stirred for 1.5 h. The resulting deep purple solution was filtered from a grey precipitate. Preparative TLC (CH$_2$Cl$_2$:hexane, 1:1, and then 9:1) gave three bands, a major purple band and two minor, one orange (Rf = 0.1) and one green (Rf = 0.03). The compound 1-C$_4$H$_3$S-3.3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$ was isolated from the purple band and orange crystals of [1-C$_4$H$_3$S-8-PMe$_2$Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_9$] [7-C$_4$H$_3$S-nido-7,8-C$_2$B$_9$H$_{11}$] from the second. Yield 0.07 g, 20%. Calculated for C$_{22}$H$_{35}$B$_9$P$_2$PdS: 44.2 C%, 5.9 H%. Found for 5: 44.3 C%, 5.6 H%.

NMR. ^{1}H (CDCl$_3$): 7.41–7.16 (m, 10 H, 2PMe$_2$Ph), 7.06 [dd, 1 H, J(H–H) 5.1, J(H–H) 1.3, C$_4$H$_3$S], 7.0 [dd, 1 H, J(H–H) 3.6, J(H–H) 1.3, C$_4$H$_3$S], 6.89 (dd, 1 H, J(H–H) 5.3, J(H–H) 3.6, C$_4$H$_3$S), 3.21 (s, 1 H, cage C–H), 1.48 [d, 6 H, J(H–^{31}P) 10.2, 2PMe$_2$Ph], 1.30 [d, 6 H, J(H–^{31}P) 9.9, 2PMe$_2$Ph]; ^{1}H (CD$_2$Cl$_2$): 7.45–7.16 (m, 10 H, 2PMe$_2$Ph), 7.10 [dd, 1 H, J(H–H) 5.1, J(H–H) 1.3, C$_4$H$_3$S], 6.99 [dd, 1 H, J(H–H) 3.6, J(H–H) 1.3, C$_4$H$_3$S], 6.91 [dd, 1 H, J(H–H) 5.3, J(H–H) 3.6, C$_4$H$_3$S], 3.18 (s, 1 H, cage C–H), 1.47 [d, 6 H, J(H–^{31}P) 10.2, 2PMe$_2$Ph], 1.31 [d, 6 H, J(H–^{31}P) 10.2, 2PMe$_2$Ph]. ^{11}B{^{1}H} (CD$_2$Cl$_2$): 9.0, −2.7, −6.2, −8.9, −14.5, −17.0. ^{11}B: doublets J = 125–154 Hz, ^{31}P{^{1}H} (CD$_2$Cl$_2$): −3.2 (vbs). Mass spectrum (FAB): m/z 597 cation.

NMR for 6. ^{1}H (CD$_2$Cl$_2$): 6.8–7.8 (multiplets, 3 Ph and 2C$_4$H$_3$S), 3.24 (s, 1 H, cage C–H), 1.89 [d, 6 H, J(H–^{31}P) 11.5, PMe$_2$Ph], 1.52 [d, 3 H, J(H–^{31}P) 9.9,

PMe$_2$Ph], 1.23 [d, 3 H, J(H–^{31}P) 10.2, PMe$_2$Ph], 1.18 [d, 3 H, J(H–^{31}P) 9.9, PMe$_2$Ph], 0.73 [d, 3 H, J(H–^{31}P) 10.2, PMe$_2$Ph]. ^{11}B{^{1}H} (CD$_2$Cl$_2$): 6.6 [d, J(^{11}B–^{31}P) 143], −4.8, −7.5, −9.2, −10.6, −13.2, −17.8, −23.0, −32.9, −35.9. ^{31}P{^{1}H} (CD$_2$Cl$_2$): 2.2 (d, J 62), −6.5 (d, J 63), −7.8 [quartet, J(^{31}P–^{11}B) 142]. Mass spectrum (positive ion FAB) 734 M$^+$.

2.1.6. 1-MeC$_4$H$_2$S-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$ 7 and [1-MeC$_4$H$_2$S-8-PMe$_2$Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_9$] [7-MeC$_4$H$_2$S-nido-7,8-C$_2$B$_9$H$_{11}$] 8

To a dry mixture of Tl$_2$[7-MeC$_4$H$_2$S-nido-7,8-C$_2$B$_9$H$_{10}$] (0.349 g, 0.55 mmol) and [PdCl$_2$(PMe$_2$Ph)$_2$] (0.247 g, 0.55 mmol) CH$_2$Cl$_2$ (30 ml) was added at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred further for 1.5 h. The resulting deep red solution was filtered from a grey precipitate. Preparative TLC (CH$_2$Cl$_2$:hexane, 1:1, and then 9:1) gave three bands, a major purple band (Rf = 0.8) and two minor, one orange (Rf = 0.27) and one green (Rf = 0.11). The compound 1-MeC$_4$H$_2$S-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$ was isolated from the purple band. Yield: 0.063 g, 19%. Calculated for C$_{23}$H$_{37}$B$_9$P$_2$PdS: 45.2 C%, 6.1 H%. Found for 7: 45.0 C%, 5.6 H%.

^{1}H (CD$_2$Cl$_2$): 7.18–7.46, (m, 10 H, 2PMe$_2$Ph), 6.77 [d, 1 H, J(H–H) 3.62], 6.56 (m, 1 H), 3.20 (s, 1 H, cage C–H), 2.46 (s, 3 H, MeC$_4$H$_2$S), 1.48 [d, 6 H, J(H–^{31}P) 9.9, 2PMe$_2$Ph], 1.32 [d, 6 H, J(H–^{31}P) 10.2, 2PMe$_2$Ph], ^{11}B{^{1}H} (CD$_2$Cl$_2$): 9.1, −3.4, −6.4, −9.1, −15.1, −17.0. ^{11}B: doublets J = 122–149 Hz. ^{31}P{^{1}H} (CD$_2$Cl$_2$): −3.2 (vbs). Mass spectrum (FAB): m/z 610 M$^+$.

NMR for 8. ^{1}H (CD$_2$Cl$_2$): 6.5–7.5 (multiplets, 3 Ph and 2C$_4$H$_3$S), 3.52 (s, 1 H, cage C–H), 2.43 (s, 3 H, MeC$_4$H$_2$S), 2.30 (s, 3 H, MeC$_4$H$_2$S) 1.86 [d, 6 H, J(H–^{31}P) 11.9, PMe$_2$Ph], 1.53 [d, 3 H, J(H–^{31}P) 10.6, PMe$_2$Ph], 1.23 [d, 3 H, J(H–^{31}P) 5.9, PMe$_2$Ph], 1.19 [d, 3 H, J(H–^{31}P) 5.9, PMe$_2$Ph], 0.80 [d, 3 H, J(H–^{31}P) 10.6, PMe$_2$Ph], ^{11}B{^{1}H} (CD$_2$Cl$_2$): 6.4 [d, J(^{11}B–^{31}P) 143], −5.0, −8.0, −9.4, −10.7, −13.4, −18.1, −23.1, −33.0, −36.0. ^{11}B: doublets J = 108–155 Hz. ^{31}P{^{1}H} (CD$_2$Cl$_2$): 0.6 (d, J 66), −6.9 (d, J 68), −7.8 [quartet, J(^{31}P–^{11}B) 142]. Mass spectrum (positive ion FAB): m/z 747 cation; (negative ion FAB): m/z 230 anion.

2.2. Crystallographic studies

2.2.1. Crystal structure determinations for 6

2.2.1.1. Crystal data for complex 6. C$_{30}$H$_{45}$B$_9$P$_3$SPd · C$_6$H$_{13}$B$_9$S, M = 948.8, orthorhombic, space group Pbca, a = 16.127(6), b = 18.557(2), c = 32.751(5) Å, V = 9801(4) Å^3, Z = 8, D$_c$ = 1.29 g cm^{-3}, μ(Mo Kα)

= 5.9 cm^{-1}, F(000) = 3896. A thin orange-red plate of dimensions 0.67 × 0.57 × 0.03 mm^3 was used.

2.2.1.2. Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. 6391 indepenedent reflections were measured (2θ ≤ 50°) of which 4068 had |F$_o$| > 4σ(|F$_o$|) and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and a semi-empirical absorption correction (based on ψ-scans) was applied; the maximum and minimum transmission factors were 0.827 and 0.741 respectively.

2.2.1.3. Structure analysis and refinement. The structure was solved by direct methods. All the major occupancy non-hydrogen atoms were refined anisotropically, the phenyl rings being treated as optimised rigid bodies. There was found to be disorder in: (i) the thiophene ring of the coordinated boron cage (65:35); (ii) the phenyl ring of the carborane-bound dimethylphenylphosphine (75:25); (iii) the boron cage of the non-coordinated thiophene-substituted carborane (60:40). In each case, two partial occupancy orientations were identified. The positions of the hydrogen atoms were idealised, assigned isotropic thermal parameters, [U(H) = 1.2U$_{eq}$(C/B); U(H) = 1.5U$_{eq}$(C–Me)], and allowed to ride on their parent atoms. Refinement was by full matrix least squares based on F^2 to give R$_1$ = 0.060, wR$_2$ = 0.134 for the observed data and 568 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.68 e Å^{-3} and −0.37 e Å^{-3} respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.003 and −0.051 respectively.

2.2.2. Crystal structure determinations for 7

2.2.2.1. Crystal data for complex 7. C$_{23}$H$_{37}$B$_9$P$_2$SPd, M = 611.2, monoclinic, space group P2$_1$/n, a = 15.180(6), b = 10.283(4), c = 19.564(7) Å, β = 105.05(3)°, V = 2949(2) Å^3, Z = 4, D$_c$ = 1.38 g cm^{-3}, μ(Cu Kα) = 68.4 cm^{-1}, F(000) = 1248. A deep-red block of dimensions 0.24 × 0.13 × 0.03 mm^3 was used.

2.2.2.2. Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Cu Kα radiation (graphite monochromator) using ω-scans. 4379 independent reflections were measured (2θ ≤ 120°) of which 3390 had |F$_o$| > 4σ(|F$_o$|) and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and a Gaussian absorption correction (face-indexed numerical) was applied; the maximum and minimum transmission factors were 0.797 and 0.421 respectively.

2.2.2.3. Structure analysis and refinement. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically, the phenyl rings being treated as optimised rigid bodies. The positions of the hydrogen atoms were located from subsequent ΔF maps, idealised, assigned isotropic thermal parameters, $[U(\text{H}) = 1.2U_{eq}(\text{C}/\text{B})$; $U(\text{H}) = 1.5U_{eq}(\text{C–Me})]$, and allowed to ride on their parent atoms. Refinement was by full matrix least squares based on F^2 to give $R_1 = 0.055$, $wR_2 = 0.129$ for the observed data and 298 parameters. The maximum and minimum residual electron densities in the final ΔF map were $0.89\,e\,\text{Å}^{-3}$ and $-1.11\,e\,\text{Å}^{-3}$ respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and -0.002 respectively.

For both structures, computations were carried out on 50 MHz 486 PC computers using the SHELXTL PC Program system [6]. Additional material available from the Cambridge Crystallographic Data Centre comprises fractional atomic coordinates, H-atom coordinates, thermal parameters and remaining bond lengths and angles.

3. Results and discussion

3.1. Synthesis and characterization

The salt $[\text{Me}_3\text{NH}][7\text{-}(\text{C}_4\text{H}_3\text{S})\text{-}nido\text{-}7,8\text{-}\text{C}_2\text{B}_9\text{H}_{11}]$ was converted into $\text{Tl}_2[7\text{-}(\text{C}_4\text{H}_3\text{S})\text{-}nido\text{-}7,8\text{-}\text{C}_2\text{B}_9\text{H}_{10}]$ by a well established method [7] and characterised by NMR and analyses. The reaction of $\text{Tl}_2[7\text{-}(\text{C}_4\text{H}_3\text{S})\text{-}nido\text{-}7,8\text{-}\text{C}_2\text{B}_9\text{H}_{10}]$ and $[\text{PdCl}_2(\text{PMe}_2\text{Ph})_2]$ gave the expected icosahedral metallocarborane product $1\text{-}\text{C}_4\text{H}_3\text{S}\text{-}3,3\text{-}(\text{PMe}_2\text{Ph})_2\text{-}3,1,2\text{-}\text{Pd}\text{-}\text{C}_2\text{B}_9\text{H}_{10}$ **5** in 20% yield after a TLC purification stage. Two other bands (orange and green) were separated on the TLC plates, and of these, the orange one was isolable and identified as $[1\text{-}\text{C}_4\text{H}_3\text{S}\text{-}8\text{-}\text{PMe}_2\text{Ph}\text{-}3,3\text{-}(\text{PMe}_2\text{Ph})_2\text{-}3,1,2\text{-}\text{Pd}\text{-}\text{C}_2\text{B}_9\text{H}_9]$ $[7\text{-}\text{C}_4\text{H}_3\text{S}\text{-}nido\text{-}7,8\text{-}\text{C}_2\text{B}_9\text{H}_{11}]$ **6** in very low yield (less than 2%). The spectroscopic data discussed below has shown that this compound also has a related icosahedral metallocarborane cage, but with one of the hydrogen substituents replaced by a phosphine.

Compound **5** was characterised by ^1H, ^{11}B, $^{31}\text{P}\{^1\text{H}\}$ NMR studies, mass spectral and elemental analyses. In the ^1H NMR spectrum of **5** the phenyl protons appear as a multiplet between 7.45 and 7.16 ppm. In the ^1H NMR spectrum the thiophene protons appear as three distinguishable doublets of doublets at 7.10, 6.99 and 6.91 ppm and the cage CH proton resonates at 3.18 ppm. Two doublets appear in the methyl region at 1.47 and 1.31 ppm which are assigned to the Me groups of the phosphine ligands. In the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum there are six peaks. All resonances show the expected doublet coupling ($^1J_{BH} = 120\text{–}150\,\text{Hz}$) in the ^{11}B NMR spectrum. The low field signal in the $^{11}\text{B}\{^1\text{H}\}$ is assigned to

the boron atom β to the carbons of the ligating $\overline{\text{CCBBB}}$ ring. This deshielding is considered diagnostic for structures in which there is a degree of distortion resulting from 'slippage' of the metal centre across the pentagonal C_2B_3 face away from the two atoms and towards the β boron atom [3]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a single very broad signal, and the FAB mass spectrum showed a highest mass peak corresponding to M^+ at 597.

Compound **6** was also characterised by NMR spectroscopy, FAB mass spectrometry and a single crystal X-ray structural analysis. The ^1H NMR spectrum of **6** in CD_2Cl_2 NMR shows several multiplets assigned to the phenyl and thiophene protons between $\delta = 6.8$ and 7.8 ppm. In the aliphatic region, five doublets are seen in the ratio 2:1:1:1:1, indicative of three PPhMe_2 groups in total. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two doublets ($\delta = 2.2$, $J = 62\,\text{Hz}$; $\delta = -6.5$, $J = 63\,\text{Hz}$) and one quartet ($\delta = -7.8$, $J = 142\,\text{Hz}$), which are assigned to two P atoms coupling to each other in the $\text{PhMe}_2\text{P–Pd–PMe}_2\text{Ph}$ moiety, and one P coupled to an ^{11}B nucleus (spin = 3/2). This assignment was confirmed by the crystal structure described below. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows at least ten distinct peaks, which were not sufficiently well resolved for accurate integration. A distinct doublet ($J = 143\,\text{Hz}$) was observed at 6.6 ppm. In the coupled spectrum, all the peaks except that doublet were split into doublets, thus indicating B–H groups, while the 6.6 ppm doublet not bearing an H is assigned as the B–P boron. The
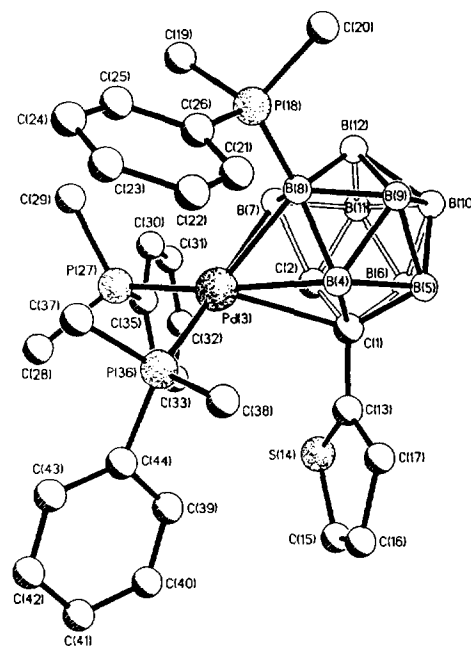

Fig. 1. The molecular structure of the cation in the salt **6**, $[1\text{-}\text{C}_4\text{H}_3\text{S}\text{-}8\text{-}\text{PMe}_2\text{Ph}\text{-}3,3\text{-}(\text{PMe}_2\text{Ph})_2\text{-}3,1,2\text{-}\text{Pd}\text{-}\text{C}_2\text{B}_9\text{H}_9][7\text{-}\text{C}_4\text{H}_3\text{S}\text{-}nido\text{-}7,8\text{-}\text{C}_2\text{B}_9\text{H}_{11}]$. For reasons of clarity the hydrogen atoms have been omitted.

Table 1
Selected bond lengths (Å) and angles (deg) for **6**

C(1)–C(13)	1.46(2)	C(1)–C(2)	1.520(11)
C(1)–B(4)	1.777(12)	C(1)–Pd(3)	2.562(7)
C(2)–B(7)	1.730(12)	C(2)–Pd(3)	2.506(7)
Pd(3)–B(7)	2.270(9)	Pd(3)–B(4)	2.290(9)
Pd(3)–B(8)	2.298(9)	Pd(3)–P(27)	2.299(2)
Pd(3)–P(36)	2.305(2)	B(4)–B(8)	1.791(14)
B(7)–B(8)	1.776(13)	B(8)–P(18)	1.927(10)
C(2)–C(1)–B(4)	109.1(6)	C(1)–C(2)–B(7)	113.2(6)
B(7)–Pd(3)–P(27)	92.2(3)	B(4)–Pd(3)–P(27)	166.4(3)
B(8)–Pd(3)–P(27)	127.2(3)	B(7)–Pd(3)–P(36)	168.3(2)
B(4)–Pd(3)–P(36)	98.2(3)	B(8)–Pd(3)–P(36)	122.9(2)
P(27)–Pd(3)–P(36)	95.00(7)	P(27)–Pd(3)–C(2)	99.2(2)
P(36)–Pd(3)–C(2)	144.5(2)	P(27)–Pd(3)–C(1)	128.0(2)
P(36)–Pd(3)–C(1)	113.7(2)	C(1)–B(4)–B(8)	107.0(7)
C(2)–B(7)–B(8)	107.0(7)	B(7)–B(8)–B(4)	102.6(7)

compound showed no EI mass spectrum, but a positive FAB mass spectrum was obtained and shows a highest mass peak at 734, $\equiv$ [1-C$_4$H$_3$S-8-PMe$_2$Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_9$]$^+$.

The crystal structure of **6** is illustrated in Fig. 1, and Table 1 lists selected bond lengths and angles. The compound is a salt [1-C$_4$H$_3$S-8-PMe$_2$Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_9$][7-C$_4$H$_3$S-*nido*-7,8-C$_2$B$_9$H$_{11}$]. The cation [1-C$_4$H$_3$S-8-PMe$_2$Ph-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_9$]$^+$ has a *closo*-icosahedral palladacarborane cage with the carbon atoms of the cage part of the face which is bonded to the metal atom. The cation is unusual since it has a PPhMe$_2$ group attached to one of the atoms of the coordinated face of the boron cage. The presence of such a grouping was indicated by the ^{11}B and ^{31}P NMR spectroscopic data discussed above. This PPhMe$_2$ group is positioned on a site two removed from the thiophene substituent; this is probably due to steric factors. In the cation the thiophene ring adopts two orientations of 65% and 35% relative occupancy which are related to each other by an approximate 180° rotation about the C(1)–C(13) bond. There is also disorder (60:40) in the uncoordinated anion [7-C$_4$H$_3$S-*nido*-7,8-C$_2$B$_9$H$_{11}$]$^-$ which takes the form of an approximate 100° rotation about a vector virtually coincident with the C (cage)–C(thiophene) bond. This disorder precludes detailed discussion of the bond lengths of the cages and of the thiophene substituents. In the cation the Pd atom attached to the nido-cage exhibits a slip factor of $\Delta = 0.31$ Å, a value very similar to that observed (0.33 Å) in the neutral compound [1-MeC$_4$H$_2$S-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$] discussed below.

It was not possible to obtain suitable crystals for a structural analysis of the main product **5**. Therefore, a similar sequence of reactions to that described above was repeated using the Me-substituted thiophene. The synthetic details for the preparation of the methyl substi-

tuted derivatives **7** and **8** are described in Section 2.1.6. Three bands were also observed on the separation of the reaction mixture on the TLC plates. The purple (major) band and orange (low yield) band were isolated to yield **7** and **8** respectively; these were found to be analogous to **5** and **6** above on the basis of spectroscopic data. Compound **7** was suitable for a single-crystal structural determination.

The crystal structure of **7** is shown in Fig. 2, and Table 2 lists selected bond lengths and angles. The compound **7**, [1-MeC$_4$H$_2$S-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$], has a structure based on a distorted closo-icosahedral palladacarborane cage. The Pd(PMe$_2$Ph)$_2$ fragment is bonded to the C$_2$B$_3$ face of the cage. In common with the majority of L$_2$MC$_2$B$_9$H$_{11}$ cage com-
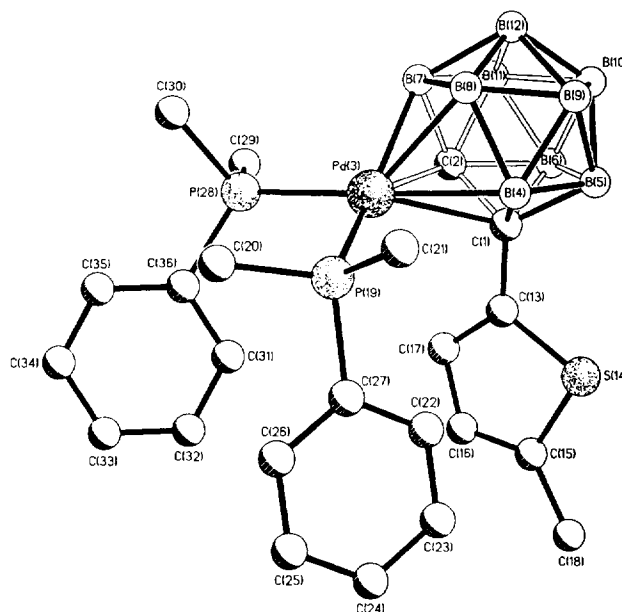

Fig. 2. The molecular structure of **7**, [1-MeC$_4$H$_2$S-3,3-(PMe$_2$Ph)$_2$-3,1,2-Pd–C$_2$B$_9$H$_{10}$]. For reasons of clarity the hydrogen atoms have been omitted.

Table 2
Selected bond lengths (Å) and angles (deg) for 7

C(1)–C(13)	1.478(10)	C(1)–C(2)	1.536(10)
C(1)–B(4)	1.764(11)	C(1)–Pd(3)	2.634(7)
C(2)–B(7)	1.746(11)	C(2)–Pd(3)	2.461(7)
Pd(3)–B(7)	2.277(9)	Pd(3)–B(8)	2.282(8)
Pd(3)–P(19)	2.293(2)	Pd(3)–P(28)	2.302(2)
Pd(3)–B(4)	2.303(8)	B(4)–B(8)	1.812(12)
B(7)–B(8)	1.785(13)		
C(2)–C(1)–B(4)	105.2(6)	C(1)–C(2)–B(7)	116.7(6)
B(7)–Pd(3)–P(19)	154.5(2)	B(8)–Pd(3)–P(19)	110.8(2)
B(7)–Pd(3)–P(28)	97.1(2)	B(8)–Pd(3)–P(28)	133.1(2)
P(19)–Pd(3)–P(28)	94.96(8)	P(19)–Pd(3)–B(4)	96.1(2)
P(28)–Pd(3)–B(4)	167.6(2)	P(19)–Pd(3)–C(2)	153.9(2)
P(28)–Pd(3)–C(2)	100.9(2)	P(19)–Pd(3)–C(1)	119.7(2)
P(28)–Pd(3)–C(1)	127.2(2)	C(1)–B(4)–B(8)	110.0(6)
C(2)–B(7)–B(8)	105.3(6)	B(7)–B(8)–B(4)	101.8(6)

pounds previously studied, the structure exhibits a slip distortion with the palladium atom moving relative to the C_2B_3 face.

The crystal structures of the cation 6 and neutral 7 demonstrate that the metallocarborane cages in both species have very similar dimensions. Thus, the average B–Pd distance is almost identical in the two compounds (2.286–2.287 Å), and the slip distortion parameters are also very similar (0.33 Å in 6, 0.31 Å in 7). The previously defined parameters which define the extent to which the C_2B_3 face is folded are also very similar: 6, $\theta = 4.4°$, $\phi = 6.1°$; $\chi = 19.6°$; 7, $\theta = 2.7°$, $\phi = 5.4°$, $\chi = 16.8°$.

The thiophenyl ligand in the carborane cage is essentially unaffected by the change from 6 to 7, and the average Pd–P distance is nearly identical in the two compounds, as are the P–Pd–P angle and the angles subtended by the Ph and two methyl groups at P.

In 6, the cage boron–PMe_2Ph distance of 1.93(1) Å falls within the range of 1.91–1.97 Å previously reported for compounds of this type. The average Pd–B distance of 2.29 Å is almost identical to that in the similar 11-vertex $nido$-$TeB_{10}H_9$ clusters such as [2-(CO)-2-(PPh_3)-$closo$-2,1-$PdTeB_{10}H_9$(PPh_3)][BF_4] [8].

3.2. Summary

The reactions of $Pd(PMe_2Ph)_2Cl_2$ with Tl_2[7-(RC_4H_2S)-7,8-$nido$-$C_2B_9H_{10}$] (R = Me or H) have led to the isolation of the neutral icosahedral metallocarboranes, 5 and 7, in good yields, and as minor products the salts 6 and 8, which resulted from the replacement of a cage hydrogen by the phosphine. The salts 6 and 8 obtained in this manner were unexpected, but they are not without precedent. Phosphine-substituted metalloborane cages have been noted in the icosahedral nickel compound [$closo$-3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{10}$]$_2$ [9], and tellurium-substituted cage compounds [2-(CO)-2-(PPh_3)-$closo$-2,1-$PdTeB_{10}H_9$(PPh_3)][BF_4] [8], [2-

(O_2CMe)-2,11-(PPh_3)$_2$-$closo$-2,1-$PdTeB_{10}H_9$] [10] and [2,2-(PMe_3)$_2$-7-PPh_3-$closo$-2,1-$PdTeB_{10}H_9$][11]. Other examples have been reported for the arsenic-substituted cage [3-Cl-3,8-(PPh_3)$_2$-$closo$-3,1,2-$PdAs_2B_9H_8$] [12] and larger cages such as [(PMe_2Ph){$PtB_{16}H_{18}$-(PMe_2Ph)}] [13]. Examples of the smaller metalloboranes such as 1-Br-1,5-(PPh_3)$_2$-1,2,3-$Ni(Et_2C_2B_4H_3$) [14] which contain a PPh_3 group on the ligand have been described. Grimes and coworkers [14], and also Hawthorne and coworkers [9] have argued in the case of the nickel compounds that they are formed by initial ligand dissociation from the metal atom, followed by phosphine attack on a B–H vertex. These workers synthesised their compounds in relatively high yields by heating the Ni–PPh_3 precursors. In the synthesis of 6 and 8, the cage-substituted phosphines were formed during the syntheses of the M–PPh_2Me 'precursor' compounds in very low yield. Heating of 5 and 7 did not give the rearranged products in significant yields and only thermal decomposition products were observed.

Acknowledgements

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