An Alternative Route to Cationic Metallaheteroboranes

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The reaction between [2-I-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] and excess of phosphine (PR_3 = PMe_3 or PMe_2Ph) afforded air-stable cationic palladatelluraboranes [2,2-$(PR_3)_2$-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]I **1** (PR_3 = PMe_3) or **2** (PR_3 = PMe_2Ph) which were characterised spectroscopically (IR and ^{11}B NMR) and by an X-ray diffraction study of **1**.

In general, the overwhelming majority of metalla-borane and -heteroborane clusters are either anionic or neutral species. Stable cationic borane-based clusters are very rare and are consequently of interest.[1,2] We recently described the synthesis of a series of air-stable cationic palladatelluraboranes formed by the displacement of the water molecule in [2-(H_2O)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]$[BF_4]$.[2] Here we present an alternative approach which may be more generally applicable to metallaborane cluster compounds containing metal–halogen bonds.

It is well known that the addition of phosphines (PR'_3) to palladium complexes such as $[PdX_2(PR_3)_2]$ or $[PdX(PR_3)(\eta^5\text{-}C_5H_5)]$ (X = halide) may cause the substitution of either halide[3] or phosphine[4] ligands. The displacement of a halide ligand affords a cationic palladium product. A particular example of this type of reaction which is of relevance to the present work is shown in equation (1).[5]

$$[PdBr(PEt_3)(\eta^5\text{-}C_5H_5)] + PEt_3 \longrightarrow [Pd(PEt_3)_2(\eta^5\text{-}C_5H_5)]Br \qquad (1)$$

We now report that cationic palladium bis(phosphine) complexes [2,2-$(PR_3)_2$-2,1-*closo*-$PdTeB_{10}H_9(PPh_3)$]I **1** (PR_3 = PMe_3) or **2** (PR_3 = PMe_2Ph) can be synthesised from [2-I-2-(PPh_3)-2,1-*closo*-$PdTeB_{10}H_9(PPh_3)$] **3**[2] in moderately low yield ($\approx$35%) according to equation (2).† The parallel feature

$$3 \xrightarrow{\text{excess } PR_3} [2,2\text{-}(PR_3)_2\text{-}2,1\text{-}closo\text{-}PdTeB_{10}H_9(PPh_3)]I + PPh_3 \qquad (2)$$

between this reaction and the reaction of equation (1) is that the C_5H_5 and $TeB_{10}H_9(PR_3)$ ligands are both five-electron η^5 donors. The reactions were carried out in solution in refluxing toluene in the presence of an excess of phosphine. The orange products were isolated either by filtering the reaction mixture (for compound **1**) or by preparative thin-layer chromatography (TLC) (for compound **2**). Compounds **1** and **2** were recrystallised from CH_2Cl_2–heptane solution and are formulated as [2,2-$(PMe_3)_2$-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]I and [2,2-$(PMe_2Ph)_2$-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]I respectively. A second product was identified from the reaction with PMe_3, namely [2-I-2-(PMe_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] **4**.†

Both **1** and **2** are indefinitely air- and moisture-stable in the solid state. Complex **1** is reasonably stable in solution and crystals suitable for an X-ray diffraction study were grown by the slow diffusion of toluene into a dichloromethane solution of **1**. In contrast, dissolution of **2** in tetrahydrofuran (thf) resulted in conversion into the green iodopalladium compound [2-I-2-(PMe_2Ph)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] **5** on standing at ambient temperature for 30 min (63.4% yield). The latter was characterised by C and H elemental analysis, and by infrared and ^{11}B NMR spectroscopy. The ^{11}B NMR chemical shift

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† [2,2-$(PMe_3)_2$-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]I **1**. A 1.0 mol dm^{-3} solution of trimethylphosphine in toluene (0.416 cm^3, 0.416 mmol) was added to a solution of **3** (0.105 g, 0.104 mmol) in toluene (25 cm^3). The solution was refluxed for 30 min and then allowed to cool. An orange precipitate was filtered off from the green solution. The solution was concentrated under reduced pressure to give a green solid. The orange precipitate was recrystallised from CH_2Cl_2–heptane (3:2) to give orange crystals of [2,2-$(PMe_3)_2$-*closo*-2.1-$PdTeB_{10}H_9(PPh_3)$]I·1.5 CH_2Cl_2 **1**·1.5CH_2Cl_2 (0.038 g, 35.4%) (Found: C, 29.65; H, 4.70. $C_{25.5}H_{45}B_{10}Cl_3IP_3PdTe$ requires C, 30.00; H, 4.25%). IR: ν_{max} 2601m(sh), 2551vs, 2545vs, 2509vs, 2501vs, 2488vs (BH) cm^{-1}. NMR (CD_3CN, 294–303 K) in order tentative assignment then $\delta(^{11}B)$ $[\delta(^1H)]$: BH(12) +17.0[+5.14], BH(7/11) +9.0[+3.75], BH(9) *ca.* +6.2[+4.86], B(11/7) +5.8[P-substituted, $^1J(^{31}P-^{11}B)$ 118 ± 16 Hz], BH(3) and BH(6) *ca.* +5.4[+2.63] and −6.6(+1.54), BH(4) and BH(5) *ca.* −10.6[+3.08] and *ca.* −11.5[+3.29], BH(8) and BH(10) −18.7[+2.12] and −20.2[+1.78]; additional ^1H data: δ +1.78 $[^2J(^{31}P-^1H)$ 11] and +1.13 $[^2J(^{31}P-^1H)$ 10 Hz] (PMe); ^{31}P (−40 °C, CD_3CN), $\delta(^{31}P_A)$ −12.3 [sp (sharp)], $\delta(^{31}P_B)$ −18.9 (sp) and $\delta(^{31}P_C)$ *ca.* +10 [br (broad)]; $^2J(^{31}P_A-^{31}P_B)$ *ca.* 47, $^2J(^{31}P_B-^{31}P_C)$ *ca.* 7, $^2J(^{31}P_A-^{31}P_C)$ *ca.* 0 Hz. The green solid was recrystallised twice from CH_2Cl_2–heptane (1:3) to give green crystals of [2-I-2-(PMe_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] **4** (0.022 g, 26.1%) (Found: C, 30.70; H, 4.05. $C_{21}H_{33}B_{10}IP_2PdTe$ requires C, 30.90; H, 4.05%). IR: ν_{max} 2576s(sh), 2543vs, 2504vs, 2486s(sh) (BH) cm^{-1}. ^{11}B-$\{^1H\}$ NMR (CH_2Cl_2, 298 K): δ (multiplicity, intensity), +16.0 (s, 1 B), +10.3 [d, 1 B, $J(^{11}B-^{31}P)$ 135 ± 5 Hz] + 8.4 (s, 1 B), +2.0 (s, 2 B), *ca.* −8.2 (s, 1 B), −11.5 (s, 2 B), −19.7 (s, 1 B), −22.6 (s, 1 B).

[2,2-$(PMe_2Ph)_2$-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]I **2**. Dimethylphenylphosphine (0.156 cm^3, 1.10 mmol) was added to a solution of **3** (0.100 g, 0.094 mmol) in toluene (30 cm^3). The solution was refluxed for 5.5 d. It was concentrated under reduced pressure and twice subjected to preparative TLC (100% CH_2Cl_2). A single major band was extracted into CH_2Cl_2 and recrystallised from CH_2Cl_2–heptane (3:2) to give orange needle crystals of **2** (0.039 g, 33.8%) (Found: C, 39.60; H, 4.45. $C_{34}H_{46}B_{10}IP_3PdTe$ requires C, 40.15; H, 4.55%). IR: ν_{max} 2553vs (BH) cm^{-1}. NMR (CD_3CN, 294–303 K), tentative assignment, $\delta(^{11}B)$ $[\delta(^1H)]$: BH(12) +16.8[+5.12], BH(7/11) +9.4[+3.93], BH(9) *ca.* + 6.5[+4.85], B(11/7) +5.9 [P-substituted, $^1J(^{31}P-^{11}B)$ 111 ± 16 Hz], BH(3) and BH(6) *ca.* +4.9[+2.79] and −6.2[+1.67], BH(4) and BH(5) *ca.* −10.0[+3.04] and *ca.* −11.8[+3.29], BH(8) and BH(10) −18.7[+2.18] and −19.8[+1.83]; additional ^1H data: δ + 0.80 $[^2J(^{31}P-^1H)$ 11], 0.91 $[^2J(^{31}P-^1H)$ 10] (PMe), +1.65 $[^2J(^{31}P-^1H)$ *ca.* 10] and +1.74 $[^2J(^{31}P-^1H)$ *ca.* 9.5 Hz]; ^{31}P (−50 °C, CD_2Cl_2–Me_2CO), $\delta(^{31}P_A)$ and $\delta(^{31}P_B)$ −8.8 (sp)(accidental coincidence), $\delta(^{31}P_C)$ *ca.* +10.2(br), $^2J(^{31}P-^{31}P)$ not observed due to resonance coincidence in this solvent.

[2-I-2-(PMe_2Ph)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$] **5**. A sample of **2** (0.030 g, 0.030 mmol) was dissolved in thf (30 cm^3). The solution was stirred for 30 min during which time it changed from orange to green. The solution was concentrated under reduced pressure and subjected to preparative TLC (CH_2Cl_2–heptane, 7:3). The single major band was extracted into CH_2Cl_2 and recrystallised from CH_2Cl_2–heptane (2:1) to give green blocks of **5** (0.018 g, 63.4%) (Found: C, 36.10; H, 4.10. $C_{26}H_{35}B_{10}IP_2PdTe$ requires C, 35.55; H, 4.00%). IR: ν_{max} 2532vs, 2470m(sh) (BH) cm^{-1}. ^{11}B-$\{^1H\}$ NMR (CH_2Cl_2, 298 K): δ (multiplicity, intensity), +17.6 (s, 1 B), +11.0 (s, 1 B), +10.3 [d, 1 B, $J(^{11}B-^{31}P)$ 128 ± 5 Hz], +3.9 (s, 2 B), −7.9 (s, 1 B), −10.6 (s, 2 B), −19.7 (s, 1 B), −21.8 (s, 1 B).

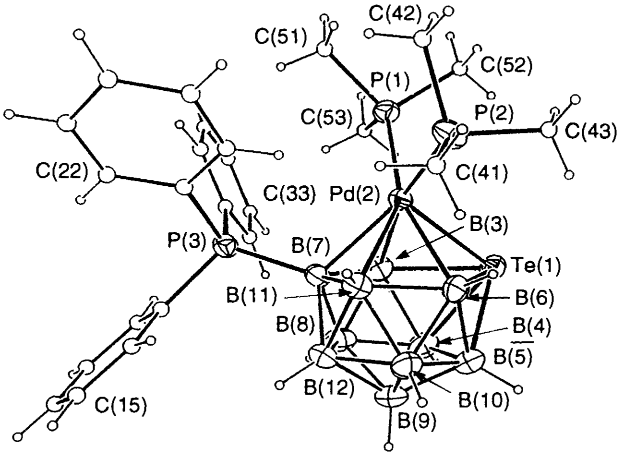

Fig. 1 An ORTEP[10] view of the cation in **1** showing the atom numbering scheme and Pd, Te, P and B atoms depicted with thermal elipsoids drawn at the 50% probability level. For clarity, the carbon and hydrogen atoms are drawn as small spheres of an arbitrary size. Selected interatomic distances (Å) and angles (°): Pd(2)–Te(1) 2.6840(5), Pd(2)–B(3) 2.305(5), Pd(2)–B(6) 2.289(6), Pd(2)–B(7) 2.298(5), Pd(2)–B(11) 2.251(5), Te(1)–B(3) 2.398(6), Te(1)–B(4) 2.278(6), Te(1)–B(5) 2.323(6), Te(1)–B(6) 2.394(6), B–B distances range from 1.739(9) for B(5)–B(9) to 1.936(8) for B(3)–B(4), B(7)–P(3) 1.961(5), Pd(2)–P(1) 2.3640(13), Pd(2)–P(2) 2.3285(13); P(1)–Pd(2)–P(2) 93.35(5), Te(1)–Pd(2)–P(1) 105.52(4), Te(1)–Pd(2)–P(2) 111.31(4), Te(1)–Pd(2)–B(3) 56.84(15), Te(1)–Pd(2)–B(6) 56.90(16), B(3)–Pd(2)–B(7) 46.27(21), B(6)–Pd(2)–B(11) 48.64(20), B(7)–Pd(2)–B(11) 46.09(20), B(3)–Te(1)–B(6) 80.31(19), Pd(2)–Te(1)–B(3) 53.59(13), Pd(2)–Te(1)–B(6) 53.22(13), B(3)–Te(1)–B(4) 48.83(20), B(4)–Te(1)–B(5) 48.41(24), B(5)–Te(1)–B(6) 46.14(21), Pd(2)–B(7)–P(3) 118.33(24)

sequence and relative intensity pattern for compound **5** were very similar to those for **3**[2] and **4**.†

The structure of **1** was confirmed by X-ray crystallography.‡ The gross $PdTeB_{10}$-cage geometry in **1** is that of a distorted icosahedron, with palladium and tellurium atoms in adjacent positions (Fig. 1). The cage molecular structure is closely similar to both (*a*) neutral compounds such as $[2,2\text{-}(PMe_2Ph)_2\text{-}closo\text{-}2,1\text{-}PdTeB_{10}H_{10}]$ **6** and $[2\text{-}(O_2CMe)\text{-}2\text{-}(PPh_3)\text{-}closo\text{-}2,1\text{-}PdTeB_{10}H_9(PPh_3)]$ **7**,[11] and (*b*) the cationic complexes $[2\text{-}(L)\text{-}2\text{-}(PPh_3)\text{-}closo\text{-}2,1\text{-}PdTeB_{10}H_9(PPh_3)][BF_4]$ (where L = H_2O **8** or CO **9**).[2] The Pd–Te distance in the cation of **1**, 2.6840(5) Å, is almost exactly the same as that in the neutral palladium bis(phosphine) compound **6**, 2.6833(2) Å, and these Pd–Te distances are shorter than those in **7**, 2.6903(4), **8**, 2.6958(6) or **9**, 2.6897(9) Å. The ranges of the Pd–B, Te–B and B–B distances in **1** and in compounds **6**, **7**,[11] **8** and **9**[2] are similar. Clearly, the $PdTeB_{10}$ cages in these compounds have closely related structures and since, in general, the species $[L_2PdTeB_{10}H_9L]^+$, $[L_2PdTeB_{10}H_{10}]$ and $[L(X)PdTeB_{10}H_9L]$ have the same number of cluster bonding electrons it can be inferred that they have similar electronic structures. The *exo*-cage B–P distance in **1** is 1.961(5) Å which is larger than the B–P distances in **7**, 1.942(4), **8**, 1.950(6) or **9**, 1.941(9) Å, but within the range of *exo*-cage B–P distances known in metallaborane clusters (1.87–1.98 Å).[1] The Pd–P distances in **1** are significantly different at 2.3285(13) and 2.3640(13) Å, whereas in **6**, the Pd–P distances are much more similar at 2.3301(7) and 2.3354(8) Å. However, *closo*-palladatelluraboranes containing phosphine ligands are known to exhibit an extensive range of Pd–P distances, *e.g.* from 2.3285(13) Å in **1** to 2.367(2) Å in **9**. It appears that Pd–P distances are extremely variable and are affected by small changes in that portion of the molecule which is *trans* to each Pd–P vector.

The shortest Te ··· I distance in **1** is 3.4841(6) Å, which is longer than the sum of the bond radii (2.87 Å) but shorter than the sum of the van der Waals' radii (4.04 Å).[12] Hence a weak Te ··· I interaction in the crystal can be inferred.

The very close similarity of the ^{11}B and $^{11}B\text{-}\{^1H\}$ NMR spectra of all the compounds **1**–**9** support the suggested similarity in the cluster electronic structures among cationic $[L_2\text{-}PdTeB_{10}H_9L]^+$, and neutral $[L_2PdTeB_{10}H_{10}]$ or $[L(X)Pd\text{-}TeB_{10}H_9L]$, compounds. The only significant difference is that in the cationic compounds the boron atom [B(7) or B(11)] bonded to PPh_3 is shielded with respect to the equivalent B–H unit in the neutral species and appears at $\delta(^{11}B)$ +5.8 and +5.9 in **1** and **2** respectively compared with an average value of *ca.* +10 for B(7/11) in the neutral compounds. An increase in ^{11}B shielding upon phosphine-for-hydrogen replacement in isoelectronic and isostructural systems is not abnormal.[13]

We are currently investigating the potential of the halide/phosphine replacement reaction for the general synthesis of cationic metalla-boranes and -heteroboranes and are studying the further chemistry of these species.

Acknowledgements

A generous loan of palladium salts from Johnson Matthey plc is gratefully acknowledged. G. F. thanks the Natural Sciences and Engineering Research Council of Canada for Grants in Aid of Research. J. D. K. acknowledges an equipment grant from the SERC, and R. M. a scholarship from the Government of the Basque Country.

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Received 20*th July* 1993; *Communication* 3/04263D

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‡ Crystal data for $C_{24}H_{42}B_{10}IP_3PdTe$ **1**: Enraf-Nonius CAD-4 diffractometer (Mo-Kα = 0.710 69 Å), orange block, crystal size 0.15 × 0.35 × 0.50 mm, M = 892.51, monoclinic, space group $P2_1/n$, a = 10.2417(7), b = 26.1983(22), c = 13.3393(11) Å, β = 101.001(7)°, U = 3513.4(5) Å^3, Z = 4, D_c = 1.69 g cm^{-3}, $F(000)$ = 1728, μ = 23.6 cm^{-1}, T = 294 K, 7644 reflections measured ($2 < 2\theta < 54°$), 7390 unique, 4918 with $[I > 3\sigma(I)]$, 362 variables. Structure solved by Patterson heavy-atom method with NRCVAX[6] and TEXSAN[7] programmes, H atoms placed in calculated geometrical positions attached to carbon or boron atoms [d(C–H) 0.95, d(B–H) 1.08 Å], empirical absorption correction,[8] secondary extinction correction applied [0.177(61)],[9] weighting scheme $w^{-1} = \sigma^2F + 0.0010F^2$, R = 0.034, $R'(\{\Sigma[w(F_o - F_c)^2]/\Sigma(wF_o^2)\}^{\frac{1}{2}})$ = 0.051, goodness-of-fit = 1.34, maximum shift/error < 0.003. All calculations carried out on a Silicon Graphics 4D-35TG computer. Atomic coordinates, thermal parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.