

Short communication

Synthesis and structural characterisation of the carbene-containing metallaheteroborane compound

[2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>]<sup>1</sup>

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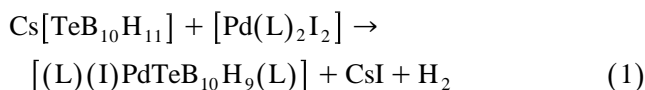
Abstract

The unique metallaheteroborane cluster compound [2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], **1**, which contains the secondary carbene (Bu<sup>t</sup>NHCH) bonded to a cage boron atom, is synthesised and structurally characterised by X-ray diffraction methods. © 1998 Elsevier Science S.A.

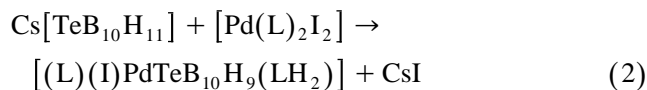
Keywords: Metallaheteroborane cluster compound; Cage boron atom; Ligand transfer

1. Introduction

The modification of a {BH<sup>-</sup>} unit in borane cluster compounds to a {B:L} unit is a well known example of Wade's rules [1]. Numerous two-electron donors (:L) have been used and examples include phosphines, amines, acetonitrile, dialkylsulphides, carbon monoxide and dinitrogen [2]. In metallaheteroborane chemistry, the transfer of a ligand (:L) from a metal to a cage boron atom is a well established reaction type. An example is the migration of a PPh<sub>3</sub> ligand from the rhodium atom in [8,8-(PPh<sub>3</sub>)<sub>2</sub>-8-CO-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] to [1,3-(PPh<sub>3</sub>)<sub>2</sub>-1-CO-*closo*-1,2-RhSB<sub>9</sub>H<sub>8</sub>] with the loss of hydrogen [3]. Alternatively, the process forming the B:L site may occur at the same time as the formation of the metallaheteroborane and an example of this is the synthesis of [2-I-2-(PPh<sub>3</sub>)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>(PPh<sub>3</sub>)] from the reaction between [TeB<sub>10</sub>H<sub>11</sub>]<sup>-</sup> and [Pd(L)<sub>2</sub>I<sub>2</sub>] [4], (Eq. (1), L = PPh<sub>3</sub>).



In a study of similar reactions to that shown in Eq. (1), we have obtained a novel secondary carbene-containing metallaheteroborane, [2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], **1**, in which an isocyanide ligand on palladium has been transferred to the telluraborane cage with the addition to two hydrogen atoms from the heteroborane, (Eq. (2), L = Bu<sup>t</sup>NC). In accordance with Wade's rules [1], the carbene ligand (LH<sub>2</sub>) is supplying two electrons.



2. Results and discussion

Three products, one major and two minor, were isolated from the reaction between Cs[*nido*-7-TeB<sub>10</sub>H<sub>11</sub>] and [Pd(Bu<sup>t</sup>NC)<sub>2</sub>I<sub>2</sub>] in thf solution. The major product, [2,2-(Bu<sup>t</sup>NC)<sub>2</sub>-*closo*-2,1-PdTeB<sub>10</sub>H<sub>10</sub>] 16%, and one of the minor products, *closo*-[2,2-(Bu<sup>t</sup>NC)<sub>2</sub>-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>(CHNBu<sup>t</sup>)] 2%, were characterised with C, H and N chemical analyses and IR and NMR spectroscopies. The compound formed in lowest yield (< 1%), **1**, was characterised solely with X-ray diffraction techniques. Suitable crystals of **1** were grown from a CH<sub>2</sub>Cl<sub>2</sub>-toluene solution.

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<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

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The analysis of the structure of [2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], **1**, showed that it had a *closo*-cage geometry based on a distorted PdTeB<sub>10</sub>-dodecahedron with palladium and tellurium in adjacent positions. Fig. 1 illustrates the *A* enantiomer which exists in the crystal in equal quantity with the *C* enantiomer. The analysis was slightly complicated by disorder of the Bu<sup>t</sup>NC moiety; brief details are in the Experimental section. Principal dimensions are listed in Table 1.

The structure, Fig. 1, is most notable for the presence of the secondary carbene ligand (Bu<sup>t</sup>NHCH) attached to the PdTeB<sub>10</sub>-cage at B(3) which is adjacent to tellurium. The formulation of the secondary carbene ligand is confirmed by its geometry and the location of the hydrogen atoms at N(2) and C(1) in difference maps. The four atoms B(3), C(1), N(2) and C(3) (torsion angle  $-179.3(10)^\circ$ ) are effectively coplanar; angle B(3)–C(1)–N(2) is  $119.8(7)^\circ$  and C(1)–N(2)–C(3) is enlarged to  $131.2(7)^\circ$ . The C(1)–N(2) distance of 1.295(9) Å is comparable with corresponding distances in a number of palladium carbene compounds, e.g., [PdCl<sub>2</sub>{C(OMe)(NHMe)}<sub>2</sub>], 1.320(12) Å, [5] and is indicative of the double bond character of C(1)=N(2). The B(3)–C(1) distance, 1.552(11)Å, suggests some multiple

bonding character and is clearly shorter than the reported mean single B–C<sub>sp<sup>3</sup></sub> bond distance of 1.597 Å [6]. The B(3)–C(1) distance may be compared with some other *exo*-bound ligands with C-donor sites for which some multiple bonding has been postulated, e.g., the isocyanide-containing complexes [6-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-6,9-(*p*-MeC<sub>6</sub>H<sub>4</sub>NC)<sub>2</sub>-*arachno*-6-RhB<sub>9</sub>H<sub>11</sub>] [7] and [1-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-2-(NHEt)-7-(EtNC)-*closo*-1,2-RhCB<sub>9</sub>H<sub>9</sub>] [8] for which B–C distances of 1.541(6)Å and 1.533(6)Å respectively were recorded. The title compound is the first with a secondary carbene attached to a borane-based cage and only the second compound to be reported with any type of carbene attached to a borane cage. Previously, the reaction between an excess of methylisocyanide and *anti*-B<sub>18</sub>H<sub>22</sub> afforded the complex 7-*L*-*anti*-B<sub>18</sub>H<sub>20</sub>, **2**, where L is the imidazole-based carbene {(MeN)<sub>2</sub>CH(CNHMe)C} [9]. The B–C distance in **2** was 1.576(2)Å. A BH<sub>3</sub> complex of another imidazole-based carbene, {(MeC)<sub>2</sub>(NEt)<sub>2</sub>C}BH<sub>3</sub>, was reported to have a B–C distance of 1.603(3)Å [10].

Although the mechanism of formation of [2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], **1** is obscure at present, it would seem likely that the carbene ligand in **1** is derived from a Bu<sup>t</sup>NC group which was originally attached to the palladium. It is noteworthy

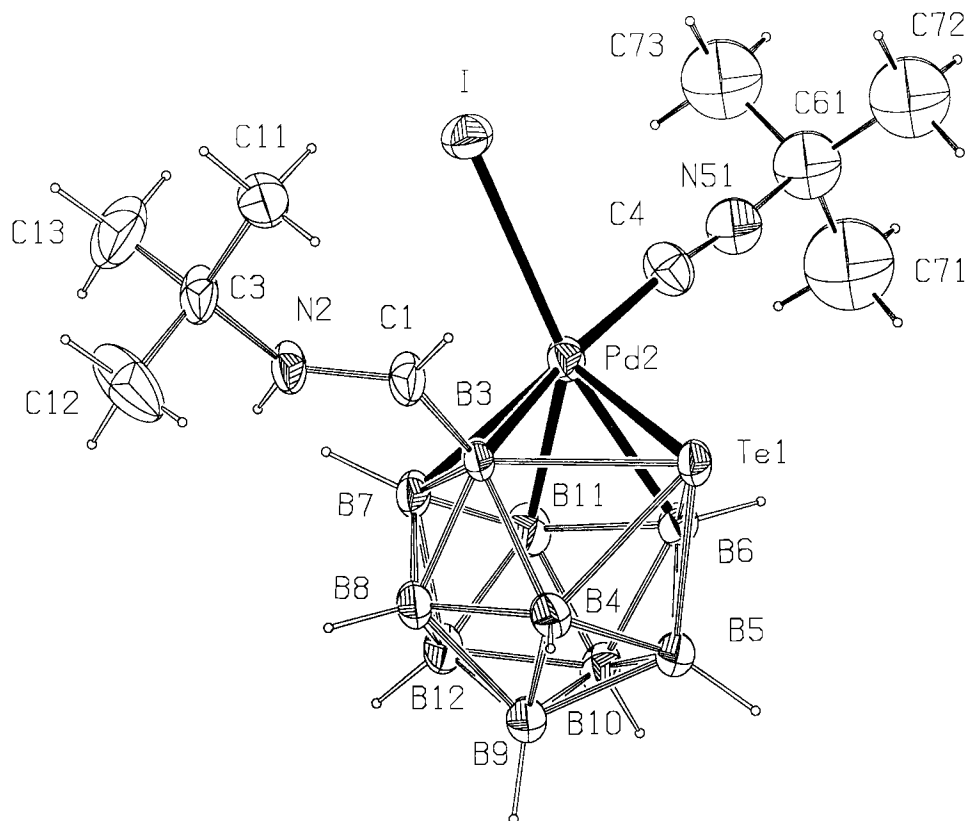


Fig. 1. A view of *A*-[2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], with numbering scheme. Displacement ellipsoids are drawn at the 20% level. For clarity, only one of the two orientations of the disordered Bu<sup>t</sup>NC moiety is shown.

Table 1  
Selected distances (Å) and angles (deg) for [2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>]

Distances (Å)					
Te(1)–Pd(2)	2.6932(8)	Te(1)–B(6)	2.408(10)	Te(1)–B(5)	2.302(10)
Te(1)–B(4)	2.307(9)	Te(1)–B(3)	2.383(8)	Pd(2)–I	2.7185(8)
Pd(2)–C(4)	1.987(9)	Pd(2)–B(6)	2.202(9)	Pd(2)–B(3)	2.244(10)
Pd(2)–B(11)	2.214(9)	Pd(2)–B(7)	2.230(9)	C(1)–N(2)	1.295(9)
C(1)–B(3)	1.552(11)	N(2)–C(3)	1.488(9)	C(4)–N(51)	1.121(12)
C(4)–N(52)	1.126(12)				
Range of B–B distances: 1.73(2) Å for B(9)–B(12) to 1.95(2) Å for B(5)–B(6)					
Angles (deg)					
I–Pd(2)–B(3)	94.9(2)	I–Pd(2)–Te(1)	113.80(3)		
C(4)–Pd(2)–I	87.1(3)	C(4)–Pd(2)–Te(1)	113.8(3)		
C(1)–B(3)–Pd(2)	114.8(6)	C(1)–B(3)–Te(1)	115.3(5)		
C(1)–B(3)–B(11)	119.4(7)	B(11)–B(3)–Te(1)	120.1(5)		
B(11)–B(6)–Te(1)	120.4(5)	N(2)–C(1)–B(3)	119.8(7)		
C(1)–N(2)–C(3)	131.2(7)	N(2)–C(3)–C(11)	110.1(7)		
N(2)–C(3)–C(12)	107.5(9)	N(2)–C(3)–C(13)	106.4(10)		
Pd(2)–C(4)–N(51)	173.8(10)	Pd(2)–C(4)–N(52)	175.1(11)		
C(4)–N(51)–C(61)	172.0(20)	C(4)–N(52)–C(62)	176.9(18)		

that the position of attachment of the carbene to the cage of **1** is at B(3). This is unique for *closo*-PdXB<sub>10</sub> derivatives containing Group VI/16 heteroboranes. All previous compounds which involved transfer of ligands from palladium had the transferred ligand attached at the B(4) position [4,11].

It was soon apparent during the development of the structure analysis that the Bu<sup>t</sup>NC group attached to the palladium had an essentially linear Pd–C–N–C<sup>t</sup>Bu geometry (Fig. 1), but was disordered slightly over two closely adjacent sites with Pd–C(4)–N(51 or 52) 174(1) and 175(1)° and C(4)–N–C<sup>t</sup>Bu 172(2) and 177(2)°, with Pd–C(4) 1.987(9), mean C(4)–N 1.124(12) Å. These data are comparable with the corresponding distances of 2.022(7) and 2.027(6) Å for Pd–C, 1.150(9) and 1.146(8) Å for C≡N in the Bu<sup>t</sup>NC group in the palladamonocarborane [1,1-(Bu<sup>t</sup>NC)<sub>2</sub>-2-NMe<sub>3</sub>-*closo*-1,2-PdCB<sub>10</sub>H<sub>10</sub>] [12]. Mean values of 1.92(4) Å for Pd–C, 1.15(3) Å for C≡N for N–C<sub>butyl</sub> were reported for [Pd(CNBu<sup>t</sup>)<sub>2</sub>I<sub>2</sub>] [13].

The Pd–Te bond distance, 2.6932(8) Å, is not unusual and the Pd–B, Te–B, and B–B distances, Table 1, which range from 2.202(9) to 2.244(10) Å, 2.302(10) to 2.408(10) Å and 1.73(2) to 1.95(2) Å, respectively, are typical of palladate lluraboranes [4,11]. The Pd–I bond length, 2.7185(8) Å, is considerably longer than both the reported mean value for such bonds of 2.624 Å [6], and 2.599(6) Å in [Pd(CNBu<sup>t</sup>)<sub>2</sub>I<sub>2</sub>] [13].

### 3. Experimental

The title compound was formed as a minor product (0.9% yield) in the reaction between Cs[7-TeB<sub>10</sub>H<sub>11</sub>] (0.178 g, 0.469 mmol) in thf (20 ml) and a solution of

[Pd(CNBu<sup>t</sup>)<sub>2</sub>I<sub>2</sub>] (0.247 g, 0.469 mmol) in thf (25 ml). The reaction mixture was refluxed for 3 h. The solvent was evaporated and the mixture purified by preparative thin layer chromatography (CH<sub>2</sub>Cl<sub>2</sub>–heptane) (7:3). One major purple band and two minor green bands were extracted into CH<sub>2</sub>Cl<sub>2</sub>. The second green band was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–toluene (2:1) to give green block-shaped crystals of [2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], **1** (0.003 g). IR:  $\nu_{\max}$  (KBr) 2540(vs) (BH), 2521(vs) (BH), 2199(vs) (C≡N) cm<sup>-1</sup>.

#### 3.1. Crystal data for **1**

[2-I-2-(Bu<sup>t</sup>NC)-3-(Bu<sup>t</sup>NHCH)-*closo*-2,1-PdTeB<sub>10</sub>H<sub>9</sub>], C<sub>10</sub>H<sub>29</sub>B<sub>10</sub>IN<sub>2</sub>PdTe,  $M_r = 646.35$ , orthorhombic, space group *Pccn*,  $a = 20.0983(13)$ ,  $b = 21.2149(15)$ ,  $c = 13.5931(13)$  Å,  $U = 5795.9(8)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.481$  g cm<sup>-3</sup>,  $F(000) = 2432$ ,  $\mu(\text{Mo K}\alpha) = 2.690$  cm<sup>-1</sup>. Diffraction data were collected using a CAD4 diffractometer and graphite monochromatised Mo K $\alpha$  radiation and corrected for Lorentz, polarisation and absorption effects (by psi-scans). Of the 6294 reflections measured in the  $\theta$  range 2–26.9°, 3861 had  $I > 2\sigma(I)$  and were labelled as observed. The structure was solved via the heavy atom method [14] and refined [15] by full-matrix least-squares calculations using all measured  $F^2$  data. Final conventional  $R$ -factors are 0.0476 ( $R(F_{\text{obs}})$ ) and 0.1735 {for  $wR(F^2(\text{all}))$ }. During the analysis, it soon became apparent that the Bu<sup>t</sup>NC moiety was slightly disordered over two adjacent sites; these atoms were allowed for using isotropic thermal parameters and appropriate constraints on the *t*-butyl C atom geometry. All other atoms were allowed anisotropic motion; H atoms were allowed for as riding

atoms. At the conclusion of the refinement there was some minor residual density (all peaks less than  $0.9 \text{ e}\text{\AA}^{-3}$ ) in a volume element around the origin; analysis of this with PLATON [16] indicated that the sum of the residual density in this area amounted to approximately 1.7 electron which we took to be coming from a partially occupied disordered solvent molecule (e.g., from approximately 3% to 4% of a toluene of solvation) but it was not possible to determine any suitable coordinates.

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