Metallaheteroborane Chemistry. Part 7.[†] Synthesis, Crystal Structure, and Characterisation of Two Dinuclear Rhodatelluraboranes, $[\{(\mathrm{PPh_3})_2\mathrm{RhTeB_{10}H_{10}}\}_2]$ and $[(\mathrm{PPh_3})(\mathrm{CO})\mathrm{Rh_2Te_2B_{20}H_{20}}]$[‡]

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The dinuclear rhodatelluraborane *closo*-$[(\mathrm{PPh_3})(\mathrm{CO})\mathrm{Rh_2Te_2B_{20}H_{20}}]$ (**2**) was obtained from the reaction between either $[\mathrm{Os_3H_2(CO)_{10}}]$ and *closo*-$[2,2\text{-}(\mathrm{PPh_3})\text{-}2\text{-H-}1,2\text{-}\mathrm{TeRhB_{10}H_{10}}]$ (**1**) in dichloromethane solvent, or $[\mathrm{Rh(cod)(PPh_3)Cl}]$ (cod = cyclo-octa-1,5-diene) and $\mathrm{Cs[TeB_{10}H_{11}]}$ in ethanol. The reaction between $[\mathrm{Mo(CO)_6}]$ and *closo*-$[2,2\text{-}(\mathrm{PPh_3})_2\text{-}2\text{-H-}1,2\text{-}\mathrm{TeRhB_{10}H_{10}}]$ in tetrahydrofuran afforded $[\{$*closo*-$(\mathrm{PPh_3})\mathrm{RhTeB_{10}H_{10}}\}_2]$, (**3**). *X*-Ray crystallographic analysis of compound (**2**) shows it to crystallise with a monoclinic space group ($P2_1/c$), containing four molecules in a unit cell of dimensions a = 16.213(4), b = 13.082(4), c = 17.048(3) Å, and β = 95.29(2)°. The final *R* factor was 0.028 for 5 992 observed reflections. *X*-Ray analysis of the $\mathrm{CH_2Cl_2}$ solvate of (**3**) shows the crystal to be monoclinic, space group $P2_1/a$ with four molecules in a unit cell that measures a = 16.384(5), b = 16.197(6), c = 19.879(5) Å, and β = 70.84(2)°. The final *R* factor was 0.039 for 3 973 observed reflections. Both (**2**) and (**3**) contain two $\{\mathrm{RhTeB_{10}}\}$ cages bonded by Rh–Rh′, Rh–B′, Rh′-B, Rh–H′–B′, and Rh′–H–B′, interactions. Principal interatomic distances are Rh–Rh′ 2.737 1(3), Rh–B′ 2.380(4), Rh′–B 2.329(4), Rh–Te 2.565 3(3), Rh′–Te′ 2.581 7(3) Å in (**2**) with the corresponding distances in (**3**), 2.834 4(12), 2.354(12), 2.341(13), 2.604 7(12), and 2.581 1(10) Å respectively. The *exo*-cage ligands ($\mathrm{PPh_3}$ or CO) in both (**2**) and (**3**) adopt *cis* configurations about the central Rh–Rh′ portions of the molecules. The ^{1}H, ^{11}B, and ^{31}P n.m.r. data for (**2**) and (**3**) show close similarities with those of (**1**).

Several unusual dinuclear rhodacarbaboranes that contain rhodium–rhodium bonds have been reported by Hawthorne and co-workers.[1–4] Intercage interactions in these compounds usually include two Rh–H–B bridged bonds and a rhodium–rhodium bond as for example in the first reported compound of this type, $[\{$*closo*-$(\mathrm{PPh_3})\mathrm{RhC_2B_9H_{11}}\}_2]$.[1,3] In some cases carbon–carbon bonds are also present, as in $[\{$*closo*-$(\mathrm{PEt_3})\mathrm{RhC_2B_9H_{10}}\}_2]$.[2,3] The preparation of $[\{(\mathrm{PPh_3})\mathrm{RhC_2B_9H_{11}}\}_2]$ was initially by the serendipitous reaction between $[3,3\text{-}(\mathrm{PPh_3})_2\text{-}3\text{-H-}3,1,2\text{-}\mathrm{RhC_2B_9H_{11}}]$ and aerial oxygen.[1] Later, benzoylperoxide was used as the oxidising agent.[1] Subsequently a more convenient synthesis was developed which involved the reaction in ether solvents of $[\mathrm{Rh(cod)(PR_3)Cl}]$ (cod = cyclo-octa-1,5-diene) and *nido*-$[7,8\text{-}\mathrm{C_2B_9H_{12}}]^-$-based anions.[2,3] The complexes mentioned above have remained as interesting oddities in the well established field of rhodium–carbaborane chemistry but in general there is a lack of other dinuclear dicluster species in metalloheteroborane chemistry. The only other related compounds are the $[\{(\mathrm{PPh_3})\mathrm{RhCB_{10}H_{10}(NH_2)}\}_2\text{-}\mathrm{H}]^-$ anion in which two bridging $\mathrm{NH_2}$ groups are present together with a hydrogen-bridged rhodium–rhodium bond (Rh–H–B bridged bonds are absent),[5] and a nickel carbaborane complex [*closo*-$\{3\text{-}(\mu\text{-CO})\text{-}8\text{-}(\mathrm{PPh_3})\text{-}3,1,2\text{-}\mathrm{NiC_2B_9H_{11}}\}_2]$, which contains two carbonyl groups bridging a single nickel–nickel bond connecting the nickelacarbaborane cages.[6] The anion was produced by the reaction of $[\mathrm{RhCl(PPh_3)_3}]$ and *nido*-$\mathrm{CB_{10}H_{12}(NH_3)}$ in methanol in the presence of hydroxide ion or $\mathrm{NEt_3}$.[5] The dinickel complex was prepared from *closo*-$[3,3\text{-}(\mathrm{PPh_3})_2\text{-}3,1,2\text{-}\mathrm{NiC_2B_9H_{11}}]$ by carbonylation with CO in refluxing benzene.[6]

In the present work we report the characterisation of two dinuclear rhodatelluraboranes. The first of these arose from an unsuccessful attempt to prepare a hybrid metal cluster–metallaheteroborane complex by the reaction between $[\mathrm{Os_3H_2(CO)_{10}}]$ and *closo*-$[2,2\text{-}(\mathrm{PPh_3})_2\text{-}2\text{-H-}1,2\text{-}\mathrm{TeRhB_{10}H_{10}}]$ (**1**), and constitutes the first dinuclear metallaheteroborane with different *exo*-cage metal-bound ligands on the two rhodium atoms present, namely $[(\mathrm{PPh_3})(\mathrm{CO})\mathrm{Rh_2Te_2B_{20}H_{20}}]$, (**2**). Previously Stone and co-workers[7] had prepared metallacarbaborane–metal cluster hybrids by the reaction of the metal carbyne function of the anion $[\mathrm{W(\equiv CR)(CO)_2(C_2R'_2B_9H_9)}]^-$ with a variety of metal substrates including $[\mathrm{Co_2(CO)_8}]$ and $[\mathrm{Fe_3(CO)_{12}}]$, and Shore *et al.*[8] had reported that the reaction of $[\mathrm{Os_3H_2(CO)_{10}}]$ and diborane affords $[\mathrm{Os_3H_3(CO)_9(BCO)}]$. From alternative attempts to synthesise (**2**) we have isolated the corresponding bis(phosphine) complex $[\{(\mathrm{PPh_3})\mathrm{RhTeB_{10}H_{10}}\}_2]$, (**3**). Compounds (**2**) and (**3**) were characterised by *X*-ray techniques and multielement n.m.r. spectroscopy.

Results and Discussion

The reaction between $[\mathrm{Os_3H_2(CO)_{10}}]$ and *closo*-$[2,2\text{-}(\mathrm{PPh_3})_2\text{-}2\text{-H-}1,2\text{-}\mathrm{TeRhB_{10}H_{10}}]$ (**1**) in a 1 : 1 molar ratio in dichloromethane was carried out at room temperature for 3 d and then the solution was heated under reflux for 20 h. Of the ten products which were observed by analytical thin-layer chromatography, only five could be isolated in sufficient amounts to enable further characterisation. Whereas all five compounds showed i.r. absorptions associated with CO ligands, only one exhibited a

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[†] Part 6, preceding paper.

[‡] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

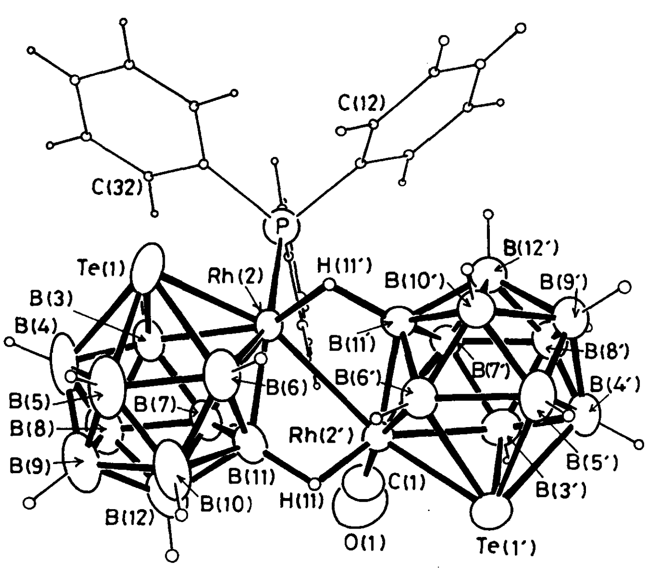


Figure 1. A view of $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$, **(2)**, with atom numbering scheme. For clarity, hydrogen and phenyl carbon atoms are shown as spheres of an arbitrary size

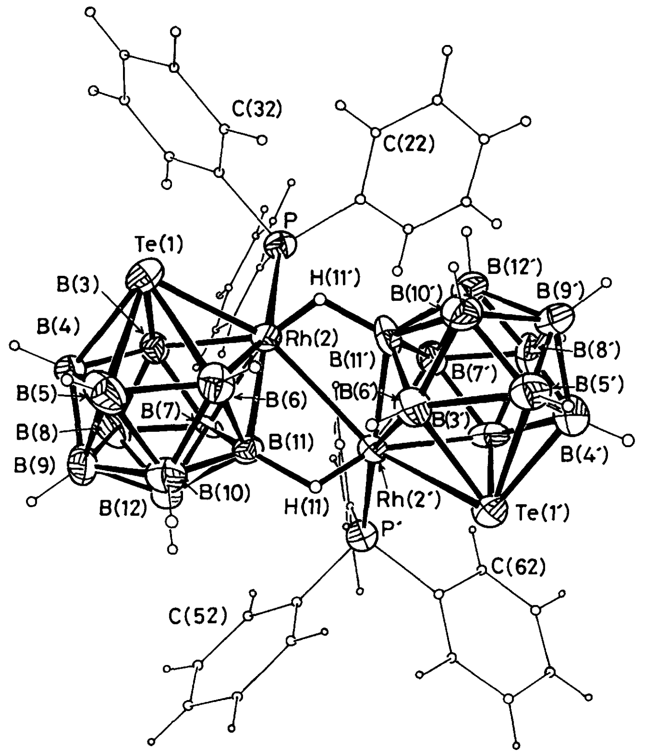


Figure 2. A view of $[\{(PPh_3)RhTeB_{10}H_{10}\}_2]$, **(3)**, with atom numbering scheme. For clarity, hydrogen and phenyl carbon atoms are shown as spheres of an arbitrary size

BH absorption (at 2 540 cm^{-1}). This dark purple compound was isolated in 45.7% yield and it was established by *X*-ray methods to be $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$ **(2)**; subsequent spectroscopic studies were in accord with this formulation. The synthesis of **(2)** contrasts to other reactions between boranes and osmium carbonyl complexes which have been reported in the literature which have afforded $Os(CO)_n$-containing cluster compounds. Examples are the preparation of *closo*-$[1,1,1-(CO)_3-2,3-(SiMe_3)_2-1,2,3-OsC_2B_4H_4]$ from $[Os_3(CO)_{12}]$ and either *nido*-$[(SiMe_3)_2C_2B_4H_6]$ or *closo*-$[(SiMe_3)_2C_2SnB_4H_4]$,[9] and the reactions of $[OsH(CO)(PPh_3)_3Cl]$ with $[B_3H_8]^-$ and $[B_5H_8]^-$ which produced *arachno*-$[OsH(CO)(PPh_3)_2(B_3H_8)]$ and *nido*-$[Os(CO)(PPh_3)_2(B_5H_9)]$ respectively.[10] The fusion of cluster systems promoted by osmium complexes has been observed previously in only one reaction, namely the formation of *anti*-$[B_{18}H_{21}]^-$ in the reaction between equimolar amounts of *nido*-$[B_9H_{12}]^-$ and $[\{Os(CO)_3Cl_2\}_2]$.[11] In an attempt to improve the preparation of **(2)**, $[Mo(CO)_6]$ was tried as an alternative source of CO.[12] The reaction of **(1)** and $[Mo(CO)_6]$ in an equimolar ratio in tetrahydrofuran (thf) solution for 16 h at room temperature gave only one major borane-containing product which was isolated in 33.1% yield and shown by spectroscopic and crystallographic analyses to be $[\{$*closo*-$(PPh_3)RhTeB_{10}H_{10}\}_2]$, **(3)**. This compound was dark purple like **(2)**. No dinuclear products were observed when the reaction between **(1)** and $[Mo(CO)_6]$ was carried out in either dichloromethane or benzene, or when **(1)** was stirred in thf solution in the absence of $[Mo(CO)_6]$.

Hawthorne and co-workers[3] had previously prepared carbaborane analogues of **(3)**, *i.e.* $[\{(PR_3)RhC_2B_9H_{11}\}_2]$ **(3)**, in good yields by the reaction between $[Rh(cod)(PR_3)Cl]$ and *nido*-$[C_2B_9H_{12}]^-$ anions in ether solvents. However, when the reaction between $[Rh(cod)(PPh_3)Cl]$ and *nido*-$[7-Ph-7,8-C_2B_9H_{11}]^-$ was carried out in refluxing methanol the yield was considerably diminished (12%). In the present work we found that the analogous reaction between $Cs[TeB_{10}H_{11}]$ and $[Rh(cod)(PPh_3)Cl]$ in ethanol at room temperature for 24 h afforded **(2)** in 20.2% yield as the only dinuclear product.

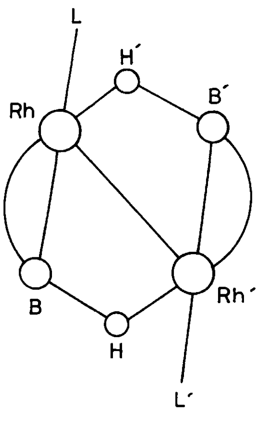
In order to establish the molecular architectures of compounds **(2)** and **(3)**, suitable single crystals were grown from dichloromethane–cyclohexane solutions and were subjected to analysis by *X*-ray diffraction techniques. Views of the overall molecular structures of **(2)** and **(3)** are given in Figures 1 and 2 respectively. The structures are mutually very similar in general, and differ only in the nature of one of the *exo*-cage ligands attached to one of the rhodium atoms. The compounds may be described as dimers of twelve-vertex rhodatelluraboranes which are bridged by Rh–Rh′, Rh–H–B′, Rh′–H–B, and B′–Rh and B–Rh′ bonding interactions. Both **(2)** and **(3)** contain the rhodium bound *exo*-cage ligands in *cis* configurations about the central Rh–Rh′ bonded portions of the molecules with the inter-rhodium linkages *trans* to the intracluster rhodium–tellurium linkages. In their overall structures and the apparently stereoselective formation of the observed isomers these compounds have strong analogies with the dirhodadicarbaboranes prepared previously by Hawthorne and co-workers[1–6] and mentioned in the Introduction.

Selected interatomic distances and angles in compounds **(2)** and **(3)** are given in Tables 1 and 2 respectively. A number of structural details are noteworthy and many of these can be associated with the centrally bridged sections, **(Ia)**. The rhodium–rhodium distances in **(2)** and **(3)** are 2.737 1(3) and 2.834 4(12) Å respectively. These values span the reported values for the analogous carbaboranes **(4)** [R = Ph, 2.763(1); Et, 2.791(1) Å][3] and are within the 'normal' range reported for rhodium–rhodium single bonds (2.7—2.8 Å).[13] However, in this context it should be noted that an upper limit for the rhodium–rhodium single bond length of 3.2 Å has been suggested,[13] and relatively few other hydrogen-bridged dinuclear rhodium complexes have been structurally characterised. In a recent analysis of a complex containing an Rh–H–Rh unit, $[\{Rh(Bu^t{}_2PH)(CO)\}_2(\mu-H)(\mu-Bu^tP)]$, the rhodium–rhodium distance was determined as 2.906(2) Å.[14]

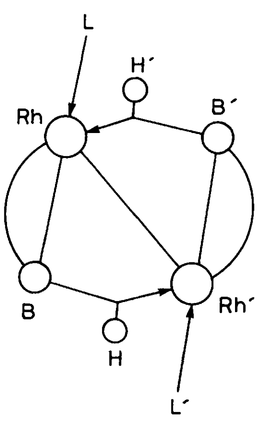
The inter-cage rhodium–boron distances are only slightly longer than the longest intra-cage rhodium–boron distances. Thus in compound **(2)** these intercage values are 2.380(4) Å [(Rh(2)–B(11′)] and 2.329(4) Å [(Rh(2′)-B(11)] compared with a range of cage Rh–B distances of 2.151(4)—2.308(4) Å, and in

Table 1. Selected interatomic distances (Å) and angles (°) in compound (**2**)

Te(1)–Rh(2)	2.565 3(3)	B(6)–B(11)	1.822(6)	Rh(2)–Te(1)–B(3)	55.5(1)	Te(1′)–Rh(2′)–B(3′)	58.1(1)
Te(1)–B(3)	2.375(4)	B(7)–B(8)	1.794(6)	Rh(2)–Te(1)–B(6)	54.9(1)	Te(1′)–Rh(2′)–B(6′)	58.3(1)
Te(1)–B(4)	2.303(5)	B(7)–B(11)	1.802(6)	B(3)–Te(1)–B(4)	49.0(2)	Te(1′)–Rh(2′)–H(11)	91.9
Te(1)–B(5)	2.303(6)	B(7)–B(12)	1.787(6)	B(3)–Te(1)–B(6)	84.0(2)	Rh(2)–Rh(2′)–C(1)	105.2(1)
Te(1)–B(6)	2.374(5)	B(8)–B(9)	1.797(7)	B(4)–Te(1)–B(5)	48.6(2)	Rh(2)–Rh(2′)–B(11)	49.5(1)
Te(1′)–Rh(2′)	2.581 7(3)	B(8)–B(12)	1.784(7)	B(5)–Te(1)–B(6)	48.1(2)	Rh(2)–Rh(2′)–B(6′)	87.5(1)
Te(1′)–B(3′)	2.371(4)	B(9)–B(10)	1.768(6)	Rh(2′)–Te(1′)–B(3′)	54.4(1)	Rh(2)–Rh(2′)–B(11′)	56.7(1)
Te(1′)–B(4′)	2.285(4)	B(9)–B(12)	1.772(7)	Rh(2′)–Te(1′)–B(6′)	54.2(1)	Rh(2)–Rh(2′)–H(11)	81.0
Te(1′)–B(5′)	2.298(5)	B(10)–B(11)	1.800(6)	B(3′)–Te(1′)–B(4′)	49.3(2)	C(1)–Rh(2′)–B(3′)	84.4(2)
Te(1′)–B(6′)	2.376(4)	B(10)–B(12)	1.804(7)	B(3′)–Te(1′)–B(6′)	83.7(1)	C(1)–Rh(2′)–B(6′)	167.2(2)
Rh(2)–Rh(2′)	2.737 1(3)	B(11)–B(12)	1.763(6)	B(4′)–Te(1′)–B(5′)	48.5(2)	C(1)–Rh(2′)–B(11′)	140.8(2)
Rh(2)–P	2.423(1)	B(11)–H(11)	1.30	B(5′)–Te(1′)–B(6′)	48.5(1)	C(1)–Rh(2′)–H(11)	96.0
Rh(2)–B(3)	2.308(4)	B(3′)–B(4′)	1.945(6)	Te(1)–Rh(2)–Rh(2′)	146.20(1)	B(11)–Rh(2′)–B(3′)	178.5(2)
Rh(2)–B(6)	2.283(4)	B(3′)–B(7′)	1.821(5)	Te(1)–Rh(2)–P	96.51(2)	B(11)–Rh(2′)–B(11′)	93.9(1)
Rh(2)–B(7)	2.226(4)	B(3′)–B(8′)	1.751(6)	Te(1)–Rh(2)–B(3)	58.1(1)	B(3′)–Rh(2′)–B(6′)	88.5(2)
Rh(2)–B(11)	2.151(4)	B(4′)–B(5′)	1.882(6)	Te(1)–Rh(2)–B(6)	58.3(1)	B(3′)–Rh(2′)–B(7′)	48.0(1)
Rh(2)–B(11′)	2.380(4)	B(4′)–B(8′)	1.759(6)	Te(1)–Rh(2)–B(11′)	125.94(9)	B(6′)–Rh(2′)–B(11′)	48.4(1)
Rh(2)–H(11′)	1.63	B(4′)–B(9′)	1.751(6)	Te(1)–Rh(2)–H(11′)	92.4	B(7′)–Rh(2′)–B(11′)	49.6(1)
Rh(2′)–C(1)	1.945(4)	B(5′)–B(6′)	1.920(6)	Rh(2′)–Rh(2)–P	116.93(2)	Rh(2′)–C(1)–O(1)	173.1(4)
Rh(2′)–B(11)	2.329(4)	B(5′)–B(9′)	1.753(6)	Rh(2′)–Rh(2)–B(6)	87.9(1)	Te(1)–B(3)–B(7)	116.9(3)
Rh(2′)–B(3′)	2.272(4)	B(5′)–B(10′)	1.768(6)	Rh(2′)–Rh(2)–B(11)	55.3(1)	Rh(2)–B(3)–B(4)	115.3(2)
Rh(2′)–B(6′)	2.268(4)	B(6′)–B(10′)	1.739(6)	Rh(2′)–Rh(2)–B(11′)	49.45(9)	B(3)–B(4)–B(5)	108.8(3)
Rh(2′)–B(7′)	2.202(4)	B(6′)–B(11′)	1.820(5)	Rh(2′)–Rh(2)–H(11′)	81.8	B(4)–B(5)–B(6)	110.1(3)
Rh(2′)–B(11′)	2.165(4)	B(7′)–B(8′)	1.805(5)	P–Rh(2)–B(3)	86.9(1)	Te(1)–B(6)–B(11)	112.9(2)
Rh(2′)–H(11′)	1.58	B(7)–B(11′)	1.833(5)	P–Rh(2)–B(6)	152.7(1)	Rh(2)–B(6)–B(5)	116.5(3)
B(3)–B(4)	1.943(6)	B(7′)–B(12′)	1.808(6)	P–Rh(2)–B(11)	155.9(1)	B(3)–B(7)–B(11)	110.8(3)
B(3)–B(7)	1.761(7)	B(8′)–B(9′)	1.788(6)	P–Rh(2)–B(11′)	96.56(9)	B(6)–B(11)–B(7)	114.4(3)
B(3)–B(8)	1.739(7)	B(8′)–B(12′)	1.798(6)	P–Rh(2)–H(11′)	92.7	Te(1′)–B(3′)–B(7′)	117.1(2)
B(4)–B(5)	1.894(7)	B(9′)–B(10′)	1.776(6)	B(3)–Rh(2)–B(6)	87.6(2)	Rh(2′)–B(3′)–B(4′)	115.0(2)
B(4)–B(8)	1.752(7)	B(9′)–B(12′)	1.752(6)	B(3)–Rh(2)–B(7)	45.7(2)	B(3′)–B(4′)–B(5′)	109.8(3)
B(4)–B(9)	1.769(8)	B(10′)–B(11′)	1.803(5)	B(3)–Rh(2)–B(11′)	174.1(2)	B(4′)–B(5′)–B(6′)	109.1(3)
B(5)–B(6)	1.906(6)	B(10′)–B(12′)	1.793(6)	B(6)–Rh(2)–B(11)	48.4(2)	Te(1′)–B(6′)–B(11′)	115.3(2)
B(5)–B(9)	1.757(8)	B(11′)–B(12′)	1.778(5)	B(7)–Rh(2)–B(11)	48.6(2)	Rh(2′)–B(6′)–B(5′)	116.3(2)
B(5)–B(10)	1.761(8)	B(11)–H(11′)	1.40	B(11)–Rh(2)–B(11′)	92.8(1)	B(3′)–B(7′)–B(11′)	110.1(3)
B(6)–B(10)	1.743(7)			Te(1′)–Rh(2′)–Rh(2)	145.61(1)	B(6′)–B(11′)–B(7′)	112.9(3)
				Te(1′)–Rh(2′)–C(1)	109.0(1)	Rh(2′)–H(11)–B(11)	107.4
				Te(1′)–Rh(2′)–B(11)	121.2(1)	Rh(2)–H(11′)–B(11′)	103.4



(Ia)



(Ib)

(**3**) the corresponding data are 2.354(12), 2.341(13), and a range of 2.153(11)—2.312(12) Å. These data and those relating to the Rh–H–B bridges are collected together with the corresponding data for the structurally characterised dirhodadicarbaborane analogues, (**4**), in Table 3. A comparison of the data in this Table clearly shows that the central sections of the complexes (**2**)—(**4**) are essentially similar.

The essentially straightforward $\{RhTeB_{10}\}$ closed cluster geometries observed in (**2**) and (**3**) and the similarity of the n.m.r. shielding patterns with those of the monomeric precursor (**1**) (discussed below) suggest that the $\{RhTeB_{10}\}$ cluster bonding in these complexes is closely similar. Compound (**1**) can be regarded as having, formally, an 18-electron rhodium centre. In compounds (**2**) and (**3**) three *exo*-polyhedral ligands on each rhodium [equivalent to H and two PPh_3 ligands in (**1**)] can be considered to be provided by the Rh–Rh bond (one electron), a PPh_3 (or CO) ligand, and donation from a two-electron B–H bond of the adjacent cage, (**Ib**), so that each rhodium is an 18-electron centre. Clearly the description given above is only one of several possible for the bonding about the rhodium atoms. Others in which full three-centre bonding interactions occur between Rh–H′–B′ and Rh–B′–Rh′ are also plausible alternatives.

It is of interest that an organometallic M←H–C equivalent to the B–H donation to Rh in compounds (**2**) and (**3**) would be described as arising from an agostic interaction.[15] In this context it is of course noted that two-electron three-centre M–H–B bonding is not an atypical feature of metal borane chemistry.[16] In both (**2**) and (**3**) each bridging section [Rh(2)–H(11′)–B(11′)–Rh(2′) and Rh(2′)–H(11)–B(11)–Rh(2)] is approximately planar, with maximum deviations from planarity of 0.178 and 0.093 Å for (**2**), and −0.050 and −0.067 Å for (**3**). The interplanar angle is 55.7° for (**2**) and 49.1° for (**3**).

The co-ordination of the *exo*-cage ligands about each rhodium atom can be initially described as being derived from an octahedral set (see previous paragraph). However the angles L–Rh–H_μ and Rh–Rh–H_μ are in general significantly less than 90° (Tables 1—3), and the L–Rh–Rh angles are considerably larger than 90°. The conformation of each Rh(ligands) unit

Table 2. Selected interatomic distances (Å) and angles (°) in compound (**3**)·CH_2Cl_2

Te(1)–Rh(2)	2.604 7(12)	B(7)–B(11)	1.837(14)	Rh(2)–Te(1)–B(3)	55.2(3)	Te(1′)–Rh(2′)–B(3′)	57.0(3)
Te(1)–B(3)	2.365(10)	B(7)–B(12)	1.782(16)	Rh(2)–Te(1)–B(6)	54.4(3)	Te(1′)–Rh(2′)–B(6′)	57.8(4)
Te(1)–B(4)	2.293(12)	B(8)–B(9)	1.772(15)	B(3)–Te(1)–B(4)	50.4(4)	Te(1′)–Rh(2′)–H(11)	99.82(4)
Te(1)–B(5)	2.287(13)	B(8)–B(12)	1.764(17)	B(3)–Te(1)–B(6)	84.0(4)	Rh(2)–Rh(2′)–P′	117.75(6)
Te(1)–B(6)	2.357(13)	B(9)–B(10)	1.780(18)	B(4)–Te(1)–B(5)	47.7(4)	Rh(2)–Rh(2′)–B(11)	48.4(3)
Te(1′)–Rh(2′)	2.581 1(10)	B(9)–B(12)	1.740(19)	B(5)–Te(1)–B(6)	47.6(5)	Rh(2)–Rh(2′)–B(6′)	87.1(4)
Te(1′)–B(3′)	2.338(11)	B(10)–B(11)	1.806(17)	Rh(2′)–Te(1′)–B(3′)	55.2(3)	Rh(2)–Rh(2′)–B(11′)	54.3(3)
Te(1′)–B(4′)	2.282(14)	B(10)–B(12)	1.770(14)	Rh(2′)–Tel(1′)–B(6′)	54.3(3)	Rh(2)–Rh(2′)–H(11)	79.45(4)
Te(1′)–B(5′)	2.322(13)	B(11)–B(12)	1.775(16)	B(3′)–Te(1′)–B(4′)	48.8(4)	P′–Rh(2′)–B(3′)	87.9(3)
Te(1′)–B(6′)	2.356(14)	B(11)–H(11)	1.355(13)	B(3′)–Te(1′)–B(6′)	83.9(5)	P′–Rh(2′)–B(6′)	152.1(3)
Rh(2)–Rh(2′)	2.834 4(12)	B(3′)–B(4′)	1.910(16)	B(4′)–Te(1′)–B(5′)	48.1(5)	P′–Rh(2′)–B(11′)	156.9(3)
Rh(2)–P	2.478(3)	B(3′)–B(7′)	1.780(19)	B(5′)–Te(1′)–B(6′)	49.1(5)	P′–Rh(2′)–H(11)	84.08(8)
Rh(2)–B(3)	2.312(12)	B(3′)–B(8′)	1.717(17)	Te(1)–Rh(2)–Rh(2′)	142.70(4)	B(11)–Rh(2′)–B(3′)	173.9(4)
Rh(2)–B(6)	2.280(11)	B(4′)–B(5′)	1.875(20)	Te(1)–Rh(2)–P	96.31(8)	B(11)–Rh(2′)–B(11′)	91.8(4)
Rh(2)–B(7)	2.218(10)	B(4′)–B(8′)	1.742(17)	Te(1)–Rh(2)–B(3)	57.1(3)	B(3′)–Rh(2′)–B(6′)	87.2(5)
Rh(2)–B(11)	2.169(12)	B(4′)–B(9′)	1.761(20)	Te(1)–Rh(2)–B(6)	57.2(3)	B(3′)–Rh(2′)–B(7′)	46.9(5)
Rh(2)–B(11′)	2.354(12)	B(5′)–B(6′)	1.945(19)	Te(1)–Rh(2)–B(11′)	124.2(3)	B(6′)–Rh(2′)–B(11′)	48.7(4)
Rh(2)–H(11′)	1.36	B(5′)–B(9′)	1.735(18)	Te(1)–Rh(2)–H(11′)	97.77(4)	B(7′)–Rh(2′)–B(11′)	48.6(4)
Rh(2′)–P′	2.404(3)	B(5′)–B(10′)	1.737(20)	Rh(2′)–Rh(2)–P	120.15(8)	Te(1)–B(3)–B(7)	116.5(6)
Rh(2′)–B(11)	2.341(13)	B(6′)–B(10′)	1.760(18)	Rh(2′)–Rh(2)–B(6)	85.5(3)	Rh(2)–B(3)–B(4)	114.7(6)
Rh(2′)–B(3′)	2.287(14)	B(6′)–B(11′)	1.822(16)	Rh(2′)–Rh(2)–B(11)	53.8(3)	B(3)–B(4)–B(5)	108.6(9)
Rh(2′)–B(6′)	2.263(11)	B(7′)–B(8′)	1.795(18)	Rh(2′)–Rh(2)–B(11′)	47.9(3)	B(4)–B(5)–B(6)	111.0(8)
Rh(2′)–B(7′)	2.177(12)	B(7′)–B(11′)	1.781(16)	Rh(2′)–Rh(2′)–H(11′)	79.67(4)	Te(1)–B(6)–B(11)	115.9(6)
Rh(2′)–B(11′)	2.153(11)	B(7′)–B(12′)	1.776(16)	P–Rh(2)–B(3)	85.8(3)	Rh(2)–B(6)–B(5)	117.7(6)
Rh(2′)–H(11)	1.41	B(8′)–B(9′)	1.774(15)	P–Rh(2)–B(6)	151.7(3)	B(3)–B(7)–B(11)	110.5(8)
B(3)–B(4)	1.983(17)	B(8′)–B(12′)	1.774(20)	P–Rh(2)–B(11)	157.0(3)	B(6)–B(11)–B(7)	112.2(8)
B(3)–B(7)	1.820(19)	B(9′)–B(10′)	1.808(20)	P–Rh(2)–B(11′)	98.5(3)	Te(1′)–B(3′)–B(7′)	116.8(7)
B(3)–B(8)	1.727(18)	B(9′)–B(12′)	1.766(17)	P–Rh(2)–H(11′)	84.37(7)	Rh(2′)–B(3′)–B(4′)	117.1(7)
B(4)–B(5)	1.852(16)	B(10′)–B(11′)	1.785(15)	B(3)–Rh(2)–B(6)	86.9(4)	B(3′)–B(4′)–B(5′)	108.9(9)
B(4)–B(8)	1.741(17)	B(10′)–B(12′)	1.810(16)	B(3)–Rh(2)–B(7)	47.3(5)	B(4′)–B(5′)–B(6′)	109.4(8)
B(4)–B(9)	1.738(18)	B(11′)–B(12′)	1.783(18)	B(3)–Rh(2)–B(11′)	175.2(4)	Te(1′)–B(6′)–B(11′)	114.1(7)
B(5)–B(6)	1.876(20)	B(11′)–H(11′)	1.399(12)	B(6)–Rh(2)–B(11)	47.9(4)	B(3′)–B(7′)–B(11′)	111.4(8)
B(5)–B(9)	1.767(17)	Cl(1)–C	1.55(4)	B(7)–Rh(2)–B(11)	49.5(4)	B(6′)–B(11′)–B(7′)	112.9(9)
B(5)–B(10)	1.748(20)	Cl(2)–C	1.89(3)	B(11)–Rh(2)–B(11′)	91.1(4)	Cl(1)–C–Cl(2)	113(2)
B(6)–B(10)	1.755(17)	Cl(2*)–C*	1.50(5)	Te(1′)–Rh(2′)–Rh(2)	144.77(4)	Rh(2′)–H(11)–B(11)	115.7(5)
B(6)–B(11)	1.810(16)			Te(1′)–Rh(2′)–P′	97.00(7)	Rh(2)–H(11′)–B(11′)	117.1(4)
B(7)–B(8)	1.789(19)			Te(1′)–Rh(2′)–B(11)	126.9(2)	Rh(2′)–B(6′)–B(5′)	116.4(7)

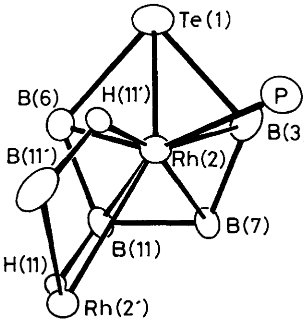
The atoms C* and Cl(2)* are disordered atoms in the CH_2Cl_2 molecule of solvation, see Table 7 for details.

Table 3. Intercage section distances (Å)

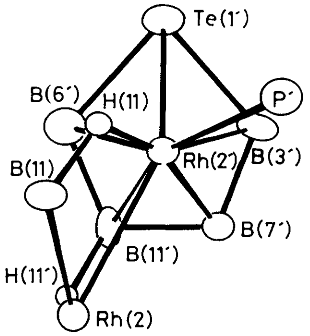
	Compound			
Distance	(2)	(3)	(4; R = Ph)	(4; R = Et)
Rh(2)–Rh(2′)	2.737 1(3)	2.834 4(12)	2.763(1)	2.791(1)
Rh(2)–B(11′)	2.380(4)	2.354(12)	2.327(8)	2.257(7)
Rh(2′)–B(11)	2.329(4)	2.341(13)	2.238(8)	2.273(7)
Range of cage Rh–B lengths	2.151(4) 2.308(4)	2.153(13) 2.312(12)	2.173(8) 2.221(8)	2.170(7) 2.211(7)
Rh(2)–H(11′)	1.63	1.36	1.78(6)	1.656
Rh(2′)–H(11)	1.58	1.41	1.77(6)	1.653
B(11)–H(11)	1.30	1.36	*	*
B(11′)–H(11′)	1.40	1.40	*	*

* Not reported in ref. 3.

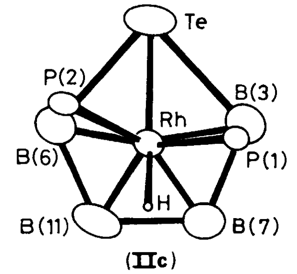
above the TeB_4 ring to which it is attached differs from that observed in the mononuclear complex (**1**). The conformations in (**3**) and (**1**) are shown in (**IIa**), (**IIb**), and (**IIc**) respectively for comparison. Both the Rh(2) phosphine unit and the Rh(2′) carbonyl unit in (**2**) adopt conformations which are closely similar to those in (**IIa**) and (**IIb**). The rhodium to cage configuration in (**2**) and (**3**) is more similar to that in the cycloboronated complex *closo*-$[2\text{-}(PPh_3)\text{-}2\text{-}H\text{-}2\text{-}(Ph_2PC_6H_4)\text{-}1,2\text{-}TeRhB_{10}H_9]$[17] than in (**1**) although it should be noted that the metal-to-cluster bonding in (**1**) is probably rotationally readily fluxional so that the metal-to-cluster bonding energies will be very similar whatever the rotational configurations. As a consequence of the rhodium–rhodium and Rh–H–B bonds relatively few geometrical isomers of (**2**) or (**3**) could be



(**IIa**)



(**IIb**)



(**IIc**)

Table 4. Measured n.m.r. properties for [(PPh$_3$)(CO)Rh$_2$Te$_2$B$_{20}$H$_{20}$] (**2**), [{(PPh$_3$)RhTeB$_{10}$H$_{10}$}$_2$] (**3**), and [(PPh$_3$)$_2$HRhTeB$_{10}$H$_{10}$] (**1**)

	Compound (**2**)[a]		Compound (**3**)[b]		Compound(**1**)[c,d]		
Assignment	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	Assignment
(11)[e]	$+33.0^{f}$	-7.65^{g}	$+26.5^{h}$	-7.28^{i}	—	—	—
	$+27.2^{j}$	-6.39^{k}			+8.3	+4.57	(7,11)[e]
(7,9,12)[e]	+18.6	+5.60					
	+17.7	+3.34	+17.0	+3.80	+19.3	+5.58	(12)[e]
	+11.5	+5.05	+9.0	+4.66			
	+10.5	+4.84	+6.0	+4.47	+14.6	+5.14	(9)[e]
	+7.6	+4.51					
	+6.0	+3.59					
(3,6)[l]	+13.3	+3.26	*ca.* +11.1	+3.03	+10.9	$+2.74^{m}$	(3,6)[l]
	ca. +5.7	+2.47	+0.8	$+2.02^{o}$			
	+3.5	$+2.15^{n}$					
	−0.1	+2.73					
(8,10)[e]	−7.0	+3.09					
	−8.0	+3.35	−9.7	+2.75	−12.9	+2.32	(8,10)[e]
	−15.5	+2.47	−16.0	+2.41			
	−16.7	+2.50					
(4,5)[f]	*ca.* −12.0	+2.56					
	−12.5	+2.32	*ca.* −14.5	+1.92			
	ca. −16.3	+2.11	*ca.* −17.7	+1.88	−14.4	+2.30	(4,5)[f]
	ca. −17.5	+2.19					

[a] $\delta(^{31}P)$ +26.1 p.p.m., $^{1}J(^{103}Rh-^{31}P)$ 118 Hz. [b] $\delta(^{31}P)$ +21.7 p.p.m., $^{1}J(^{103}Rh-^{31}P)$ 124 Hz. [c] Data from ref. 19. [d] $\delta(^{31}P)$ +29.1 p.p.m., $^{1}J(^{103}Rh-^{31}P)$ 97 Hz; ^{31}P data measured at 213 K. [e] (7,11), (8,10), (9), and (12) ^{11}B resonances sharper than the (3,6) and (4,5) ones. [f] $^{1}J(^{11}B-^{1}H)$ *ca.* 83 Hz. [g] Apparent 1:2:1 triplet $[J(^{103}Rh-^{1}H) + J(^{31}P-^{1}H)]/2$ *ca.* 15 Hz (mean value). [h] $^{1}J(^{11}B-^{1}H)$ *ca.* 82 Hz. [i] Apparent 1:2:1 triplet, $[J(^{103}Rh-^{1}H) + J(^{31}P-^{1}H)]/2$ *ca.* 17 Hz (mean value). [j] $^{1}J(^{11}B-^{1}H)$ *ca.* 75 Hz. [k] Doublet, 1:1, $J(^{103}Rh-^{1}H)$ 20.5 Hz. [l] (3,6) and (4,5) ^{11}B resonances broader than the (7,11), (8,10), (9), and (12) ones. [m] Doublet structure, $^{4}J(^{31}P-^{1}H)$ *ca.* 14.5 Hz. [n] Doublet structure, $^{4}J(^{31}P-^{1}H)$ *ca.* 13 Hz. [o] Possible doublet structure.

envisaged. However, it is not entirely clear why the single isomers obtained in this work should be formed so stereoselectively.

It is of interest that the Rh–C bond distance of the carbonyl ligand to rhodium in compound (**2**) is long [1.945(4) Å] compared with the reported value for Rh–C in *closo*-[3-(PPh$_3$)-3-(CO)-4-(py)-3,1,2-RhC$_2$B$_9$H$_{10}$] (**5**) (py = pyridine) [1.795(6) Å]. Concomitantly, the C–O distance in (**2**) is short [1.122(5) Å] and this correlates with the relatively high CO stretching frequency (2 062 cm^{-1}). Even higher values of ν_{CO} (2 088 cm^{-1}) were reported for the *closo*-[3-(PPh$_3$)-3-(CO)-3-X-3,1,2-RhC$_2$B$_9$H$_{11}$] complexes (X = Cl or NO$_3$), whereas lower values were observed for a series of mutually isomeric anions *closo*-[(PPh$_3$)(CO)RhC$_2$B$_9$H$_{11}$]$^-$,[18] for example for the 3,1,2-RhC$_2$ isomer ν_{CO} was 1 910 cm^{-1}.

The tellurium atoms in compound (**2**) (Table 1) and (**3**) (Table 2) are bonded in essentially the same manner as in the *closo* complex [2,2-(PPh$_3$)$_2$-2-H-1,2-TeRhB$_{10}$H$_{10}$], (**1**),[19] *i.e.* by two shorter interactions to boron atoms B(4), B(5) [2.296(4) and 2.300(4) Å in (**1**)] and two longer interactions to B(3), B(6) [2.374(5) and 2.399(4) Å in (**1**)]. Likewise the rhodium atom in (**1**) has been found to bond with shorter equal-length interactions to B(7), B(11) of 2.238(4) and 2.239(4) Å and longer interactions to B(3), B(6) of 2.333(5) and 2.317(4) Å respectively which are not significantly different. In comparison the rhodium atoms in (**2**) and (**3**) are also bonded with two shorter and two longer interactions to the cages but in a much less symmetrical fashion. For example in (**2**) (Table 1) the rhodium atom bearing the phosphine ligand has longer interactions to B(3), B(6) [2.308(4) and 2.283(4) Å], which are not significantly different at the 3σ level, but the two shorter interactions to B(7), B(11) [2.226(4) and 2.151(4) Å] are significantly different. The carbonyl-bonded rhodium atom experiences a similarly distorted environment with longer interactions to B(3′), B(6′) [2.272(4) and 2.268(4) Å] and non-equivalent shorter interactions to B(7′), B(11′) [2.202(4) and 2.165(4) Å]. Analogous effects are observed in (**3**) (Table 2). The reduction in rhodium–tellurium distance of 2.617 2(4) Å in compound (**1**) to 2.565 3(3) and 2.581 7(3) Å in (**2**) or 2.581 1(10) and 2.604 7(12) Å in (**3**) correlates with the removal of the strongly *trans*-influencing H ligand on formation of (**2**) and (**3**). Rhodium–phosphorus bonding distances in (**2**) and (**3**) are not unusual. The value in (**2**), 2.423(1) Å, is intermediate between the values in (**3**) [2.478(3) and 2.404(3) Å]. The ranges of boron–boron distances in (**2**) and (**3**) [1.739(7)—1.945(6) and 1.717(17)—1.983(17) Å respectively] are large but not at all uncommon for metallaboranes and -heteroboranes.[20]

The measured ^{11}B, ^{1}H, and ^{31}P n.m.r. properties of compounds (**2**) and (**3**) (Table 4) were consistent with the binuclear structures, and the overall ^{11}B shielding patterns, as mentioned above, were closely similar to those observed for the mononuclear *closo*-[2,2-(PPh$_3$)$_2$-2-H-1,2-TeRhB$_{10}$H$_{10}$] species (**1**) (see Figure 4).[19] With appropriate experiments (see below) twenty different ^{11}B resonance positions could be discerned for the asymmetric compound (**2**), with an agglomerate of twelve resonances to lower field, corresponding to the two sets (primed and unprimed in Figure 1) of (3,6), (7,11), (9), and (12) positions, and eight at higher field, corresponding[19] to the two sets of (4,5) and (8,10) positions. The ^{11}B n.m.r. spectra of the symmetrical compound (**3**) were somewhat broader, due to the larger molecular size,[19] but were nevertheless simpler because only ten resonance positions were of course observed. These were also grouped into two agglommerates, corresponding to the (3,6), (7,11), (9), (12), (4,5), and (8,10) positions. Within these agglomerates it was apparent for each compound that some signals were substantially broader than others, the broad ones

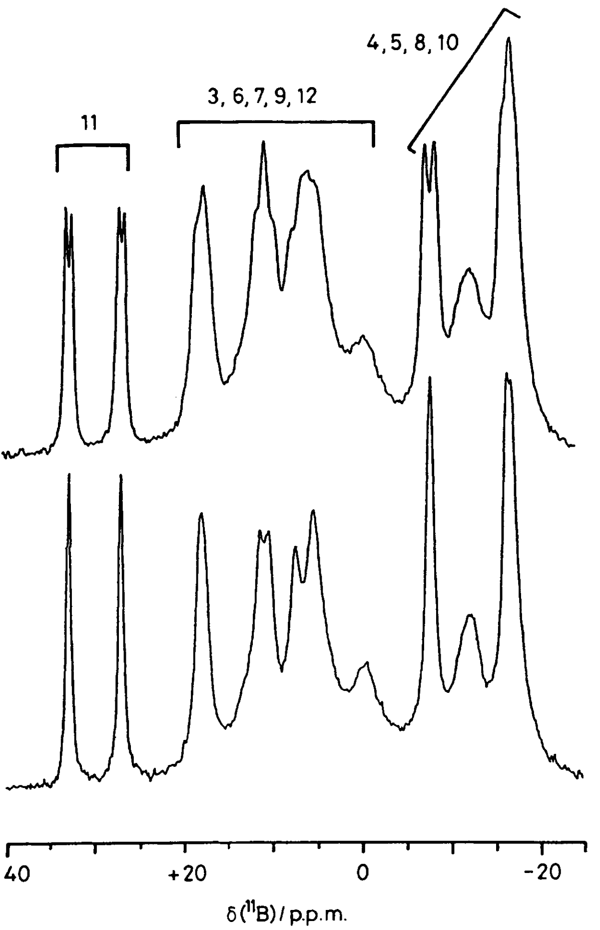


Figure 3. 128-MHz ^{11}B (top) and ^{11}B-{^{1}H(broad-band noise)} n.m.r. spectra (bottom) for the asymmetric dinuclear species $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$ (**2**) in CD_2Cl_2 solution at 294 K

being assignable to the ^{11}B (3,4,5, and 6) positions flanking the tellurium atom which are known from the studies on the mononuclear species to have substantially shorter ^{11}B relaxation times than the others. Although further assignment of individual resonances to precise particular positions is not feasible, these considerations nevertheless enable their assignment for each compound into four positional groups *i.e.* [(3,6)], [(7,11)(9)(12)], [(4,5)], and [(8,10)].

For the asymmetric compound (**2**) the two resonances at extreme lowest field in the [(7,11)(9)(12)] grouping appear to be somewhat sharper than the others, and are characterised by lower coupling constants $^{1}J(^{11}B-^{1}H)$. These resonances are readily assignable to the ^{11}B(11) and ^{11}B(11′) positions associated with the Rh–H–B linkages, with a specific assignment between these two positions arising from the incidence of a coupling $^{2}J(^{31}P-^{1}H)$ of *ca.* 11 Hz to the ^{11}B ^{1}H(11′) proton but not to the ^{11}B ^{1}H(11) proton. In the symmetrical dimer (**3**) only one such bridging proton resonance is observed; this exhibits coupling $^{2}J(^{31}P-^{1}H)$ because each monomer unit has a phosphine ligand associated with it.

For each of compounds (**2**) and (**3**) much of the 128-MHz ^{11}B n.m.r. spectrum was too closely packed for the individual resonance positions to be distinguished satisfactorily by inspection [see Figure 3 for (**2**)], but the deviations from linear correlation between δ(^{11}B) and δ(^{1}H) for the individual {BH} units gave sufficient dispersion at 9.4 T for each unit to be resolved in a δ(^{11}B):δ(^{1}H) correlation matrix so that ^{1}H-{^{11}B(selective)} n.m.r. spectroscopy was able to resolve both the ^{11}B and ^{1}H chemical shift positions whilst assigning the ^{1}H resonances to their directly bound boron atoms. With these ^{1}H-{^{11}B(selective)} experiments it was possible to confirm and distinguish the hidden and/or overlapping broader ^{11}B resonances as being broad, by (*a*) their less-intense ^{1}H sharpening responses when ν(^{11}B) was exactly on resonance, and by (*b*) their correspondingly greater ^{1}H responses, compared to those associated with sharper ^{11}B resonances, when ν(^{11}B) was somewhat off-resonance. The identification of the broader resonances is useful in the positional assignments as discussed above.

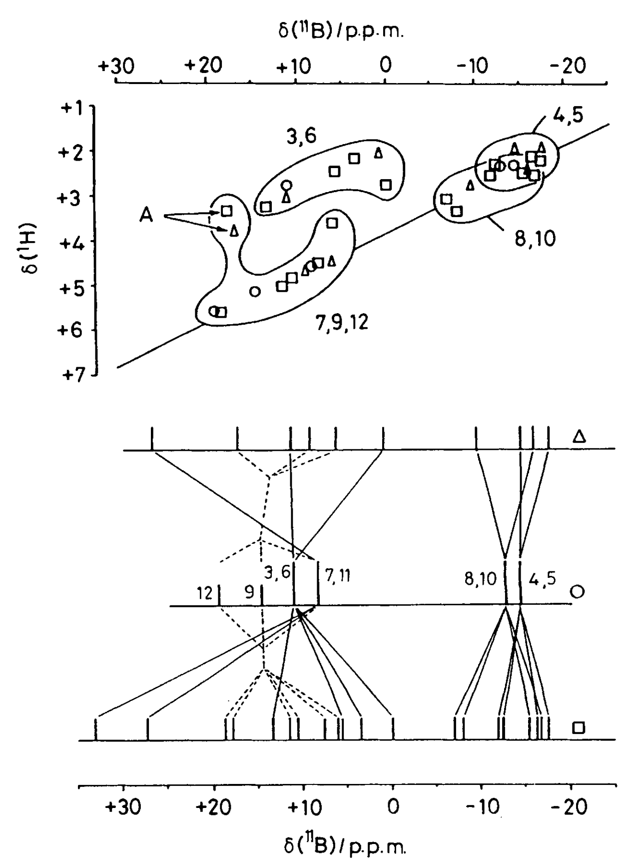


Figure 4. N.m.r. data for the dinuclear species $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$ (**2**) and $[\{(PPh_3)RhTeB_{10}H_{10}\}_2]$ (**3**), together with those of their monomeric precursor $[(PPh_3)_2HRhTeB_{10}H_{10}]$ (**1**).[19] The uppermost diagram shows a plot of δ(^{11}B) *versus* δ(^{1}H) for directly bound BH(*exo*) units [○, compound (**1**); □, (**2**); △, (**3**)]. The line drawn has gradient δ(^{11}B):δ(^{1}H) 10:1, intercept +3.75 in δ(^{1}H) (compare ref. 19). For an explanation of points A see text. The lower diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B n.m.r. spectra of the three compounds. Lines join equivalent positions in the four different {*closo*-$RhTeB_{10}H_{10}$} subclusters involved [so far as can be defined; the hatched connections indicate the uncertainty among some of the (7), (9), and (12) assignments]

The measured n.m.r. data for compounds (**2**) and (**3**) are presented in Table 4, and the ^{11}B and ^{1}H results are presented graphically in Figure 4. Compound (**1**) is also included for comparison. As mentioned above, it can be seen that the overall ^{11}B and ^{1}H shielding behaviour is very similar to that observed for the monomeric *closo*-$[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}1,2\text{-}TeRhB_{10}H_{10}]$ (**1**). The principal deviations from (**1**) for each compound are (*a*) for the (3,6) positions, which are quite spread out (but note that these are not only adjacent to the intracluster linkage but are also known to be considerably affected by ligand variation on the Rh atom in these *closo*-2,1-$RhTeB_{10}$ species),[19] and (*b*) for the unique point A, one of the (7)(9)(12) positions, which is some

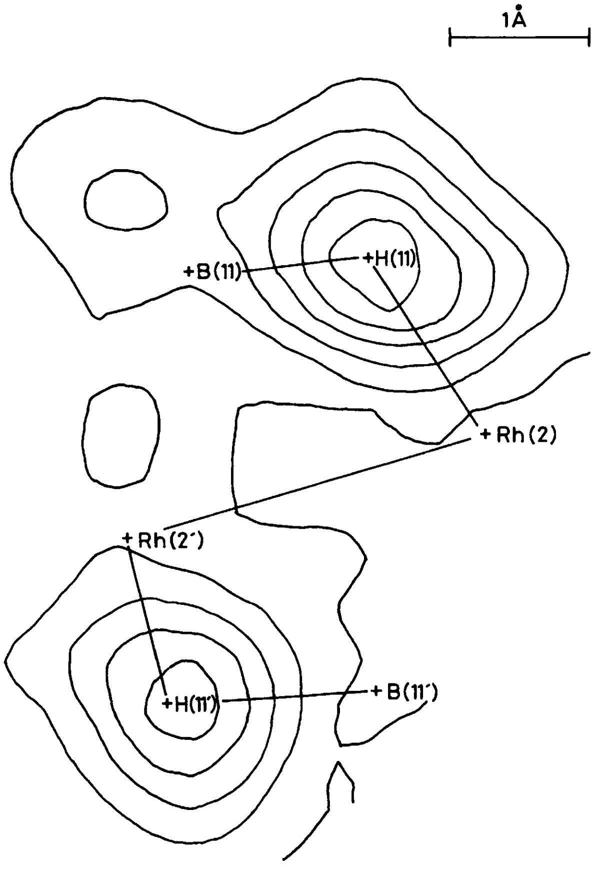


Figure 5. A section of the difference map calculated in the B(11')H(11)-H(11') plane in the compound $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$, (2), showing the bridging H atoms. Contours are at approximately 0.1 e Å^{-3}

2 p.p.m. in $\delta(^1H)$ more shielded than its fellows. That only one of these BH units in (2) is, whereas two in (3) are, so affected, is of some significance, and may indicate it is assignable to B(7') or B(12') [rather than B(9')] because the former two are in the shielding core of the PPh groups on the opposing cluster (unprimed, Figure 1).

Experimental

General.—All experiments and recrystallisations were carried out in an inert atmosphere.[19] The compounds $Cs[TeB_{10}H_{11}]$, $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}1,2\text{-}TeRhB_{10}H_{10}]$,[19] $[Rh(cod)(PPh_3)Cl]$,[21] and $[Os_3H_2(CO)_{10}]$[22] were prepared by literature methods and $[Mo(CO)_6]$ was purchased from Alfa-Ventron Inc. and used as supplied. Infrared spectra were recorded as KBr discs on Perkin-Elmer 682 or Mattson Polaris FT spectrometers.

Reactions of $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}1,2\text{-}TeRhB_{10}H_{10}]$ (1).—*With* $[Os_3H_2(CO)_{10}]$. Compound (1) (0.114 g, 0.13 mmol) was added to a solution of $[Os_3H_2(CO)_{10}]$ (0.098 g, 0.13 mmol) in CH_2Cl_2 (30 cm^3). The mixture was stirred at room temperature for 3 d then heated to reflux for 20 h. It was concentrated under reduced pressure (rotary film evaporator, 25 °C). Preparative t.l.c. on silica gel (Merck, Kieselgel 60, PF 254) with benzene–light petroleum (b.p. 60—80 °C) (2:3) produced ten bands. Five bands were isolated and the compounds extracted into CH_2Cl_2. Infrared spectroscopic analysis showed only one compound, the major component, to exhibit BH absorptions. Recrystallisation from CH_2Cl_2–cyclohexane afforded dark purple *crystals* of $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$, (2) (0.045 g, 45.7%). I.r.: $\nu_{max.}$ 3 050w, 2 950w, 2 920m, 2 845w, 2 540vs (BH), 2 062vs (CO), 1 870w, 1 845w, 1 825w, 1 770w, 1 750vw, 1 715m, 1 700w, 1 685w, 1 650vw, 1 635vw, 1 572w, 1 555w, 1 540w, 1 505w, 1 475m, 1 455w, 1 430s, 1 370vw, 1 360vw, 1 280w, 1 180w, 1 155w, 1 115vw, 1 090m, 1 075vw, 1 020vw, 985s, 900m, 855vw, 745s, 720vw, 692s, 665vw, 650vw, and 635vw cm^{-1}. Proton and ^{11}B n.m.r. data are given in Table 4.

With $[Mo(CO)_6]$. Compound (1) (0.085 g, 0.097 mmol) was added to a solution of $[Mo(CO)_6]$ (0.026 g, 0.097 mmol) in thf (4 cm^3). The mixture was stirred at room temperature for 18 h. The solution was concentrated under reduced pressure (rotary film evaporator, 25 °C) and subjected to preparative t.l.c. on silica gel with CH_2Cl_2–hexane (4:1) as eluant. The only major component was extracted into CH_2Cl_2. Recrystallisation from CH_2Cl_2 gave dark purple *crystals* of $[\{(PPh_3)RhTeB_{10}H_{10}\}_2]\cdot CH_2Cl_2$, (3)·$CH_2Cl_2$ (0.021 g, 33.1%). I.r.: $\nu_{max.}$ 3 040w, 2 550vs (BH), 2 515vs (BH), 2 060vw (Rh–μH), 1 580vw, 1 568vw, 1 473m, 1 429s, 1 310w, 1 259w, 1 180w, 1 155vw, 1 090m, 1 022vw, 990s, 898m, 855w, 738s, and 692s cm^{-1}. Proton and ^{11}B n.m.r. data are given in Table 4.

Crystal Structure Analyses for Compounds (2) *and* (3).—*Crystal data.* $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$, (2). $C_{19}H_{35}B_{20}OPRh_2Te_2$, $M = 987.69$, monoclinic, $a = 16.213(4)$, $b = 13.082(4)$, $c = 17.048(3)$ Å, $\beta = 95.29(2)°$, $U = 3\,601$ Å^3, $Z = 4$, $D_c = 1.82$ g cm^{-3}, $F(000) = 1\,864$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 25.6$ cm^{-1}, space group $P2_1/c$ determined uniquely from systematic absences ($0k0$ absent if $k = 2n + 1$; $h0l$ absent if $l = 2n + 1$).

$[\{(PPh_3)RhTeB_{10}H_{10}\}_2]\cdot CH_2Cl_2$, (3)·$CH_2Cl_2$. $C_{37}H_{52}B_{20}Cl_2P_2Rh_2Te_2$, $M = 1\,306.91$, monoclinic, $a = 16.384(5)$, $b = 16.197(6)$, $c = 19.879(5)$ Å, $\beta = 70.84(2)°$, $U = 4\,983$ Å^3, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 2\,528$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 19.3$ cm^{-1}, space group $P2_1/a$ determined uniquely from systematic absences ($0k0$ absent if $k = 2n + 1$; $h0l$ absent if $h = 2n + 1$).

Structure determinations. Both compounds (2) and (3) were analyzed in a similar way (details of data collection and structure determination are summarised in Table 5). Dark purple crystals of (2) and (3) were grown from CH_2Cl_2. Accurate cell dimensions and the crystal orientation matrix were determined by a least-squares treatment of 25 reflections. Data were collected on a CAD4 diffractometer using graphite-monochromated Mo-K_α radiation. Intensities of three reflections measured every 2 h showed no decay. Data were corrected for Lorentz, polarisation and absorption effects.

The co-ordinates of the heavy atoms were determined from analysis of the three-dimensional Patterson functions and those of the remaining non-hydrogen atoms were found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of most of the hydrogen atoms. For compound (3) a difference Fourier map calculated at this stage also revealed the position of a disordered CH_2Cl_2 solvate molecule. The co-ordinates of the bridging hydrogen atoms bonded to rhodium atoms were obtained from difference maps calculated near the conclusion of the refinements (see Figure 5), and in the final rounds of calculations other hydrogen atoms were positioned on geometrical grounds (C–H 0.95, B–H 1.10 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 5.0 Å^2 for (2) [4.7 Å^2 for phenyl hydrogens and 3.7 Å^2 for other hydrogens for (3)·CH_2Cl_2]. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.050(F_o)^2]$. There were no chemically significant features in the final difference maps. Scattering factors and anomalous dispersion corrections were taken from ref. 23. All calculations were performed on a

Table 5. Details of data collection and refinement

	(**2**)	(**3**)·CH_2Cl_2
Crystal size (mm)	0.48 × 0.51 × 0.13	0.11 × 0.28 × 0.28
Range of reflections from which cell data were calculated (°)	$12 < \theta < 15$	$10 < \theta < 13$
hkl collected	*h* 0—20	0—18
	k 0—16	0—18
	l −21 to 21	−22 to 22
Scan type	ω—2θ	ω—2θ
Scan width	0.70 + 0.35tanθ	0.70 + 0.35tanθ
2θ limits (°)	2—54	2—46
Reflections collected	8 417	7 439
Independent reflections	7 846	6 892
Observed reflections [$I > 3\sigma(I)$]	5 992	3 973
Max. and min. transmission factors	0.717, 0.314	0.835, 0.597
Least-squares parameters	407	560
R	0.028	0.039
R'	0.037	0.046
Goodness of fit	1.40	1.26
Max. shift/error	<0.01	<0.01
Max. Δ(ρ) (e Å^{-3})	±1.16(10)	±0.81(12)

Table 6. Positional parameters and their estimated standard deviations for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Te(1)	0.222 00(2)	0.375 44(3)	−0.061 04(2)	C(36)	0.264 9(3)	0.625 8(6)	−0.120 4(3)
Te(1′)	0.049 91(2)	0.394 97(2)	0.307 59(2)	B(3)	0.338 9(3)	0.378 8(4)	0.033 8(3)
Rh(2)	0.222 20(2)	0.452 80(2)	0.077 25(2)	B(4)	0.320 0(3)	0.252 6(4)	−0.025 2(3)
Rh(2′)	0.173 01(2)	0.430 29(2)	0.225 60(2)	B(5)	0.209 3(3)	0.209 8(5)	−0.018 0(3)
P	0.281 48(6)	0.616 23(8)	0.046 07(6)	B(6)	0.153 5(3)	0.304 6(4)	0.043 6(3)
O(1)	0.331 6(2)	0.446 1(3)	0.337 3(2)	B(7)	0.321 3(3)	0.350 7(4)	0.131 9(3)
C(1)	0.274 7(3)	0.434 0(4)	0.295 7(3)	B(8)	0.367 5(3)	0.259 0(4)	0.071 2(3)
C(11)	0.210 0(3)	0.724 7(3)	0.041 2(2)	B(9)	0.292 6(4)	0.161 0(4)	0.044 1(4)
C(12)	0.136 2(3)	0.720 5(3)	−0.005 9(2)	B(10)	0.198 4(3)	0.192 6(4)	0.083 0(4)
C(13)	0.083 1(3)	0.803 5(4)	−0.013 3(3)	B(11)	0.216 1(3)	0.309 2(4)	0.137 9(3)
C(14)	0.102 0(3)	0.890 8(4)	0.028 7(3)	B(12)	0.296 3(3)	0.218 2(4)	0.138 6(4)
C(15)	0.173 0(4)	0.895 6(4)	0.079 0(3)	B(3′)	0.127 7(3)	0.548 6(4)	0.309 2(3)
C(16)	0.227 6(3)	0.811 7(4)	0.085 0(3)	B(4′)	0.007 9(3)	0.561 7(4)	0.306 0(3)
C(21)	0.371 3(3)	0.660 5(3)	0.109 3(3)	B(5′)	−0.042 9(3)	0.482 9(4)	0.222 7(3)
C(22)	0.390 2(3)	0.614 8(4)	0.181 0(3)	B(6′)	0.041 4(3)	0.417 1(4)	0.168 7(3)
C(23)	0.457 6(4)	0.651 5(5)	0.229 5(3)	B(7′)	0.155 1(3)	0.596 7(3)	0.214 8(3)
C(24)	0.503 6(4)	0.731 3(6)	0.206 9(4)	B(8′)	0.072 2(3)	0.651 5(4)	0.264 9(3)
C(25)	0.484 8(3)	0.775 0(5)	0.136 7(4)	B(9′)	−0.024 4(3)	0.614 3(4)	0.213 8(3)
C(26)	0.418 1(3)	0.742 8(4)	0.086 8(3)	B(10′)	−0.005 8(3)	0.530 4(4)	0.135 4(3)
C(31)	0.318 8(3)	0.615 6(4)	−0.052 2(3)	B(11′)	0.104 9(3)	0.519 5(3)	0.134 3(2)
C(32)	0.402 1(3)	0.595 7(4)	−0.062 0(3)	B(12′)	0.060 3(3)	0.637 8(4)	0.159 5(3)
C(33)	0.427 9(3)	0.583 7(5)	−0.135 8(3)	H(11)	0.1794	0.3136	0.2026
C(34)	0.372 1(4)	0.592 6(6)	−0.202 0(3)	H(11′)	0.1276	0.4948	0.0596
C(35)	0.291 4(4)	0.613 3(7)	−0.192 7(3)				

The co-ordinates of H(11) and H(11′) were determined from difference maps and were included in the calculations with a B_{iso} value of 5 Å^2.

PDP11/73 computer using SDP-Plus.[24] Atomic co-ordinates are listed in Tables 6 and 7 and principal details of the molecular geometry are given in Tables 1 and 2. Figures 1 and 2 are general views of the molecules prepared using ORTEP II.[25]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

Reaction of [Rh(cod)(PPh_3)Cl] *with* Cs[7-$TeB_{10}H_{11}$].—A mixture of [Rh(cod)(PPh_3)Cl] (0.13 g, 0.26 mmol) and Cs[$TeB_{10}H_{11}$] (0.10 g, 0.26 mmol) in absolute EtOH (60 cm^3) was stirred at room temperature for 24 h. The resulting solution was concentrated (rotary film evaporator, 25 °C) and subjected to preparative t.l.c. on silica gel with CH_2Cl_2 as eluant. The major band which was purple in colour was extracted into CH_2Cl_2 and recrystallised (0.020 g, 20.2%). This compound was characterised spectroscopically (i.r., n.m.r.) as (**2**).

N.M.R. Spectroscopy.—N.m.r. spectroscopy was performed at 9.4 T using commercially available instrumentation and techniques as described and exemplified by us in previous Parts of this series (see ref. 19). Chemical shifts δ are given in p.p.m. positive to higher frequency (lower nuclear shielding) from Ξ 100 ($SiMe_4$) for ^1H (quoted ±0.05 p.p.m.), Ξ 40.480 730 (nominally 85% H_3PO_4) for ^{31}P (quoted ±0.5 p.p.m.), and Ξ 32.083 971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 p.p.m.), Ξ being defined as in ref. 26. Data were recorded at 294—297 K for CD_2Cl_2 solutions unless otherwise indicated.

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Table 7. Positional parameters and their estimated standard deviations for compound (**3**)$\cdot CH_2Cl_2$

Atom	*x*	*y*	*z*
Te(1)	0.136 04(4)	0.032 41(5)	0.431 53(4)
Te(1′)	−0.182 71(4)	0.095 61(5)	0.261 13(4)
Rh(2)	0.094 33(5)	0.018 35(5)	0.316 38(4)
Rh(2′)	−0.021 91(5)	0.078 34(5)	0.249 08(4)
P	0.181 6(2)	−0.106 9(2)	0.270 4(1)
P′	0.036 3(2)	0.161 6(2)	0.144 0(1)
C(11)	0.279 7(6)	−0.100 6(7)	0.192 9(5)
C(12)	0.325 5(6)	−0.174 3(7)	0.164 7(5)
C(13)	0.402 2(7)	−0.168 6(8)	0.108 3(6)
C(14)	0.436 5(7)	−0.093 4(9)	0.079 8(6)
C(15)	0.393 8(8)	−0.022 8(9)	0.108 1(6)
C(16)	0.315 3(7)	−0.027 2(7)	0.163 6(6)
C(21)	0.133 2(6)	−0.203 1(6)	0.249 8(5)
C(22)	0.105 8(7)	−0.267 0(7)	0.297 7(6)
C(23)	0.068 0(7)	−0.336 8(7)	0.279 3(7)
C(24)	0.054 0(6)	−0.339 3(7)	0.214 5(6)
C(25)	0.082 2(7)	−0.277 3(7)	0.167 1(6)
C(26)	0.122 7(6)	−0.211 2(7)	0.182 9(5)
C(31)	0.222 4(6)	−0.142 5(6)	0.341 4(5)
C(32)	0.162 0(6)	−0.163 9(7)	0.407 8(5)
C(33)	0.191 2(7)	−0.190 8(7)	0.461 9(5)
C(34)	0.278 0(7)	−0.196 1(8)	0.452 4(6)
C(35)	0.336 6(7)	−0.175 0(9)	0.387 9(6)
C(36)	0.310 4(6)	−0.146 5(7)	0.332 0(5)
C(41)	0.131 1(6)	0.125 4(7)	0.073 4(5)
C(42)	0.172 7(6)	0.055 5(7)	0.081 3(5)
C(43)	0.241 3(7)	0.023 4(8)	0.024 0(6)
C(44)	0.269 3(8)	0.068 3(8)	−0.039 1(6)
C(45)	0.227 1(7)	0.138 5(8)	−0.047 4(5)
C(46)	0.160 3(6)	0.166 4(7)	0.007 6(5)
C(51)	0.059 6(6)	0.267 6(6)	0.164 3(5)
C(52)	0.137 0(6)	0.306 5(7)	0.131 1(6)
C(53)	0.153 7(7)	0.385 0(8)	0.150 5(6)
C(54)	0.090 8(8)	0.427 2(7)	0.200 6(7)
C(55)	0.012 6(8)	0.390 1(7)	0.233 9(6)
C(56)	−0.002 3(7)	0.309 4(7)	0.217 1(6)
C(61)	−0.035 6(6)	0.181 8(7)	0.090 4(5)
C(62)	−0.031 6(7)	0.128 1(7)	0.034 8(5)
C(63)	−0.086 1(6)	0.140 9(8)	−0.005 2(6)
C(64)	−0.143 4(6)	0.205 3(9)	0.010 9(6)
C(65)	−0.145 8(7)	0.258 1(8)	0.064 3(6)
C(66)	−0.094 7(7)	0.245 0(7)	0.105 5(6)
B(3)	0.222 4(7)	0.077 6(8)	0.317 2(6)
B(4)	0.210 8(8)	0.153 5(8)	0.398 1(6)
B(5)	0.094 5(8)	0.167 8(8)	0.447 9(6)
B(6)	0.026 0(7)	0.107 1(8)	0.406 3(6)
B(7)	0.166 4(7)	0.129 6(7)	0.263 9(6)
B(8)	0.226 1(7)	0.184 0(8)	0.310 8(6)
B(9)	0.154 9(7)	0.239 1(8)	0.383 4(6)
B(10)	0.047 2(7)	0.212 7(8)	0.389 7(6)
B(11)	0.052 1(7)	0.145 3(7)	0.316 1(6)
B(12)	0.128 7(7)	0.225 8(7)	0.306 1(6)
B(3′)	−0.088 6(8)	0.000 1(7)	0.186 6(7)
B(4′)	−0.202 0(8)	−0.039 4(9)	0.237 2(7)
B(5′)	−0.226 1(8)	−0.018 8(8)	0.334 6(7)
B(6′)	−0.129 9(7)	0.040 9(8)	0.348 7(7)
B(7′)	−0.016 2(7)	−0.052 3(8)	0.222 0(6)
B(8′)	−0.109 8(7)	−0.101 2(8)	0.211 7(7)
B(9′)	−0.188 3(7)	−0.113 9(8)	0.297 2(6)
B(10′)	−0.146 7(8)	−0.066 1(8)	0.361 5(6)
B(11′)	−0.040 1(7)	−0.030 7(7)	0.314 3(6)
B(12′)	−0.077 4(7)	−0.123 9(8)	0.286 5(7)
Cl(1)	0.046 1(6)	0.615 4(5)	0.473 8(4)
Cl(2)	0.112 4(6)	0.511 9(5)	0.562 2(5)
Cl(2*)	0.014(3)	0.561(2)	0.588(2)
C	0.124(2)	0.604(2)	0.501(2)
C*	−0.0306	0.5820	0.5350

Atom C was refined isotropically and the positional and thermal parameters of C* were fixed, Cl(2) and Cl(2*) are disordered chlorine atom sites with occupancies 0.8 and 0.2, C has occupancy 0.8 and C* has occupancy 0.2.

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