Metallaheteroborane Chemistry. Part 4.† The Synthesis of *closo*-[2,2-$(PPh_3)_2$-2-H-1,2-$XMB_{10}H_{10}$] (X = Se or Te, M = Rh or Ir) Compounds, their Characterisation by Nuclear Magnetic Resonance Techniques, and the Crystal and Molecular Structure of the X = Te, M = Rh Complex‡

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The reactions between [$M(PPh_3)_3Cl$] (M = Rh or Ir) and the *nido*-[7-$XB_{10}H_{11}$]$^-$ (X = Se or Te) anions in ethanol afford air-stable *closo*-[2,2-$(PPh_3)_2$-2-H-1,2-$XMB_{10}H_{10}$] complexes in moderate to high yields. N.m.r. data confirm the presence of the $M(PPh_3)_2H$ units and the *closo* nature of the metallaheteroboranes. An *X*-ray diffraction study of *closo*-[2,2-$(PPh_3)_2$-2-H-1,2-$TeRhB_{10}H_{10}$]·0.5-C_6H_{12} shows the triclinic crystals to belong to the $P\bar{1}$ space group with $Z = 2$ and cell dimensions $a = 12.406(1)$, $b = 17.872(4)$, $c = 10.010(1)$ Å, $\alpha = 94.30(1)$, $\beta = 107.25(1)$, and $\gamma = 94.31(1)$°. The final *R* factor was 0.033 for 5 380 observed reflections. Principal interatomic distances include Rh–Te 2.617 2(4), Rh–B 2.238(4)—2.333(5), and Te–B 2.296(4)—2.399(4) Å. The conformation of the $Rh(PPh_3)_2H$ unit above the TeB_4 face to which it is bonded has the Rh–H and Rh–Te vectors *trans* to each other. The conformational preferences of $M(PPh_3)_2H$ units in the new complexes and in electronically related metallacarbaboranes are discussed. The detailed n.m.r. properties indicate a close electronic relationship with the previously reported [2,2-$(PR_3)_2$-1,2-$XPtB_{10}H_{10}$] (X = Se or Te) species.

Apart from the metallacarbaborane compounds of the general formula [$(PR_3)_2M(H)R'_2C_2B_9H_9$] (M = Rh or Ir) which have been studied extensively by Hawthorne and co-workers,[2] there appear to be almost no contiguous cage-bonded rhodium or iridium heteroborane complexes in the literature. The thiaborane derivative [$(PPh_3)_2Rh(H)SB_{10}H_{10}$] was reported by Thompson and Rudolph[3] but its complete characterisation does not appear to have been published (possibly because of the untimely death of the senior author Professor R. W. Rudolph). As part of our developing and continuing interest in heteroboranes and their metal derivatives,[1,4–6] we decided to prepare some rhodium and iridium complexes of the $XB_{10}H_{10}$ ligands (X = Se or Te). Here we describe the moderate to high yield syntheses of the compounds [2,2-$(PPh_3)_2$-2-H-1,2-$XMB_{10}H_{10}$] [X = Se, M = Rh (**1**) or Ir (**2**); X = Te, M = Rh (**3**) or Ir (**4**)], and their characterisation by spectroscopic and, for (**3**), *X*-ray diffraction methods.

Results and Discussion

Reaction between [$M(PPh_3)_3Cl$] (M = Rh or Ir) and M′[7-$XB_{10}H_{11}$] (M′ = Cs or $NHEt_3$, X = Se or Te) in methyl or ethyl alcohol at room temperature for 1—3 d afforded the complexes [2,2-$(PPh_3)_2$-2-H-1,2-$XMB_{10}H_{10}$] according to equation (1). The complexes precipitated as air-stable yellow

$$[M(PPh_3)_3Cl] + M'[XB_{10}H_{11}] \longrightarrow [(PPh_3)_2M(H)XB_{10}H_{10}] + M'Cl + PPh_3 \quad (1)$$

powders from the reaction mixtures. Recrystallisation from MeOH–CH_2Cl_2 then gave yellow crystalline solids in 30—90% yields.

The i.r. spectra of (**1**)—(**4**) all showed characteristic M–H terminal stretching modes [2 080 (**1**), 2 200 (**2**), 2 045 (**3**), and 2 170 cm^{-1} (**4**)] and strong B–H absorptions [2 590, 2 530 (**1**); 2 580, 2 530 (**2**); 2 555, 2 525 (**3**); and 2 560, 2 520 cm^{-1} (**4**)]. The former may be compared with absorptions due to the Rh–H mode found in the electronically related metallacarbaboranes of the general type *closo*-[$(PR_3)_2Rh(H)C_2B_9H_{10}R$] which are usually[7] in the range 2 030—2 170 cm^{-1} although Rh–H frequencies have been found below 2 000 cm^{-1} in, for example, *closo*-[1,2-$(Me)_2$-3,3-$(PEt_3)_2$-3-H-3,1,2-$RhC_2B_9H_9$] (1 970 cm^{-1}).[8] Corresponding iridium–hydride frequencies in metallacarbaboranes are generally higher than their rhodium counterparts,[9] reflecting the trend observed in the pairs of compounds (**1**), (**2**), and (**3**), (**4**).

In the case of the rhodatelluraborane compound (**3**), crystals grown by diffusion of cyclohexane into a CH_2Cl_2 solution of (**3**) were suitable for single-crystal *X*-ray diffraction analysis. The crystal selected contained discrete molecules of [$(PPh_3)_2$-$Rh(H)TeB_{10}H_{10}$] and C_6H_{12} molecules of solvation. The analysis unambiguously established the cluster architecture of (**3**) as shown in Figure 1. The *closo*-$TeRhB_{10}$ cage is based on the icosahedron and has the tellurium adjacent to the rhodium atom. A list of interatomic distances and angles is given in Table 1. The conformation of the $Rh(PPh_3)_2(H)$ unit above the TeB_4 ring to which it is attached is shown in Figure 2. It is noteworthy

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† For Part 3 see ref. 1.

‡ *closo*-2-Hydrido-2,2-bis(triphenylphosphine)-1-tellura-2-rhodadodecaborane(10).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

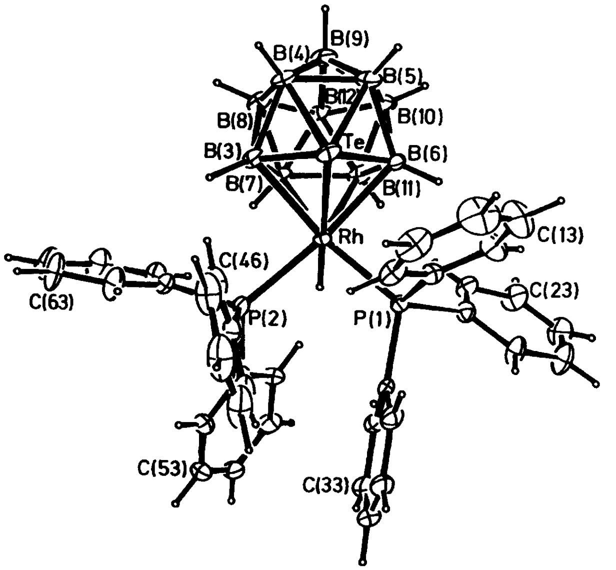


Figure 1. A general view of (**3**) showing the crystallographic numbering scheme. Ellipsoids are at the 25% level except for H atoms which are shown as spheres of arbitrary radius

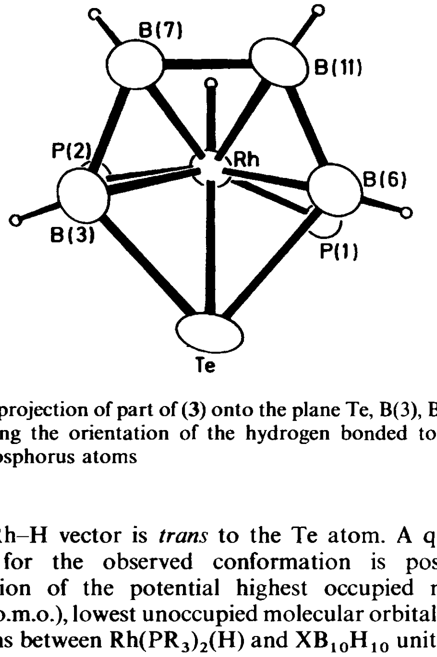
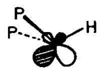
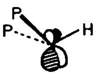


Figure 2. A projection of part of (**3**) onto the plane Te, B(3), B(7), B(11), B(6), showing the orientation of the hydrogen bonded to rhodium, and the phosphorus atoms

that the Rh–H vector is *trans* to the Te atom. A qualitative rationale for the observed conformation is possible by consideration of the potential highest occupied molecular orbital (h.o.m.o.), lowest unoccupied molecular orbital (l.u.m.o.) interactions between $Rh(PR_3)_2(H)$ and $XB_{10}H_{10}$ units. Results from extended Hückel (e.h.) m.o. calculations suggest that the frontier orbitals of the metal-containing ML_2H unit will contain strong contributions of the forms shown in (**I**) and (**II**),[10] and will involve substantial metal d_{xz} (**I**) and d_{yz} (**II**) components. In the corresponding $M(CO)_3$ units that contain d^6 metal centres these orbitals would be degenerate and unfilled.[11] In ML_2H units (M = Rh or Ir) however, the degeneracy is removed because of the point group (C_s) of such units;[10] (**II**) is now found at lower energy than (**I**) and also becomes filled in the ML_2H units, *i.e.* orbital (**II**) becomes the h.o.m.o. and orbital (**I**) becomes the l.u.m.o. E.h.m.o. predictions of dominant contributions to the h.o.m.o. and l.u.m.o. of the $XB_{10}H_{10}$ unit are shown in (**III**) and (**IV**) respectively.[4] Interactions of either (**I**) and (**III**) or (**II**) and (**IV**), or both sets, would lead to the observed ML_2H–$XB_{10}H_{10}$ conformation (**V**). The alternative conformation (**VI**) is also in principle possible but presumably (**V**) is preferred on mainly steric grounds. Support for this suggestion is found in the structural chemistry of the electronically related ML_2H-containing metallacarbaboranes.[2,12,13] The frontier orbitals of the $C_2B_9H_{11}$ unit which contains adjacent carbon atoms [h.o.m.o. (**VII**) and l.u.m.o. (**VIII**)][14] are of similar form to those of $XB_{10}H_{10}$, and a similar sequence of interactions (**I**)—(**VII**) and (**II**)—(**VIII**) may be expected with a similar choice of final conformation, *i.e.* (**IX**) or (**X**). Both of these conformations have been observed: thus the μ-*o*-xylyl-C^1C^2-bridged species *closo*-[1,2-(μ-1′,2′-$CH_2C_6H_4CH_2$)-3,3-$(PPh_3)_2$-3-H-$RhC_2B_9H_9$][12] (**5**) exhibits the least sterically demanding conformation with the Rh–H vector above the C–C bond, (**XI**), whereas in *closo*-[3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] the conformation is basically (**X**) (although the assessment of this is complicated because of some disorder in the carbon and adjacent boron atoms).[13] In the compound *closo*-[1-Me-2,2-$(PEt_3)_2$-2-H-8-Ph-2,1,8-$RhC_2B_9H_9$] which contains a CB_4 ring bonded to Rh and is possibly more closely related to the TeB_4–Rh system of (**3**), the conformation is (**XII**),[12] *i.e.* equivalent to that in the rhodatelluraborane, (**V**). The molecular structure of only one other Rh–Te metallaheteroborane has been reported, namely that of the *ortho* cycloboronated compound *closo*-[2-(PPh_3)-2-H-2-$(Ph_2PC_6H_4)$-1,2-$TeRhB_{10}H_9$] (**6**),[6] but in this compound the conformation of the RhP_2H section, (**XIII**), is determined by the C_{Ph}–B bond formed between B(6) and an *ortho* carbon of a phosphinophenyl group and hence is not the same as in (**3**).



(I)



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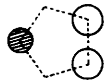

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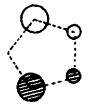

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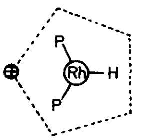

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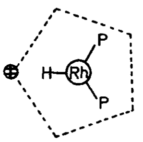

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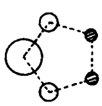

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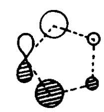

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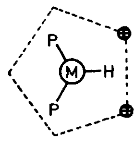

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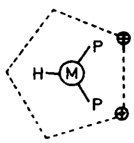
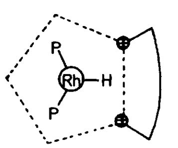
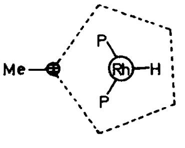


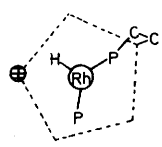
(X)



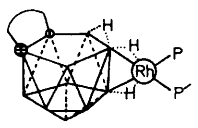
(XI)



(XII)



(XIII)



(XIV)

The Rh–Te distance of 2.617 2(4) Å in (**3**) is significantly longer than the value of 2.565 6(4) Å in the cycloboronated species *closo*-[2-(PPh_3)-2-H-2-$(Ph_2PC_6H_4)$-1,2-$TeRhB_{10}H_9$] (**6**),[6] and this may be attributable either to the strong *trans* influence of the H ligand, or to 'slippage' of the ML_2H unit towards B(7) and B(11) caused by (**I**)—(**III**) and (**II**)—(**IV**) bonding interactions, or to both, since neither would be as

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

Rh–Te	2.617 2(4)	C(13)–C(14)	1.349(8)	C(44)–C(45)	1.353(9)	B(4)–B(9)	1.758(6)
Rh–P(1)	2.398(1)	C(14)–C(15)	1.386(9)	C(45)–C(46)	1.378(6)	B(5)–B(6)	1.962(7)
Rh–P(2)	2.354(1)	C(15)–C(16)	1.374(7)	C(51)–C(52)	1.396(5)	B(5)–B(9)	1.748(7)
Rh–B(3)	2.333(5)	C(21)–C(22)	1.372(5)	C(51)–C(56)	1.377(5)	B(5)–B(10)	1.768(8)
Rh–B(6)	2.317(4)	C(21)–C(26)	1.399(6)	C(52)–C(53)	1.381(7)	B(6)–B(10)	1.767(5)
Rh–B(7)	2.238(4)	C(22)–C(23)	1.394(6)	C(53)–C(54)	1.370(6)	B(6)–B(11)	1.791(6)
Rh–B(11)	2.239(4)	C(23)–C(24)	1.354(7)	C(54)–C(55)	1.369(5)	B(7)–B(8)	1.817(7)
Te–B(3)	2.374(5)	C(24)–C(25)	1.357(7)	C(55)–C(56)	1.392(6)	B(7)–B(11)	1.808(7)
Te–B(4)	2.296(4)	C(25)–C(26)	1.375(6)	C(61)–C(62)	1.366(5)	B(7)–B(12)	1.771(6)
Te–B(5)	2.300(4)	C(31)–C(32)	1.401(6)	C(61)–C(66)	1.393(5)	B(8)–B(9)	1.768(7)
Te–B(6)	2.399(4)	C(31)–C(36)	1.377(5)	C(62)–C(63)	1.386(6)	B(8)–B(12)	1.774(7)
P(1)–C(11)	1.834(4)	C(32)–C(33)	1.388(5)	C(63)–C(64)	1.359(7)	B(9)–B(10)	1.763(7)
P(1)–C(21)	1.825(4)	C(33)–C(34)	1.358(7)	C(64)–C(65)	1.367(6)	B(9)–B(12)	1.765(8)
P(1)–C(31)	1.838(3)	C(34)–C(35)	1.372(9)	C(65)–C(66)	1.378(6)	B(10)–B(11)	1.779(7)
P(2)–C(41)	1.837(3)	C(35)–C(36)	1.395(6)	B(3)–B(4)	1.925(7)	B(10)–B(12)	1.758(7)
P(2)–C(51)	1.832(4)	C(41)–C(42)	1.381(6)	B(3)–B(7)	1.801(6)	B(11)–B(12)	1.753(6)
P(2)–C(61)	1.849(4)	C(41)–C(46)	1.381(7)	B(3)–B(8)	1.743(5)	C(1)–C(2)	1.431(14)
C(11)–C(12)	1.376(6)	C(42)–C(43)	1.387(6)	B(4)–B(5)	1.885(8)	C(1)–C(3′)	1.470(17)
C(11)–C(16)	1.406(5)	C(43)–C(44)	1.372(10)	B(4)–B(8)	1.743(7)	C(2)–C(3)	1.438(14)
C(12)–C(13)	1.373(8)						

Te–Rh–P(1)	95.87(3)	Rh–P(1)–C(31)	121.9(1)	B(3)–B(7)–B(8)	57.6(2)
Te–Rh–P(2)	110.06(3)	C(11)–P(1)–C(21)	104.3(2)	B(8)–B(7)–B(12)	59.2(3)
Te–Rh–B(3)	57.0(1)	C(11)–P(1)–C(31)	103.3(2)	B(11)–B(7)–B(12)	58.6(2)
Te–Rh–B(6)	57.8(1)	C(21)–P(1)–C(31)	98.1(2)	B(3)–B(8)–B(4)	67.0(3)
Te–Rh–B(7)	93.9(1)	Rh–P(2)–C(41)	111.0(1)	B(3)–B(8)–B(7)	60.8(2)
Te–Rh–B(11)	93.6(1)	Rh–P(2)–C(51)	116.8(1)	B(4)–B(8)–B(9)	60.1(3)
P(1)–Rh–P(2)	96.26(3)	Rh–P(2)–C(61)	120.2(1)	B(7)–B(8)–B(12)	59.1(3)
P(1)–Rh–B(3)	151.6(1)	C(41)–P(2)–C(51)	108.6(2)	B(9)–B(8)–B(12)	59.8(3)
P(1)–Rh–B(6)	85.4(1)	C(41)–P(2)–C(61)	102.6(2)	B(4)–B(9)–B(5)	65.0(3)
P(1)–Rh–B(7)	157.2(1)	C(51)–P(2)–C(61)	95.8(2)	B(4)–B(9)–B(8)	59.3(3)
P(1)–Rh–B(11)	111.1(1)	Rh–B(3)–Te	67.5(1)	B(5)–B(9)–B(10)	60.5(3)
P(2)–Rh–B(3)	86.8(1)	Rh–B(3)–B(7)	64.0(2)	B(8)–B(9)–B(12)	60.3(3)
P(2)–Rh–B(6)	167.8(1)	Te–B(3)–B(4)	63.6(2)	B(10)–B(9)–B(12)	59.8(3)
P(2)–Rh–B(7)	99.6(1)	B(4)–B(3)–B(8)	56.5(3)	B(5)–B(10)–B(6)	67.4(3)
P(2)–Rh–B(11)	141.8(1)	B(7)–B(3)–B(8)	61.7(3)	B(5)–B(10)–B(9)	59.3(3)
B(3)–Rh–B(6)	86.1(2)	Te–B(4)–B(3)	67.8(2)	B(6)–B(10)–B(11)	60.7(2)
B(3)–Rh–B(7)	46.4(2)	B(3)–B(4)–B(8)	56.5(2)	B(9)–B(10)–B(12)	60.2(3)
B(3)–Rh–B(11)	81.4(2)	Te–B(4)–B(5)	65.9(2)	B(11)–B(10)–B(12)	59.4(3)
B(6)–Rh–B(7)	82.5(2)	B(5)–B(4)–B(9)	57.2(3)	Rh–B(11)–B(6)	69.2(2)
B(6)–Rh–B(11)	46.2(2)	B(8)–B(4)–B(9)	60.6(3)	Rh–B(11)–B(7)	66.1(2)
B(7)–Rh–B(11)	47.6(2)	Te–B(5)–B(4)	65.7(2)	B(6)–B(11)–B(10)	59.4(3)
Rh–Te–B(3)	55.5(1)	Te–B(5)–B(6)	68.0(2)	B(7)–B(11)–B(12)	59.6(3)
Rh–Te–B(4)	95.3(1)	B(4)–B(5)–B(9)	57.5(3)	B(10)–B(11)–B(12)	59.7(3)
Rh–Te–B(5)	95.2(1)	B(6)–B(5)–B(10)	56.3(2)	B(7)–B(12)–B(8)	61.7(3)
Rh–Te–B(6)	54.8(1)	B(9)–B(5)–B(10)	60.2(3)	B(7)–B(12)–B(11)	61.7(2)
B(3)–Te–B(4)	48.6(2)	Rh–B(6)–Te	67.4(1)	B(8)–B(12)–B(9)	59.9(3)
B(3)–Te–B(5)	83.3(2)	B(5)–B(6)–B(10)	56.3(3)	B(9)–B(12)–B(10)	60.1(3)
B(3)–Te–B(6)	83.4(2)	Rh–B(6)–B(11)	64.6(2)	B(10)–B(12)–B(11)	60.9(3)
B(4)–Te–B(5)	48.4(2)	Te–B(6)–B(5)	62.7(2)	C(2)–C(1)–C(3′)	111.9(10)
B(4)–Te–B(6)	83.9(2)	B(10)–B(6)–B(11)	60.0(3)	C(1)–C(2)–C(3)	110.5(7)
B(5)–Te–B(6)	49.3(2)	Rh–B(7)–B(3)	69.6(2)	C(1′)–C(3)–C(2)	114.1(9)
Rh–P(1)–C(11)	110.3(1)	Rh–B(7)–B(11)	66.2(2)		
Rh–P(1)–C(21)	116.7(1)				

* The ′ refers to equivalent position $1 - x, 1 - y, 1 - z$.

effective in the 'twisted' cycloboronated complex (**6**). However, comparison data are limited. The authors are unaware of any other published Rh–Te bond distances. The Rh–B distances to the boron atoms which are also bound to the tellurium atom, *i.e.* B(3) and B(6), have a mean value of 2.325(8) Å. The Rh–B distances to the other boron atoms, B(7) and B(11), are significantly shorter [mean 2.239(1) Å]. Thus, as with the Pt–Te compound $[2,2\text{-}(PEt_3)_2\text{-}1,2\text{-}TePtB_{10}H_{10}]$,[1] there is significant displacement of the metal unit away from the Te site and this may have an electronic component analogous to the 'slippage' of the $Pd(CNBu^t)_2$ unit in *closo*-$[1\text{-}(NMe_3)\text{-}2,2\text{-}(CNBu^t)_2\text{-}2,1\text{-}PdCB_{10}H_{10}]$.[14] It is noteworthy that whilst the shorter Rh–B distances could be regarded as typical in the sense that they are within the range reported for such bonds in rhodaboranes [2.049(6)—2.302(5) Å],[15] the longer values are significantly outside this range. The equivalent Rh–B distances in the cycloboronated complex (**6**) [2.283(20) and 2.330(1) Å][6] show similar behaviour. In reported rhodacarbaboranes the Rh–B distances are generally *ca.* 2.2 Å but values as low as 2.106(5) and high as 2.331(14) Å have been observed. The last distance is that measured for the Rh–B interaction opposite the Rh–H vector in compound (**5**) mentioned above.[12] In a closely related *exo–nido* quasi-tautomer of (**5**), $[6,10\text{-}(\mu\text{-}[Rh(\mu\text{-}H)_2(PPh_3)\text{-}\{P(C_6H_{11})_3\}])\text{-}7,8\text{-}(\mu\text{-}1',2'\text{-}CH_2C_6H_4CH_2)\text{-}10,11\text{-}(\mu\text{-}H)\text{-}7,8\text{-}$

Table 2. Proton and boron-11 n.m.r. data for [2,2-$(PPh_3)_2$-2-H-1,2-$XMB_{10}H_{10}$] (**1**)—(**4**) (CD_2Cl_2[a] or $CD_3C_6D_5$[b] solutions, δ in p.p.m.)

	X = Se			X = Te				
	Rh[a] (**1**)		Ir[a] (**2**)	Rh[a] (**3**)		Ir[a,b] (**4**)		
Assignment (intensity)	δ(^{11}B)[c]	δ(^{1}H)[d]	δ(^{11}B)[c]	δ(^{11}B)[c]	δ(^{1}H)[d]	δ(^{11}B)[a,c]	δ(^{11}B)[b,c]	δ(^{1}H)[d]
12 (1 BH)	+17.1	+4.19	+15.3	+19.3	+5.58	+16.3	+19.5	+5.99
9 (1 BH)	+12.9	+4.46	+13.2	+14.3	+5.14	+13.6	+16.3	+6.74
3,6 (2 BH)	+10.9	+2.31[e]	+8.6	+10.9	+2.74[f]	+6.5	+7.2	+2.79[g]
7,11 (2 BH)	+7.6	+3.82	+1.7	+8.3	+4.57	+1.2	+3.0	+4.61
8,10 (2 BH)	−14.1	+1.83	−16.2	−12.9	+2.32	−15.9	−14.1	+2.52
4,5 (2 BH)	−12.5	+2.00	−15.0	−14.4	+2.30	−17.3	−16.3	+2.42
2 (1 MH)		−6.23[h]			−3.96[i]			−5.55[j]

[a] At ambient temperature, 298 K. [b] At 363 K. [c] δ(^{11}B) ±0.5 p.p.m. to high frequency of $BF_3(OEt_2)$. [d] δ(^{1}H) ±0.5 p.p.m. to high frequency of $SiMe_4$, ^{1}H resonances related to directly bound ^{11}B resonances by selective ^{1}H-{^{11}B} experiments. [e] Doublet structure, $^{3}J(^{31}P\text{–Rh–B–}^{1}H)$ *ca.* 15 Hz. [f] Doublet structure, $^{3}J(^{31}P\text{–Rh–B–}^{1}H)$ *ca.* 14.5 Hz. [g] Doublet structure, $^{3}J(^{31}P\text{–Ir–B–}^{1}H)$ 15.3 Hz. [h] Triplet [$^{2}J(^{31}P\text{–}^{1}H)$ 21 Hz] of doublets [$^{1}J(^{103}Rh\text{–}^{1}H)$ 17 Hz]. [i] Triplet (^{2}J *ca.* 19 Hz) of doublets (^{1}J *ca.* 17 Hz). [j] Triplets, ^{2}J 20 Hz.

Table 3. [^{1}H–^{1}H]-COSY correlations for (**1**) and (**4**) and T_1 (^{11}B) relaxation times (ms) and $^{1}J(^{11}B\text{–}^{1}H)$ coupling constant data for (**4**) (CD_2Cl_2 solution, ambient temperature 298 K)[a]

	[^{1}H–^{1}H]-COSY correlations[b]		(**4**) Ir–Te	
Assignment	(**1**) Rh–Se	(**4**) Ir–Te	T_1 (approx.)	$^{1}J(^{11}B\text{–}^{1}H)$[c]
12	(7,11)m, (8,10)w	(7,11)s, (8,10)m, (9)w	3.5	139
9	(8,10)m, (4,5)w	(8,10)s, (4,5)m, (12)w	2.6	142
3,6		(8,10)w?	0.5	*d*
7,11	(8,10)s, (12)m	(8,10)s, (12)s	2.1	133
8,10	(7,11)s, (9)m, (12)w, (4,5)w?	(9)s, (7,11)s, (4,5)s, (12)m, (3,6)w?	3.4	145
4,5	(9)w, (8,10)w?	(8,10)s, (9)m	< *ca.* 1[d]	*d*

[a] $^{1}J(^{11}B\text{–}^{1}H)$ 130—160 Hz. [b] Measured with {^{11}B (broad-band noise)} decoupling; s = stronger, w = weaker, m = intermediate. [c] ±8 Hz; measured from ^{11}B spectrum with resolution enhancement to separate doublet components. [d] Accurate measurement of these parameters precluded because of the ^{11}B linewidths and/or overlap with adjacent ^{11}B lines.

$C_2B_9H_7$], which has a rhodium-to-cluster interaction as depicted in (**XIV**), one of the *exo* cluster Rh–H bridged interactions is 2.338(8) Å.[12] Similar Rh–(μ-H)–B distances, but for a Rh atom in one rhodacarbaborane unit interacting with a B atom in a second unit, have been reported in the dimeric rhodacarbaboranes [{$(PPh_3)RhC_2B_9H_{11}$}$_2$], [{$(PEt_3)RhC_2B_9H_{10}$}$_2$], and [{$(PPh_3)RhC_2B_9H_{10}Ph$}$_2$] as varying between 2.257(7) and 2.327(8) Å. However each of these complexes is held together by a Rh–Rh interactions as well as the Rh–(μ-H)–B bonds.[16] Clearly it is difficult to make detailed assessments of the significance of metal–cluster interactions to cluster bonding when such assessments are based simply on a comparison of metal–cluster interatomic distances.

The Rh–P bond distances in (**3**) are significantly different [2.354(1) and 2.398(1) Å] but typical of rhodium–phosphine bond lengths. A similar Rh–P non-equivalence has been reported in *closo*-[3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$].[13] The differences may arise from a dependence on the Rh–P and P–C rotamers and the Rh-B_4Te twistomer (Figure 2) as well as on other crystallographic considerations.

The TeB(3)B(7)B(11)B(6) ring is notably planar. The Te–B distances to B(3) and B(6) adjacent to the metal atom [mean 2.387(13) Å] are significantly longer than the distances to B(4) and B(5) [mean 2.298(2) Å]. This difference was also marked in the cycloboronated complex (**6**) [2.409(30) and 2.298(4) Å], reflecting the differences in electronic character produced on changing the ML_2H unit configuration,[6] and similar differences are also observed in the *closo*-[2,2-$(PR_3)_2$-1,2-$XPtB_{10}H_{10}$] (X = Se or Te) species that we have reported.[1,4]

Within the borane cage section of (**3**), the B–B distances are between 1.743(7) and 1.962(7) Å, with the three B–B interactions flanking the Te atom notably longer than any others (Table 1). Again, this behaviour is paralleled in the $PtTeB_{10}$ and $PtSeB_{10}$ analogues.[1,4]

The measured n.m.r. parameters relating to the BH and MH units of (**1**)—(**4**) are given in Tables 2 and 3. The presence of the $M(PPh_3)_2H$ unit in (**1**)—(**4**) was confirmed by the observation of the M–H proton signal split by coupling to two equivalent phosphorus nuclei [$^{2}J(^{31}P\text{–M–}^{1}H)$ *ca.* 20, 23, *ca.* 19, and 20 Hz respectively for (**1**)—(**4**)], and the rhodium nucleus [$^{1}J(^{103}Rh\text{–}^{1}H)$ *ca.* 17 Hz] for both (**1**) and (**3**). The coupling constants $^{2}J(^{31}P\text{–M–}^{1}H)$ are at the lower end of the range of values (20—42 Hz) reported for seventeen *closo*-rhodacarbaboranes whereas the $^{1}J(^{103}Rh\text{–}^{1}H)$ value is in the middle of the range of such values (13—23 Hz) in the rhodacarbaboranes.[7]

Compounds (**1**)—(**4**) all show 1:1:2:2:2:2 relative intensity patterns in both their ^{11}B and ^{1}H n.m.r. spectra, and an absence of bridging ^{1}H resonances, consistent with the *closo* nature of the cage and the retention of a time-average mirror plane of symmetry in solution. The assignment of the resonances reported in Table 2 to the borane cage positions was achieved using intensity data and selective ^{1}H-{^{11}B} spectroscopy for (**1**)—(**4**), together with [^{1}H–^{1}H]-COSY experiments, which were carried out in the presence of {^{11}B(broad-band noise)} decoupling,[17] for (**1**) and (**4**) (Table 3).

Of the compounds (**1**)—(**4**), the iridium–tellurium complex, (**4**), was the one studied in most detail by n.m.r. techniques and some specific comments pertaining to this compound are relevant here, although the points will apply generally. Additionally in this discussion, comparison with similar data from the electronically related [2,2-$(PR_3)_2$-1,2-$TePtB_{10}H_{10}$]

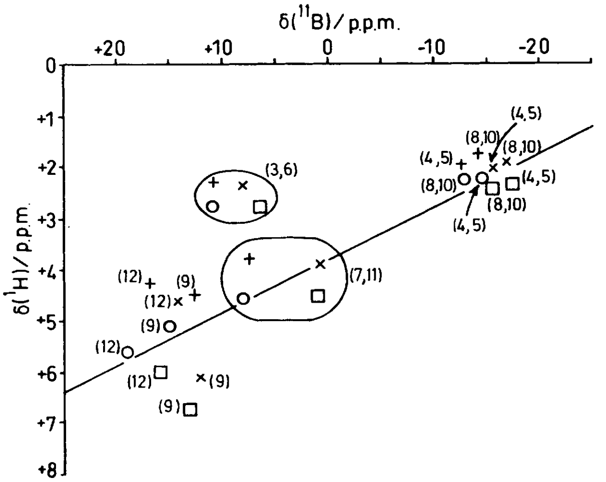


Figure 3. Plot of $\delta(^{11}B)$ *versus* $\delta(^{1}H)$ for directly bound boron and hydrogen atom pairs in compounds (**1**) (RhSe, +), (**2**) (IrTe, ○), (**3**) (RhTe, ×), and (**4**) (IrTe, □). The line drawn has slope $\delta(^{11}B)\delta(^{1}H)$ 9.7:1 with intercept $\delta(^{1}H) = +3.80$ p.p.m., comparable with values of 11:1 and 3.75 p.p.m. from the platinatelluraborane analogues in ref. 1. The largest deviations from this line occur for the BH(3,6) position, possibly arising from an increased ^{1}H shielding due to the anisotropy of the phosphine groups [configuration (**V**) and Figures 1 and 2], and for the BH(9) positions in compounds (**2**) and (**4**) which are antipodal to the heavier transition element iridium. Note also that BH(12) in compounds (**3**) and (**4**), which is antipodal to the heavier chalcogen Te, exhibits a lower proton shielding than in (**1**) or (**2**)

complexes is of interest in an assessment of the electronic similarities among these *closo* systems.[1]

The ^{11}B resonance lines were somewhat broader for (**4**) than those from the $[(PR_3)_2PtTeB_{10}H_{10}]$ compounds (where R_3 = Et_3 or PMe_2Ph)[1] because of the increase in ^{11}B relaxation rates arising from the larger molecular bulk of the iridium compound (in which $R_3 = Ph_3$). This phenomenon precluded the resolution of certain of the coupling constants $^{1}J(^{11}B-^{1}H)$ and inhibited the observation of correlations in $[^{11}B-^{11}B]$ COSY experiments. Interestingly, the relative magnitudes of the various measured relaxation times $T_1(^{11}B)$ paralleled those measured for equivalent cluster sites in the platinum species. Unfortunately the iridium compound was too insoluble in $CD_3C_6D_5$ at higher temperatures for $[^{11}B-^{11}B]$-COSY experiments to be performed within a reasonable time interval, even though the ^{11}B lines at these higher temperatures were sharper, as expected. The higher temperature work in $CD_3C_6D_5$ did however reveal both absolute and differential effects on $\delta(^{11}B)$. Shielding changes $\Delta\sigma(^{11}B)$ of -0.5 to -3.2 p.p.m. were apparent, *i.e.* an overall deshielding effect with change of solvent and temperature ($CD_3C_6D_5$ at 363 K from CD_2Cl_2 at 298 K). It is noteworthy that the magnitudes of the individual changes [except for that at $^{11}B(3,6)$] were essentially the same as those observed for equivalent sites in the previously examined platinum compounds.[1]

The absence of $[^{11}B-^{11}B]$ cross-correlations in the COSY experiment on (**4**) prevented peak assignment by this method, but the cluster ^{1}H resonances were readily related to their directly bound boron atoms by selective $^{1}H-\{^{11}B\}$ spectroscopy, and $[^{1}H-^{1}H]$-COSY experiments, carried out in the presence of $\{^{11}B$(broad-band noise)$\}$ decoupling,[17] thence revealed the cluster connectivities and permitted the structural assignment of the spectra. Further support for these assignments was obtained from the shielding pattern parallels, and also relaxation-time parallels, with the previously investigated[1] platinatelluradodecaboranes for which the incidence of structure arising from couplings $^{1}J(^{195}Pt-^{11}B)$ in the ^{11}B spectra removed any ambiguity of assignment. The shielding parallels are in fact quite close [see Figure 3 (and compare Figure 4 in ref. 1)], indicating close similarities in electronic structure, with the $^{11}B(9)$ and $^{11}B(12)$ resonances tending to be at higher frequency, the $^{11}B(8,10)$ and $^{11}B(7,11)$ resonances at lower frequency, and those of $^{11}B(4,5)$ and $^{11}B(3,6)$ at intermediate frequency. Again there is an approximate parallel between $\delta(^{11}B)$ and $\delta(^{1}H)$ for directly bound B and H atoms (the line drawn has slope 11:1), the principal deviations occurring at BH(3,6) which flanks the metal–chalcogen linkage, and in compounds (**2**) and (**4**), at BH(9) which is antipodal to the third-row transition element iridium. Again, both these effects are observed for the platinum analogues,[1] emphasizing the general impression and conclusion that the compounds have very similar cluster electronic structures.

Experimental

General.—All preparative experiments and recrystallisations were carried out in an inert atmosphere. The compounds $[Rh(PPh_3)_3Cl]$,[18] $[Ir(PPh_3)_3Cl]$,[19] $[NHEt_3][7\text{-}SeB_{10}H_{11}]$,[20] and $Cs[7\text{-}TeB_{10}H_{11}]$[20] were prepared according to literature methods. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 682 spectrometer.

Reaction of $[Rh(PPh_3)_3Cl]$ *with* $[NHEt_3][7\text{-}SeB_{10}H_{11}]$.—A suspension of $[Rh(PPh_3)_3Cl]$ (0.75 g, 0.81 mmol) in ethanol (50 cm^3) was added to a solution of $[NHEt_3][7\text{-}SeB_{10}H_{11}]$ (0.246 g, 0.82 mmol) in ethanol (50 cm^3). After stirring at room temperature for 20 h, the reaction mixture was filtered, yielding a *yellow solid* $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1\text{-}RhSeB_{10}H_{10}]$ (**1**) (0.6 g, 89.7%). I.r.: $\nu_{max.}$ at 3 050m, 2 923m, 2 850w, 2 590s (BH), 2 530s (BH), 2 080w (RhH), 1 590vw, 1 575vw, 1 482s, 1 438s, 1 315w, 1 188w, 1 160w, 1 095s, 1 075 (sh), 1 020s, 1 003m, 935w, 915w, 890w, 745w, 730vw, 698vs, and 645vw cm^{-1}.

Reaction of $[Ir(PPh_3)_3Cl]$ *with* $[NHEt_3][7\text{-}SeB_{10}H_{11}]$.—A solution of $[NHEt_3][7\text{-}SeB_{10}H_{11}]$ (0.29 g, 0.97 mmol) in methanol (20 cm^3) was added to a stirred suspension of $[Ir(PPh_3)_3Cl]$ (0.97 g, 0.96 mmol) in methanol (20 cm^3). On stirring at room temperature for 3 d, the initially pink reaction mixture became yellow-white. Filtration yielded a beige solid (0.702 g). Recrystallization from CH_2Cl_2–CH_3OH afforded *yellow crystals* of $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}2,1\text{-}IrSeB_{10}H_{10}]$ (**2**) (0.274 g, 30.0%). I.r.: $\nu_{max.}$ at 3 045m, 2 920w, 2 850vw, 2 580s (BH), 2 530s (BH), 2 200w (IrH), 1 483s, 1 438s, 1 312wbr, 1 186w, 1 160w, 1 092s, 1 023s, 1 000m, 930w, 918w, 765mbr, 740s, and 695vs cm^{-1}.

Reaction of $[Rh(PPh_3)_3Cl]$ *with* $Cs[7\text{-}TeB_{10}H_{11}]$.—Degassed absolute alcohol (200 cm^3) was added to a mixture of $Cs[7\text{-}TeB_{10}H_{11}]$ (0.69 g, 1.81 mmol) and $[Rh(PPh_3)_3Cl]$ (1.67 g, 1.81 mmol). The mixture was stirred for 14 h at room temperature. A *yellow precipitate* of $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}1,2\text{-}TeRhB_{10}H_{10}]$ (**3**) (1.50 g, 95%) was produced. The precipitate was filtered off and dried under inert gas (Found: C, 49.45; H, 4.40. $C_{36}H_{41}B_{10}P_2RhTe$ requires C, 49.45; H, 4.75%). I.r.: $\nu_{max.}$ at 3 045w, 2 915vw, 2 840vw, 2 555s (BH), 2 525s (BH), 2 045w (RhH), 1 582w, 1 566vw, 1 540vw, 1 478s, 1 431s, 1 310w, 1 182w, 1 158w, 1 115vs, 1 090s, 1 010s, 998s, 935vw, 920vw, 900vw, 882vw, 850vw, 815vw, 740s, 722vw, 692s, 650vw, and 635w cm^{-1}.

X-Ray Analysis of $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}1,2\text{-}TeRhB_{10}H_{10}]\cdot 0.5C_6H_{12}$ (**3**).—*Crystal data.* $C_{39}H_{47}B_{10}P_2RhTe$, M = 916.37, triclinic, a = 12.406(1), b = 17.872(4), c = 10.010(1) Å, α = 94.30(1), β = 107.25(1), γ = 94.31(1)°, U = 2 102 Å^3, Z = 2,

Table 4. Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*
Rh	−0.100 75(2)	0.247 20(1)	0.174 44(2)
Te	0.030 22(2)	0.237 50(2)	0.012 74(2)
P(1)	−0.226 45(7)	0.327 00(5)	0.035 24(8)
P(2)	−0.232 75(7)	0.139 39(5)	0.125 64(9)
C(11)	−0.184 3(3)	0.346 2(2)	−0.120 7(3)
C(12)	−0.137 6(4)	0.415 9(3)	−0.137 0(4)
C(13)	−0.099 3(5)	0.424 7(4)	−0.250 8(5)
C(14)	−0.108 4(5)	0.366 7(4)	−0.349 1(5)
C(15)	−0.155 4(5)	0.295 8(3)	−0.335 7(4)
C(16)	−0.193 3(3)	0.285 2(2)	−0.221 9(4)
C(21)	−0.232 3(3)	0.420 3(2)	0.118 9(3)
C(22)	−0.174 8(3)	0.442 6(2)	0.257 6(4)
C(23)	−0.187 4(4)	0.513 0(3)	0.317 7(5)
C(24)	−0.255 1(5)	0.559 9(3)	0.239 6(6)
C(25)	−0.313 2(5)	0.539 0(3)	0.102 4(6)
C(26)	−0.303 7(4)	0.469 2(2)	0.041 7(5)
C(31)	−0.379 9(3)	0.299 5(2)	−0.037 1(4)
C(32)	−0.441 1(3)	0.297 3(2)	0.059 9(4)
C(33)	−0.557 7(4)	0.278 3(3)	0.014 2(5)
C(34)	−0.614 6(4)	0.266 0(3)	−0.125 4(7)
C(35)	−0.557 0(4)	0.270 5(3)	−0.222 6(6)
C(36)	−0.439 4(3)	0.287 9(2)	−0.178 2(4)
C(41)	−0.286 9(4)	0.110 4(2)	−9.064 3(4)
C(42)	−0.396 6(4)	0.115 9(2)	−0.146 4(4)
C(43)	−0.427 2(6)	0.097 1(3)	−0.290 7(5)
C(44)	−0.349 7(6)	0.072 1(3)	−0.352 5(5)
C(45)	−0.242 1(6)	0.066 4(3)	−0.273 1(4)
C(46)	−0.210 6(4)	0.086 1(3)	−0.130 0(4)
C(51)	−0.353 6(3)	0.144 8(2)	0.194 5(4)
C(52)	−0.446 8(4)	0.090 3(2)	0.147 2(5)
C(53)	−0.533 4(3)	0.089 9(2)	0.207 7(5)
C(54)	−0.528 5(3)	0.142 3(2)	0.316 8(5)
C(55)	−0.436 6(3)	0.195 2(3)	0.368 3(4)
C(56)	−0.350 0(3)	0.196 0(2)	0.306 1(4)
C(61)	−0.189 6(3)	0.050 5(2)	0.198 9(3)
C(62)	−0.197 7(4)	−0.016 6(2)	0.119 9(4)
C(63)	−0.176 5(5)	−0.082 8(3)	0.182 4(5)
C(64)	−0.149 2(5)	−0.083 5(2)	0.324 2(5)
C(65)	−0.140 4(4)	−0.016 8(3)	0.405 0(4)
C(66)	−0.161 5(4)	0.049 4(2)	0.344 1(4)
B(3)	0.039 6(4)	0.164 6(3)	0.204 0(5)
B(4)	0.182 3(4)	0.202 4(3)	0.182 4(5)
B(5)	0.185 0(4)	0.307 3(3)	0.170 9(5)
B(6)	0.041 5(3)	0.341 2(3)	0.184 7(4)
B(7)	0.029 7(4)	0.214 5(3)	0.362 5(4)
B(8)	0.163 3(4)	0.187 3(3)	0.344 4(5)
B(9)	0.246 1(4)	0.269 1(3)	0.328 3(5)
B(10)	0.166 4(4)	0.346 7(3)	0.329 0(5)
B(11)	0.033 9(3)	0.315 1(3)	0.351 1(4)
B(12)	0.157 1(4)	0.274 7(3)	0.436 8(4)
C(1)	0.551 6(9)	0.441 1(5)	0.451 0(12)
C(2)	0.475 6(9)	0.481 6(6)	0.352 3(8)
C(3)	0.472 5(11)	0.556 5(5)	0.413 7(9)

D_c = 1.45 g cm^{-3}, $F(000)$ = 916, λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 11.8 cm^{-1}, space group $P\bar{1}$.

Structure determination. Pale yellow prismatic crystals were grown by diffusion of cyclohexane into a solution of (**3**) in CH_2Cl_2. Accurate cell dimensions and the crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range 10 < θ < 15°. Crystal dimensions were 0.23 × 0.35 × 0.55 mm and the intensities of reflections with indices h 0 to 10, k 0 to 21, l −18 to 18, with 2 < 2θ < 48° were measured using ω–2θ scans with an ω scan width (0.80 + 0.35tanθ) and graphite monochromatized Mo-K_α radiation. Intensities of three reflections were measured every 2 h and showed no evidence of crystal decay. 7 153 Reflections were measured, of which 6 552 were unique, and the 5 380 with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement; R_{int} = 0.017. Data were corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0.824, 0.672). Space group $P\bar{1}$ was assumed and confirmed by the refinement. The co-ordinates of the Rh and Te atoms were determined from analysis of the three-dimensional Patterson function 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 and 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. The co-ordinates of the hydrogen bonded to rhodium were obtained from a difference map near the conclusion of the refinement and in the final rounds of calculations the other hydrogen atoms were positioned on geometrical grounds (C–H 0.95 Å, B–H 1.10 Å) and included (as riding atoms) in the structure factor calculations with an overall B_{iso} of 7.0 Å^2. The final cycle of refinement included 478 variable parameters, R = 0.033, R' = 0.044, goodness-of-fit 1.49, $w = 1/[\sigma^2(F_o) + 0.050(F_o)^2]$; the maximum shift/error was less than 0.01. Largest peaks and valleys in final difference map were ±0.93 e Å^{-3}, adjacent to Rh and Te; there were no chemically significant features. Scattering factors and anomalous dispersion corrections were taken from International Tables.[21] All calculations were performed on a PDP11/73 computer using SDP-Plus.[22] Atomic co-ordinates and details of molecular geometry are given in Tables 4 and 1. Figures 1 and 2 are views of the molecule prepared using ORTEP II.[23] A molecule of cyclohexane of solvation was also found lying about a crystallographic inversion centre.

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

Reaction of [Ir(PPh$_3$)$_3$Cl] *with* Cs[7-TeB$_{10}$H$_{11}$].—[Ir(PPh$_3$)$_3$Cl] (0.3521 g, 0.3472 mmol) and Cs[7-TeB$_{10}$H$_{11}$] (0.132 g, 0.347 mmol) were placed in a 250-cm^3 flask and absolute alcohol (60 cm^3) added. The mixture was stirred for 5 d.* An impure sample of *closo*-[2,2-(PPh$_3$)$_2$-2-H-1,2-TeIrB$_{10}$H$_{10}$] (**4**) (0.294 g, 88%) was filtered off. Preparative t.l.c. (Merck, Kieselgel 60, PF 254; CH_2Cl_2) produced three bands. The major band was extracted into CH_2Cl_2 and recrystallized as *yellow microcrystals* of *closo*-[2,2-(PPh$_3$)$_2$-2-H-1,2-TeIrB$_{10}$H$_{10}$]·CH_2Cl_2 (**4**) (Found: C, 42.80; H, 4.30. $C_{37}H_{43}B_{10}Cl_2IrP_2Te$ requires C, 42.40; H, 4.10%). I.r.: $\nu_{max.}$ at 3 045w, 2 900vw, 2 860vw, 2 560s (BH), 2 520s (BH), 2 170w (IrH), 1 582vw, 1 570vw, 1 478s, 1 432s, 1 310w, 1 185w, 1 158w, 1 090s, 1 020s, 998w, 925vw, 885vw, 850vw, 750w, 740s, 695s, and 635 vw cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy.—N.m.r. spectroscopy was carried out at 8.5 or 9.4 T using commercially

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* Stirring for a short time (up to 2 h) gave a pure product but in lower yield (63%).

available instrumentation with the general techniques, and also the techniques of the ^1H-{^{11}B}[24] and the COSY[17,25] experiments, being essentially as described and illustrated in other papers of this series.[1,4] Relaxation times $T_1(^{11}B)$ were measured by the π-delay-$\pi/2$-acquire inversion-recovery method. Chemical shifts δ are given in p.p.m. to high frequency (low field) of Ξ 100 ($SiMe_4$) for ^1H, Ξ 40.480 730 (nominally 85% H_3PO_4) for ^{31}P, and Ξ 32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$][26] for ^{11}B, Ξ being defined as in ref. 27. The shifts were measured using solvent deuteron or residual proton resonances as internal secondary standards.[27]

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