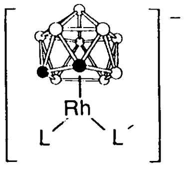
# Synthesis of $\eta^4$-1,3-Diphosphacyclobutadiene($\eta^5$-1,2-dicarbaborane)rhodium Complexes; Crystal Structures of the Compounds $[NEt_4][Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$, $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$, and $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ *

**Helen F. Dare, Judith A. K. Howard, Massimino U. Pilotti, F. Gordon A. Stone, and Jürgen Szameitat**
*Department of Inorganic Chemistry, The University, Bristol BS8 1TS*

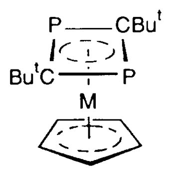
Treatment of a thf (tetrahydrofuran) solution of $K[Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ with $Bu^tC{\equiv}P$, followed by addition of $NEt_4Cl$, affords the salt $[NEt_4][Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**3**), the structure of which has been established by *X*-ray diffraction. Compound (**3**) reacts with $[AuCl(PPh_3)]$ and with $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ to afford, respectively, the complexes $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**4**) and $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**5**). The structures of the products (**4**) and (**5**) have also been determined by *X*-ray diffraction. In all three compounds the rhodium is $\eta^5$ ligated by a *nido*-icosahedral $C_2B_9H_{11}$ fragment, and by a 1,3-diphosphacyclobutadiene group. Within the latter the P–C distances are equal, and the four-membered CPCP rings are close to planar. In the compounds (**4**) and (**5**) a phosphorus atom in the $\eta^4\text{-}Bu^t{}_2CP_2$ group co-ordinates to the $Au(PPh_3)$ and the $Co(CO)_2(\eta^4\text{-}C_4Me_4)$ groups, respectively. The n.m.r. data ($^1H$, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) are reported, and where appropriate discussed.

We are currently investigating the reactivity of salts of the anions $[Rh(L)L'(\eta^5\text{-}C_2B_9H_9R_2)]^-$ (**1a**; R = H, L = L′ = $PPh_3$), (**1b**; R = H, L = CO, L′ = $PPh_3$), and (**1c**; R = Me, L = L′ = CO).[1] As part of our work we have examined the reaction between the potassium salt of (**1a**) and the phospha-alkyne $Bu^tC{\equiv}P$. There is considerable interest currently in the ligating properties of phospha-alkynes, and the species $Bu^tC{\equiv}P$ has been frequently employed to model the co-ordinating properties of $C{\equiv}P$ groups.[2]

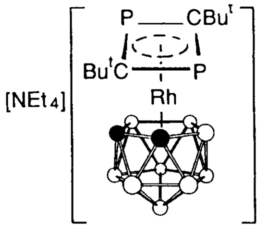
The studies reported herein were stimulated by the independent report by two groups[3,4] that the compound $Bu^tC{\equiv}P$ undergoes a cyclodimerisation reaction with the complexes $[M(C_2H_4)_2(\eta\text{-}C_5H_5)]$ (M = Co or Rh) to afford the species $[M(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta\text{-}C_5H_5)]$ (**2a**; M = Co) and (**2b**; M = Rh). We have drawn attention[1b] to the isolobal relationship between the fragments $Rh(\eta^5\text{-}C_2B_9H_9R_2)^-$ and $M(\eta\text{-}C_5R_5)$ (M = Co or Rh, R = H or Me), and it thus seemed possible that salts of one or other of the species (**1**) would also react readily with $Bu^tC{\equiv}P$, although the nature of the resulting product remained to be established. A preliminary account of our results has been given.[5]



| | ● | L | L′ |
|---|---|---|---|
| (**1a**) | CH | $PPh_3$ | $PPh_3$ |
| (**1b**) | CH | CO | $PPh_3$ |
| (**1c**) | CMe | CO | CO |

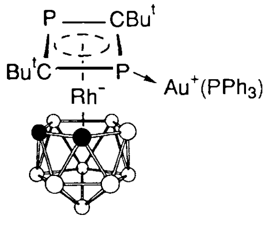


| | M |
|---|---|
| (**2a**) | Co |
| (**2b**) | Rh |



(**3**)

● CH ○ BH



(**4**)

● CH ○ BH

## Results and Discussion

Treatment of the potassium salt of complex (**1a**) with $Bu^tC{\equiv}P$ in thf (tetrahydrofuran) followed by addition of $NEt_4Cl$ afforded the brown salt $[NEt_4][Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**3**). This complex was characterised by microanalysis, and by $^1H$, $^{13}C\text{-}\{^1H\}$, $^{11}B\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (Tables 1 and 2). The structure of the anion of (**3**) (Figure 1) was established by an *X*-ray diffraction study, selected data from which are listed in Table 3.

It is immediately apparent that the reaction between (**1a**) and $Bu^tC{\equiv}P$ parallels that between $[Rh(C_2H_4)_2(\eta\text{-}C_5H_5)]$ and the phospha-alkyne in leading to cyclodimerisation of the latter, and capture of the resulting 1,3-diphosphacyclobutadiene molecule by the rhodium atom. In (**2a**) the P–C distances are closely similar, averaging 1.797 Å.[4] This is also the case for the $C_2P_2$ ring in (**3**) (average P–C separation 1.785 Å), and in both complexes these distances reflect partial double-bond character of these bonds in the four-membered ring systems. The rhodium atom in (**3**) is as expected $\eta^5$ co-ordinated by the *nido*-icosahedral $C_2B_9H_{11}$ fragment, with structural parameters similar to those of other structures containing the $Rh(\eta^5\text{-}C_2B_9H_{11})$ group.[1,6]

The n.m.r. data for complex (**3**) (Tables 1 and 2) are in accord

---

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

**Table 1.** Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

| Compound | $^1H$[b](δ) | $^{13}C$[c](δ) |
|---|---|---|
| (3) | 0.97 (s, 18 H, $Bu^t$), 1.32 [t, 12 H, $MeCH_2N$, $J$(HH) 7], 3.22 [q, 8 H, $MeCH_2N$, $J$(HH) 7], 3.52 [s br, 2 H, CH ($C_2B_9H_{11}$)] | 111.2 [t of d, CP, $J$(PC) 52, $J$(RhC) 12], 53.2 ($MeCH_2N$), 39.9 [br, $C_2$ ($C_2B_9H_{11}$)], 35.2 [t, $CMe_3$, $J$(PC) 6], 31.4 ($CMe_3$), 8.0 ($MeCH_2N$) |
| (4) | 1.08 (s, 18 H, $Bu^t$), 3.98 [s br, 2 H, CH ($C_2B_9H_{11}$)], 7.51—7.53 (m, 15 H, Ph) | 134.4 [d, $C^2$ (Ph), $J$(PC) 12], 132.5 [$C^4$ (Ph)], 129.9 [d, $C^3$ (Ph), $J$(PC) 12], 129.1 [d, $C^1$ (Ph), $J$(PC) 56], 44.0 [br, $C_2$ ($C_2B_9H_{11}$)], 35.8 ($CMe_3$), 32.2 ($CMe_3$) |
| (5)[d] | 0.97 (s, 9 H, $Bu^t$), 1.05* (s, 18 H, $Bu^t$), 1.10 (s, 9 H, $Bu^t$), 1.61 [d, 12 H, $C_4Me_4$, $J$(PH) 6], 1.93* [d, 12 H, $C_4Me_4$, $J$(PH) 5], 2.22 [s br, 2H, CH ($C_2B_9H_{11}$)] | 110.0 (br, CP), 42.4 [br, $C_2$ ($C_2B_9H_{11}$)], 35.6, 35.3 ($CMe_3$), 32.3, 32.0 ($CMe_3$), 32.2* ($CMe_3$), 10.4 ($C_4Me_4$), 10.1* ($C_4Me_4$) |

[a] Chemical shifts in p.p.m., coupling constants in Hz, measurements in $CD_2Cl_2$. [b] Resonances for the B–H protons are not resolved due to $^{11}B$–$^1H$ coupling, and very broad weak signals may be seen in the range δ 0—5. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 p.p.m.). [d] Complex exists in solution as a *ca.* 3:1 mixture of two diastereoisomers (see text). Peaks due to minor isomer are asterisked, but not all signals are observed due to insolubility of complex.

**Table 2.** Boron-11 and phosphorus-31 n.m.r. data[a] for the complexes

| Compound | $^{11}B$[b](δ) | $^{31}P$[c](δ) |
|---|---|---|
| (3) | −40.0, −35.4, −27.9, −24.2, −19.2, −14.1, −13.2, −10.7, −3.2 | 61.5 [d, $J$(RhP) 24] |
| (4) | −26.2 (1B), −21.2 (2B), −11.0 (4B), −3.4 (1B), −0.4 (1B) | [d] −21.3 [d(br), $PCBu^t$, $J$(PP) 213], 40.0 [d, $PCBu^t$, $J$(PP) 213], 51.9 (s, $PPh_3$) |
| (5) | −26.8, −22.9, −13.0, −12.3, −11.4, −8.3, −6.9, −1.2 0.6 | [d,e] 37.8 [d, $J$(PP) 30], 42.5* [d, $J$(PP) 28], 69.1* [d(br), $J$(PP) 28], 92.1 [d(br), $J$(PP) 30] |

[a] Chemical shifts in p.p.m., coupling constants in Hz, measurements in $CD_2Cl_2$ at ambient temperatures, unless otherwise stated. [b] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of 85% $H_3PO_4$ (external). [d] Measured at −60 °C to reduce line broadening. [e] Peaks due to minor diastereoisomer (see text) are asterisked.

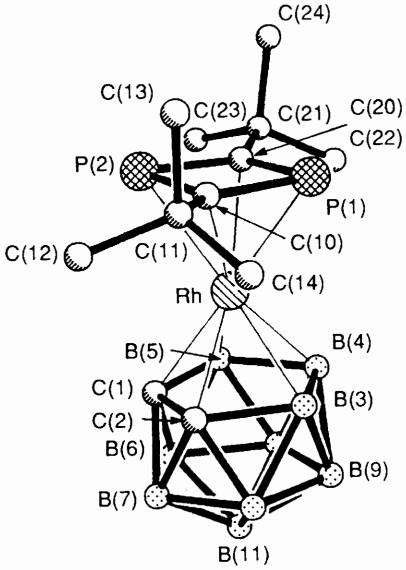


**Figure 1.** Structure of the anion of $[NEt_4][Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (3) showing the crystallographic numbering scheme

with the structure established by *X*-ray diffraction. In the $^1H$ spectrum there is one singlet resonance for the $Bu^t$ groups and one peak for the CH groups of the $C_2B_9H_{11}$ cage. The $^{13}C$-{$^1H$} spectrum shows the expected signals for the $Bu^t$ and CH groups, but also reveals a resonance for the CP nuclei at δ 111.2 p.p.m. This signal appears as a triplet of doublets due to $^{31}P$–$^{13}C$ (52 Hz) and $^{103}Rh$–$^{13}C$ (12 Hz) coupling. The corresponding *C*P resonance of (2a) is seen at δ 107.6 p.p.m., with $J$(PC) 54 Hz.[4] The $^{31}P$-{$^1H$} n.m.r. spectrum of (3) displays a doublet resonance at δ 61.5 p.p.m. [$J$(RhP) 24 Hz], and the $^{11}B$-{$^1H$} n.m.r. spectrum shows nine broad peaks, each corresponding in intensity to one $^{11}B$ nucleus. The orientation of the $Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)$ fragment with respect to the pentagonal face of the *nido*-$C_2B_9H_{11}$ cage (Figure 1) introduces an asymmetry into the latter leading to inequivalence of the boron nuclei and the observation of nine resonances. Although two peaks for the cage-carbon nuclei were not observed in the $^{13}C$-{$^1H$} n.m.r. spectrum, the resonance at δ 39.9 p.p.m. for these atoms was very broad, and therefore probably corresponds to two overlapping signals.

It was hoped that protonation of complex (3) might afford a neutral and stable compound; either a hydridorhodium species or a compound in which the proton was attached to a phosphorus atom in the 1,3-diphosphacyclobutadiene ring. However, treatment of (3) with $HBF_4{\cdot}Et_2O$ led only to decomposition. Since the fragment $[Au(PPh_3)]^+$ is isolobal with the proton,[7] the reaction of the gold species with (3) was next investigated.

A thf solution of complex (3) was treated with $[AuCl(PPh_3)]$ in the presence of $TlBF_4$. The latter reagent was added to remove chloride as TlCl, thereby generating *in situ* the species $[Au(PPh_3)]^+$. Column chromatography of the reaction mixture afforded the yellow crystalline complex $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (4) in essentially quantitative yield. The structure of this product (Figure 2) was established by *X*-ray diffraction, and selected data from this study are given in Table 4.

The $Au(PPh_3)$ group in (4) is ligated by a phosphorus atom of the 1,3-diphosphacyclobutadiene ring [Au–P(1) 2.269(3), Au–P(3) 2.281(3) Å] in such a manner that the P(1)–Au–P(3) [174.5(1)°] fragment is nearly linear. Attachment of the gold atom to P(1) has no discernible effect on the P–C separations in the four-membered ring which are essentially the same (average 1.77 Å), and close to those found in (3).

The n.m.r. data for complex (4) (Tables 1 and 2) are in agreement with the results of the *X*-ray structure analysis. In

**Table 3.** Selected internuclear distances (Å) and angles (°) for $[NEt_4][Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**3**), with estimated standard deviations (e.s.d.s) in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh–P(1) | 2.334(6) | Rh–P(2) | 2.374(6) | Rh–C(10) | 2.21(2) | Rh–C(20) | 2.20(2) |
| Rh–C(1) | 2.17(2) | Rh–C(2) | 2.19(2) | Rh–B(3) | 2.21(2) | Rh–B(4) | 2.24(3) |
| Rh–B(5) | 2.23(3) | P(1)–C(10) | 1.78(2) | P(1)–C(20) | 1.80(2) | P(2)–C(10) | 1.77(2) |
| P(2)–C(20) | 1.79(2) | C(10)–C(11) | 1.47(3) | C(20)–C(21) | 1.49(3) | C(1)–C(2) | 1.55(3) |
| C(1)–B(5) | 1.68(3) | C(2)–B(3) | 1.72(3) | B(3)–B(4) | 1.83(3) | B(4)–B(5) | 1.79(4) |

| | | | | | |
|---|---|---|---|---|---|
| P(1)–Rh–P(2) | 70.5(2) | P(1)–Rh–C(10) | 46.0(5) | P(2)–Rh–C(10) | 45.4(5) |
| P(1)–Rh–C(20) | 46.8(6) | P(2)–Rh–C(20) | 45.8(6) | C(10)–Rh–C(20) | 63.3(7) |
| C(10)–P(1)–C(20) | 80(1) | C(10)–P(2)–C(20) | 81(1) | P(1)–C(10)–P(2) | 100(1) |
| P(1)–C(20)–P(2) | 99(1) | | | | |

**Table 4.** Selected internuclear distances (Å) and angles (°) for $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**4**), with e.s.d.s in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Au–P(1) | 2.269(3) | Au–P(3) | 2.281(3) | Rh–P(1) | 2.326(3) | Rh–P(2) | 2.368(3) |
| Rh–C(1) | 2.21(1) | Rh–C(2) | 2.17(1) | Rh–B(3) | 2.19(1) | Rh–B(4) | 2.21(1) |
| Rh–B(5) | 2.21(1) | Rh–C(10) | 2.17(1) | Rh–C(20) | 2.21(1) | P(1)–C(10) | 1.77(1) |
| P(1)–C(20) | 1.76(1) | P(2)–C(10) | 1.78(1) | P(2)–C(20) | 1.77(1) | C(1)–C(2) | 1.64(2) |
| C(1)–B(5) | 1.68(2) | C(2)–B(3) | 1.70(2) | B(3)–B(4) | 1.78(2) | B(4)–B(5) | 1.83(2) |

| | | | | | |
|---|---|---|---|---|---|
| P(1)–Au–P(3) | 174.5(1) | P(1)–Rh–C(10) | 46.0(3) | P(2)–Rh–C(10) | 46.0(3) |
| P(1)–Rh–C(20) | 45.5(2) | P(2)–Rh–C(20) | 45.4(3) | C(10)–Rh–C(20) | 65.1(3) |
| C(10)–P(1)–C(20) | 84.0(4) | C(10)–P(2)–C(20) | 83.1(4) | P(1)–C(10)–P(2) | 95.8(4) |
| P(1)–C(20)–P(2) | 96.5(4) | | | | |

**Table 5.** Selected internuclear distances (Å) and angles (°) for $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**5**), with e.s.d.s in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh–P(1) | 2.398(10) | Rh–P(2) | 2.296(10) | Rh–C(1) | 2.21(3) | Rh–C(2) | 2.15(4) |
| Rh–B(3) | 2.21(4) | Rh–B(4) | 2.19(4) | Rh–B(5) | 2.19(4) | Rh–C(10) | 2.16(3) |
| Rh–C(20) | 2.16(3) | Co–P(2) | 2.22(1) | Co–C(3) | 1.98(4) | Co–C(4) | 1.71(4) |
| Co–C(30) | 2.00(4) | Co–C(40) | 2.10(4) | Co–C(50) | 2.00(4) | Co–C(60) | 1.98(4) |
| P(1)–C(10) | 1.69(4) | P(1)–C(20) | 1.77(3) | P(2)–C(10) | 1.78(4) | P(2)–C(20) | 1.74(4) |
| C(30)–C(40) | 1.36(5) | C(40)–C(50) | 1.41(6) | C(50)–C(60) | 1.38(5) | C(30)–C(60) | 1.40(6) |
| C(1)–C(2) | 1.62(5) | C(1)–B(5) | 1.76(6) | C(2)–B(3) | 1.64(6) | B(3)–B(4) | 1.65(6) |
| B(4)–B(5) | 1.75(6) | C(3)–O(3) | 1.28(6) | C(4)–O(4) | 1.22(4) | | |

| | | | | | |
|---|---|---|---|---|---|
| P(1)–Rh–P(2) | 69.7(4) | P(1)–Rh–C(10) | 43(1) | P(2)–Rh–C(10) | 47(1) |
| P(1)–Rh–C(20) | 45(1) | P(2)–Rh–C(20) | 46(1) | C(10)–Rh–C(20) | 62(1) |
| P(2)–Co–C(3) | 94(1) | P(2)–Co–C(4) | 102(1) | C(3)–Co–C(4) | 96(2) |
| C(40)–C(30)–C(60) | 97(3) | C(30)–C(40)–C(50) | 84(3) | C(30)–C(60)–C(50) | 84(3) |
| C(40)–C(50)–C(60) | 95(3) | C(10)–P(1)–C(20) | 80(2) | C(10)–P(2)–C(20) | 79(2) |
| P(1)–C(10)–P(2) | 101(2) | P(1)–C(20)–P(2) | 100(2) | Co–C(3)–O(3) | 176(3) |
| Co–C(4)–O(4) | 172(3) | | | | |

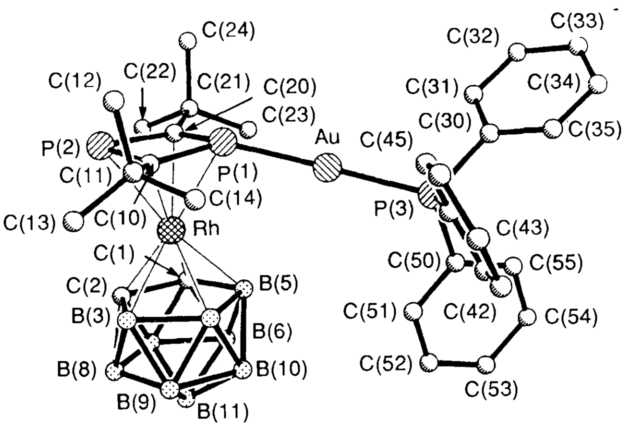


**Figure 2.** Molecular structure of $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**4**) showing the crystallographic numbering scheme

particular, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum displays resonances for the three non-equivalent phosphorus nuclei. The singlet signal at δ 51.9 p.p.m. may be ascribed to the $PPh_3$ group, and the two doublet resonances [*J*(PP) 213 Hz] at δ −21.3 and 40.0 p.p.m. to the phosphorus atoms in the four-membered ring. The signal at −21.3 p.p.m. is assigned to P(1) (Figure 2). This doublet is broader than the other due to the $^{197}Au$ (spin $\frac{3}{2}$) quadrupolar effect, and indeed was not observed in the room-temperature spectrum.

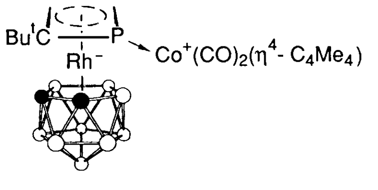
If it is assumed that the P(1) atom in (**4**) donates an electron pair to the gold atom, which is also ligated by the $PPh_3$ group, then this metal centre may be regarded as $Au^+$ ($d^{10}$), like the gold atom in the salt $[Au(PPh_3)_2][PF_6]$.[8] The rhodium centre would then formally carry a uninegative charge, as in the salt (**3**), and overall complex (**4**) would be neutral with a zwitterionic structure.

The reaction between (**3**) and the salt $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ was also studied. Addition of the latter to a $CH_2Cl_2$ solution of the former gave yellow crystals of the complex $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**5**) in *ca.* 80% yield. Examination of the i.r. spectrum, and the $^1H$, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. data, for this product revealed that in solution it existed as a mixture of two diastereoisomers in *ca.* 3:1 proportions, based on peak intensities in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (Table 2). Discussion of this data is

**Table 6.** Data for crystal structure analyses[a]

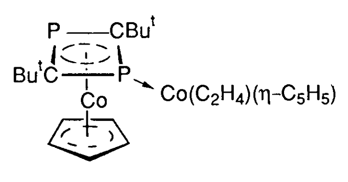
| Compound | (3) | (4) | (5) |
|---|---|---|---|
| Molecular formula | $C_{20}H_{49}B_9NP_2Rh$ | $C_{30}H_{44}AuB_9P_3Rh$ | $C_{22}H_{41}B_9CoO_2P_2Rh$ |
| $M$ | 865.8 | 894.9 | 658.9 |
| Crystal shape and colour | Amber prisms | Yellow-orange rhombs | Yellow platelets |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic |
| Space group | $P2_12_12_1$ (no. 19) | $P2_1/a$ (non-standard, no. 14) | $P2_1/c$ (no. 14) |
| $a$/Å | 10.152(3) | 18.51(1) | 16.181(8) |
| $b$/Å | 12.205(4) | 10.363(4) | 10.361(5) |
| $c$/Å | 23.919(6) | 19.00(1) | 19.51(1) |
| $\beta$/° |  | 96.17(5) | 101.70(5) |
| $U$/Å$^3$ | 2 965(1) | 3 623(3) | 3 203(3) |
| $Z$ | 4 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.35 | 1.65 | 1.37 |
| $F(000)$ | 1 184 | 1 704 | 1 344 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 6.8 | 46.4 | 11.4 |
| $2\theta$ range/° | $3 \leqslant 2\theta \leqslant 50$ | $3 \leqslant 2\theta \leqslant 50$ | $3 \leqslant 2\theta \leqslant 45$ |
| Approx. crystal size (mm) | 0.10 × 0.40 × 0.20 | 0.72 × 0.80 × 0.84 | 0.05 × 0.20 × 0.20 |
| No. of unique data | 3 820 | 5 422 | 4 206 |
| No. of observed data | 2 033 | 3 895 | 1 786 |
| Criterion for observed data, $n$ in $[F \geqslant n\sigma(F)]$ | 2.0 | 5.0 | 3.5 |
| Refinement solution method | Patterson | Patterson | Patterson |
| Anisotropic atoms | C of $C_2Bu^t_2$ group, P, Rh | C, B, P, Rh, Au | P, Co, Rh |
| Isotropic atoms | H, B, C | H | H, B, C |
| Final $R(R')$[b] | 0.097 (0.084) | 0.043 (0.046) | 0.13 (0.12) |
| Residual index $S$ | 1.12 | 1.61 | 1.64 |
| $g$ | 0.002 50 | 0.000 475 | 0.001 |
| Largest final difference electron-density features (e Å$^{-3}$) | +1.2, −1.4 | +0.8, −1.1 | +1.7, −1.8 |

[a] Common to all: data collected at 298 K using graphite-monochromated Mo-$K_\alpha$ $X$-radiation, $\bar{\lambda}$ = 0.710 73 Å; diffractometer Siemens R3m/V. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$ ($\Delta = |F_o| - |F_c|$, $N_o$,$N_v$ = number of observations and variables); $w^{-1} = [\sigma_c^2(F_o) + gF^2]$, $\sigma_c^2(F_o)$ = variance in $F_o$ due to counting statistics; $g$ was chosen so as to minimise variation in $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$.



(5)

● CH ○ BH



(6)

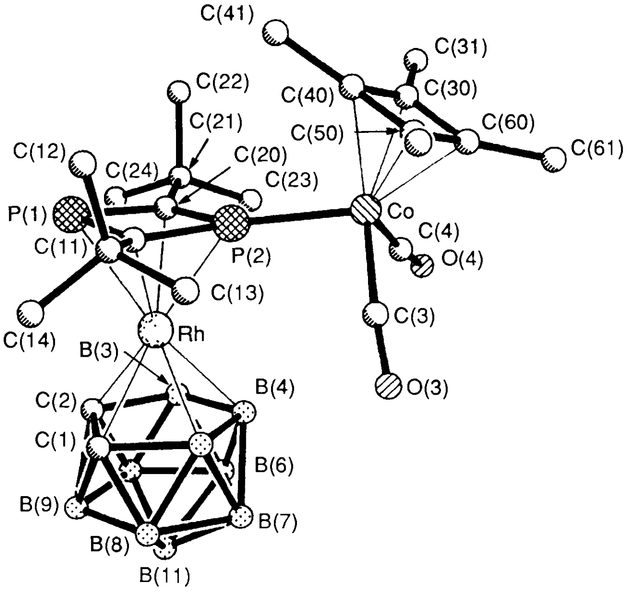


**Figure 3.** Molecular structure of $[Rh\{\eta^4\text{-}Bu^t_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (5) showing the crystallographic numbering scheme

deferred until the results of an $X$-ray diffraction study are described.

It was impossible to grow good-quality single crystals of (5), only thin platelets being obtained. Consequently the $X$-ray study led to a relatively poor structure determination (see Experimental section). Nevertheless, the results left no doubt about the overall molecular structure (Figure 3 and Table 5). The complex is derived from (3) by co-ordination of a $Co(CO)_2(\eta^4\text{-}C_4Me_4)$ fragment to one of the phosphorus atoms in the four-membered 1,3-diphosphacyclobutadiene ring of the latter species. As in the complexes (3) and (4), the P–C distances in the 1,3-diphosphacyclobutadiene ring (5) (average 1.75 Å) are equal, within the limits of the available data. Moreover, in all three structures reported herein the $\eta^4$-$C_2P_2$ rings deviate little from planarity [mean deviation: ±0.023, (3); ±0.048, (4); and ±0.039 Å, (5)]. The cobalt atom in (5) carries the tetramethylcyclobutadiene ligand, as well as two terminally bound CO groups. The rhodium atom is co-ordinated by the $C_2B_9H_{11}$ cage in the usual manner *via* the open pentagonal face of this *nido*-icosahedral fragment.

The structure established for complex (5) is novel in that it contains both a cyclobutadiene and a diphosphacyclobutadiene ligand. The cobalt atom acquires an electron pair from P(2), and together with its other ligands attains a filled 18-electron valence shell for Co$^+$ ($d^8$). As in complex (**4**), the Rh($\eta^5$-$C_2B_9H_{11}$) fragment in (**5**) would retain a uninegative charge, and overall the compound is thus neutral.

**Table 7.** Atomic positional parameters (fractional co-ordinates, × $10^4$) for complex (**3**), with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Rh | 1 044(2) | 10 792(1) | 770(1) |
| P(1) | 963(7) | 9 050(5) | 369(2) |
| P(2) | −204(5) | 10 863(6) | −68(2) |
| C(10) | 1 325(20) | 10 160(15) | −87(9) |
| C(11) | 2 467(22) | 10 366(18) | −451(8) |
| C(12) | 2 587(23) | 11 569(18) | −641(9) |
| C(13) | 2 266(23) | 9 666(19) | −1 009(8) |
| C(14) | 3 757(22) | 9 985(20) | −210(9) |
| C(20) | −565(20) | 9 798(19) | 420(8) |
| C(21) | −1 844(19) | 9 504(16) | 683(9) |
| C(22) | −1 683(23) | 8 940(19) | 1 242(11) |
| C(23) | −2 769(22) | 10 426(18) | 741(11) |
| C(24) | −2 486(25) | 8 694(22) | 275(10) |
| C(1) | 1 251(23) | 12 444(16) | 1 095(8) |
| C(2) | 2 623(21) | 11 955(19) | 961(8) |
| B(3) | 2 826(20) | 10 727(21) | 1 303(10) |
| B(4) | 1 291(28) | 10 553(23) | 1 691(11) |
| B(5) | 268(23) | 11 698(21) | 1 511(11) |
| B(6) | 1 022(33) | 12 943(23) | 1 760(13) |
| B(7) | 2 549(24) | 13 070(24) | 1 395(14) |
| B(8) | 3 559(25) | 11 970(18) | 1 530(10) |
| B(9) | 2 751(23) | 11 109(24) | 2 022(12) |
| B(10) | 1 180(28) | 11 718(23) | 2 157(10) |
| B(11) | 2 544(34) | 12 583(28) | 2 060(13) |
| N | 2 964(17) | 6 858(14) | 1 935(7) |
| C(30) | 3 866(28) | 6 460(20) | 1 504(10) |
| C(31) | 4 214(29) | 7 350(21) | 1 064(10) |
| C(40) | 2 653(22) | 5 902(21) | 2 300(9) |
| C(41) | 3 763(28) | 5 422(22) | 2 613(12) |
| C(50) | 1 712(24) | 7 235(21) | 1 690(11) |
| C(51) | 995(27) | 6 452(19) | 1 321(10) |
| C(60) | 3 586(27) | 7 754(22) | 2 250(10) |
| C(61) | 2 828(26) | 8 154(21) | 2 769(10) |

As mentioned above, in solution complex (**5**) exists as a mixture of more than one diastereoisomer. Thus the i.r. spectrum shows three absorptions in the CO stretching region, rather than two. The $^{31}P$-{$^1H$} n.m.r. spectrum (Table 2) shows two pairs of resonances, with each signal a doublet due to $^{31}P$–$^{31}P$ coupling. The relative intensity of the two pairs is *ca.* 3:1. If a single isomer were present only one pair of signals would have been observed.

The $^1H$ and $^{13}C$-{$^1H$} n.m.r. spectra of (**5**) were informative. However, because of the insolubility of the complex leading to weak signals, and band broadening caused by the presence of the quadrupolar $^{59}Co$ nucleus, not all peaks due to the minor isomer were observed in the $^{13}C$-{$^1H$} n.m.r. spectrum. For the symmetrical structure of the diastereoisomer established by *X*-ray diffraction, the Bu$^t$ groups should give rise to one signal in the $^1H$ n.m.r. spectrum, and two ($CMe_3$ and $CMe_3$) in the $^{13}C$-{$^1H$} spectrum. The resonance in the $^1H$ n.m.r. spectrum for the Bu$^t$ groups occurs at δ 1.05, and surprisingly corresponds to the minor isomer, based on peak intensity. Only one resonance (δ 32.2 p.p.m.) for the Bu$^t$ group was observed in the $^{13}C$-{$^1H$} n.m.r. spectrum and this can be assigned to the $C\mathit{Me}_3$ nuclei. The absence of the $\mathit{C}Me_3$ resonance, as well as signals for the CO groups, is attributed to the measurement difficulties mentioned above. The major diastereoisomer present in solutions of (**5**) has a less symmetrical structure since the Bu$^t$ groups are inequivalent. In the $^1H$ n.m.r. spectrum of the mixture two resonances for the Bu$^t$ group for this species are seen (δ 0.97 and 1.10), and correspondingly in the $^{13}C$-{$^1H$} n.m.r. spectrum there are two sets of peaks at δ 35.6 and 35.3 p.p.m. ($\mathit{C}Me_3$), and 32.3 and 32.0 p.p.m. ($C\mathit{Me}_3$). We suggest that the n.m.r. data imply a restricted rotation about the Co–P(2) bond in (**5**) in solution, so that the bulky $Co(CO)_2(\eta^4$-$C_4Me_4)$ fragment adopts different orientations with respect to the remainder of the molecule.

It has been previously reported[4] that treatment of complex (**2a**) with 1 equivalent of [$Co(C_2H_4)_2(\eta$-$C_5H_5)$] affords the complex [Co{$\eta^4$-Bu$^t_2C_2P_2Co(C_2H_4)(\eta$-$C_5H_5)$}($\eta$-$C_5H_5$)] (**6**), the structure of which was deduced from n.m.r. spectroscopy. It is evident that the structures of (**5**) and (**6**) can be mapped isolobally.[9] The $\eta^4$-$C_4Me_4$ and $\eta$-$C_5H_5$ rings in (**5**) and (**6**) can be viewed as bi- and tri-dentate groups respectively, with the $C_5H_5$ ring formally carrying a negative charge. The $Co(CO)_2$-($\eta^4$-$C_4Me_4$) and $Co(C_2H_4)(\eta$-$C_5H_5)$ moieties can thus both be

**Table 8.** Atomic positional parameters (fractional co-ordinates, × $10^4$) for complex (**4**), with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Au | 8 753(1) | 1 059(1) | 7 556(1) | C(21) | 9 016(6) | 2 106(10) | 9 869(5) |
| Rh | 8 033(1) | 3 757(1) | 8 566(1) | C(22) | 9 008(7) | 3 196(12) | 10 410(6) |
| P(1) | 8 150(1) | 1 526(3) | 8 503(1) | C(23) | 9 698(6) | 2 189(12) | 9 492(6) |
| P(2) | 7 439(2) | 2 696(3) | 9 446(1) | C(24) | 8 975(7) | 831(11) | 10 259(7) |
| P(3) | 9 254(1) | 539(3) | 6 547(1) | C(30) | 9 847 | −833 | 6 630 |
| C(1) | 8 860(5) | 5 299(11) | 8 733(6) | C(31) | 10 244(4) | −1 098(6) | 7 280(3) |
| C(2) | 8 037(6) | 5 792(10) | 8 839(6) | C(32) | 10 743 | −2 111 | 7 338 |
| B(3) | 7 434(6) | 5 449(11) | 8 122(7) | C(33) | 10 845 | −2 859 | 6 746 |
| B(4) | 7 944(7) | 4 663(11) | 7 505(6) | C(34) | 10 448 | −2 594 | 6 096 |
| B(5) | 8 872(6) | 4 562(10) | 7 947(7) | C(35) | 9 949 | −1 581 | 6 038 |
| B(6) | 9 199(7) | 6 163(12) | 8 116(8) | C(40) | 8 553 | 133 | 5 848 |
| B(7) | 8 678(7) | 6 938(12) | 8 687(7) | C(41) | 8 546(4) | 659(6) | 5 171(3) |
| B(8) | 7 786(7) | 7 030(10) | 8 287(7) | C(42) | 7 997 | 321 | 4 643 |
| B(9) | 7 740(6) | 6 361(11) | 7 438(7) | C(43) | 7 455 | −542 | 4 790 |
| B(10) | 8 630(7) | 5 846(11) | 7 315(7) | C(44) | 7 462 | −1 068 | 5 467 |
| B(11) | 8 536(7) | 7 238(11) | 7 780(7) | C(45) | 8 011 | −731 | 5 996 |
| C(10) | 7 272(5) | 2 159(9) | 8 552(5) | C(50) | 9 770 | 1 823 | 6 209 |
| C(11) | 6 575(6) | 1 861(10) | 8 095(6) | C(51) | 9 492(3) | 3 072(6) | 6 232(3) |
| C(12) | 6 248(7) | 658(12) | 8 395(8) | C(52) | 9 865 | 4 101 | 5 966 |
| C(13) | 6 045(6) | 2 944(12) | 8 093(9) | C(53) | 10 516 | 3 882 | 5 677 |
| C(14) | 6 716(8) | 1 616(17) | 7 358(8) | C(54) | 10 794 | 2 634 | 5 654 |
| C(20) | 8 342(5) | 2 219(8) | 9 345(5) | C(55) | 10 421 | 1 604 | 5 920 |

**Table 9.** Atomic positional parameters (fractional co-ordinates, × $10^4$) for complex (**5**), with e.s.d.s in parentheses

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Rh | 3 086(2) | 5 003(3) | 5 241(1) |
| Co | 1 750(3) | 2 606(5) | 6 313(3) |
| P(1) | 4 426(7) | 4 321(11) | 5 907(6) |
| P(2) | 2 901(6) | 3 498(9) | 6 060(5) |
| C(1) | 2 997(22) | 7 024(33) | 4 874(18) |
| C(2) | 3 320(23) | 6 039(35) | 4 344(19) |
| B(3) | 2 607(25) | 4 919(51) | 4 098(20) |
| B(4) | 1 846(26) | 5 123(51) | 4 538(20) |
| B(5) | 2 071(23) | 6 438(34) | 5 109(19) |
| B(6) | 1 737(32) | 5 573(44) | 3 696(26) |
| B(7) | 1 328(30) | 6 682(45) | 4 296(24) |
| B(8) | 2 104(32) | 7 797(49) | 4 535(26) |
| B(9) | 2 936(26) | 7 550(42) | 4 053(21) |
| B(10) | 2 664(24) | 6 139(36) | 3 513(20) |
| B(11) | 1 882(24) | 7 282(35) | 3 651(20) |
| C(3) | 1 158(22) | 4 282(33) | 6 312(18) |
| O(3) | 729(26) | 5 323(42) | 6 306(21) |
| C(4) | 1 215(22) | 2 109(33) | 5 506(19) |
| O(4) | 895(17) | 1 613(25) | 4 946(15) |
| C(10) | 3 653(22) | 4 741(34) | 6 331(18) |
| C(11) | 3 712(23) | 5 685(35) | 6 950(19) |
| C(12) | 4 259(21) | 5 220(38) | 7 607(17) |
| C(13) | 2 847(24) | 6 021(40) | 7 162(20) |
| C(14) | 4 055(27) | 6 979(39) | 6 770(23) |
| C(20) | 3 650(19) | 3 156(27) | 5 563(16) |
| C(21) | 3 764(25) | 1 969(35) | 5 090(20) |
| C(22) | 4 228(25) | 923(38) | 5 562(20) |
| C(23) | 2 967(25) | 1 436(41) | 4 711(21) |
| C(24) | 4 351(23) | 2 356(38) | 4 626(19) |
| C(30) | 1 946(25) | 859(38) | 6 747(20) |
| C(31) | 2 050(29) | −422(40) | 6 354(23) |
| C(40) | 2 462(26) | 1 671(37) | 7 189(21) |
| C(41) | 3 378(23) | 1 643(37) | 7 478(19) |
| C(50) | 1 700(25) | 2 203(37) | 7 307(21) |
| C(51) | 1 617(25) | 3 093(38) | 7 891(21) |
| C(60) | 1 185(24) | 1 384(34) | 6 848(19) |
| C(61) | 322(27) | 972(46) | 6 756(23) |

regarded as $Co^{I}L_4[Co^{I}(d^8)$, L an electron-pair donor] groups.[9] The isolobal relationship between the fragments $Co(\eta\text{-}C_5H_5)$ and $Rh(\eta^5\text{-}C_2B_9H_{11})^-$ was mentioned earlier.

## Experimental

All experiments were carried out under nitrogen, using Schlenk-tube techniques, and all solvents were freshly distilled over appropriate drying agents prior to use. Chromatography columns were of silica gel (Fluka, 70—230 mesh). The instrumentation used for the spectroscopic measurements has been described previously.[10] The reagents $K[Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$,[6] $Bu^tC{\equiv}P$,[11] $[AuCl(PPh_3)]$,[12] and $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$[13] were prepared by previously reported methods.

*Synthesis of the Salt* $[NEt_4][Rh(\eta^4\text{-}Bu^t_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**3**).—The compound $Bu^tC{\equiv}P$ (0.10 g, 1.0 mmol) was added to a thf (25 $cm^3$) solution of $K[Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ (0.30 g, 0.38 mmol). The mixture was stirred at room temperature for 3 d, during which time the colour changed from dark brown to dark red. The salt $[NEt_4]Cl$ (0.30 g, 1.52 mmol) was then added, and the mixture was stirred for 2 h, after which it was filtered through a Celite pad (*ca.* 3 cm). Solvent was reduced in volume to *ca.* 3 $cm^3$, and hexane (*ca.* 50 $cm^3$) was added dropwise to avoid formation of an oil, while stirring vigorously. This procedure afforded dark brown microcrystals from which the supernatant liquid was removed with a syringe. The residue was washed with hexane–$Et_2O$ (1:1, 4 × 20 $cm^3$) to remove $PPh_3$, and then dried *in vacuo* for *ca.* 12 h to give brown *microcrystals* of $[NEt_4][Rh(\eta^4\text{-}Bu^t_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**3**) (0.20 g, 75%) (Found: C, 43.4; H, 8.1. $C_{20}H_{49}B_9NP_2Rh$ requires C, 42.5; H, 8.7%).

*Preparation of the Dimetal Compounds.*—(*i*) A thf (25 $cm^3$) solution of complex (**3**) (0.10 g, 0.18 mmol) was treated with $[AuCl(PPh_3)]$ (0.09 g, 0.18 mmol) and $TlBF_4$ (0.07 g, 0.20 mmol), and the mixture was stirred for 2 h, and then filtered through a Celite pad (*ca.* 3 cm) to remove TlCl. Solvent was removed *in vacuo*, and the residue was dissolved in $CH_2Cl_2$ (1 $cm^3$) and chromatographed at −20 °C on a 2 × 20 $cm^3$ silica-gel column, eluting with the same solvent. A yellow eluate was collected from which solvent was removed *in vacuo*. Recrystallisation of the residue from $CH_2Cl_2$–hexane (20 $cm^3$, 1:20) gave yellow *microcrystals* of $[Rh\{\eta^4\text{-}Bu^t_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**4**) (0.15 g, 95%) (Found: C, 40.3; H, 5.0. $C_{30}H_{44}AuB_9P_3Rh$ requires C, 40.3; H, 5.0%).

(*ii*) The salt $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ (0.74 g, 0.18 mmol) was added to a solution of (**3**) (0.10 g, 0.18 mmol) in $CH_2Cl_2$ (25 $cm^3$) and the mixture was stirred for *ca.* 4 h, after which the reaction was complete (monitored by i.r. spectroscopy). Solvent was reduced *in vacuo* to *ca.* 2 $cm^3$, and the mixture was chromatographed (at −20 °C, 2 × 20 cm column), using $CH_2Cl_2$ as eluant. A yellow fraction was collected, reduced in volume to *ca.* 1 $cm^3$, and hexane (20 $cm^3$) was added. This procedure afforded yellow microcrystals from which the supernatant liquid was removed with a syringe. Drying of the residue *in vacuo* gave yellow *microcrystals* of $[Rh\{\eta^4\text{-}Bu^t_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**5**) (0.10 g, 84%) (Found: C, 40.9; H, 6.5. $C_{22}H_{41}B_9CoO_2P_2Rh$ requires C, 40.1; H, 6.3%); $\nu(CO)_{max.}$ at 2 074w, 2 040w(sh), and 2 023vs $cm^{-1}$ (in $CH_2Cl_2$).

*Crystal Structure Determinations.*—Details of the data-collection procedures and structure solution and refinement are given in Table 6. Data were collected on single crystals mounted under nitrogen in thin-walled glass capillaries, and were corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an empirical method based upon azimuthal scan data.[14]

The structures were solved by conventional heavy-atom and Fourier difference methods, and were refined by blocked-cascade least squares. All the hydrogen atoms were included in calculated positions (C–H 0.96, B–H 1.10 Å)[15] with fixed isotropic thermal parameters. In order to distinguish C from B atoms in the $C_2B_9H_{11}$ cages, initially all these atoms were treated as borons until sufficient data became available to allow a distinction to be made on the basis of thermal parameters and bond lengths. In general, C–C distances are 1.65 Å or less, and B–B 1.70 Å or greater. For complex (**3**), $P2_12_12_1$ is a chiral space group. Enantiomer tests during refinement showed that the final co-ordinates correspond to the correct form. The goodness of fit ($S$) for (**5**) (Table 6) indicates that the model refined is a satisfactory one, and the high $R$ values are a result of low scattering power of the crystal. All calculations were performed on a DEC micro-Vax II computer using the SHELXTL PLUS system of programs. Scattering factors were from ref. 16. Atomic co-ordinates for complexes (**3**)—(**5**) are listed in Tables 7—9, respectively.

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

## Acknowledgements

We thank the S.E.R.C. for support, SHELL for a C.A.S.E.

research studentship (to M. U. P.), and the Deutsche-Forsschungsgemeinschaft for a fellowship (to J. S.).

## References

1 (*a*) J. R. Fernandez, G. F. Helm, J. A. K. Howard, M. U. Pilotti, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1990, 1747; (*b*) N. Carr, M. C. Gimeno, J. E. Goldberg, M. U. Pilotti, F. G. A. Stone, and I. Topaloğlu, *ibid.*, p. 2253.

2 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327; M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484.

3 P. B. Hitchcock, M. J. Maah, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 737.

4 P. Binger, R. Milczarek, R. Mynott, M. Regitz, and W. Rösch, *Angew. Chem., Int. Ed. Engl.*, 1986, **98**, 645; P. Binger, R. Milczarek, R. Mynott, Yi-Hung Tsay, E. Raable, C. Krüger, and M. Regitz, *Chem. Ber.*, 1988, **121**, 637.

5 H. F. Dare, J. A. K. Howard, M. U. Pilotti, F. G. A. Stone, and J. Szameitat, *J. Chem. Soc., Chem. Commun.*, 1989, 1409.

6 J. A. Walker, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1985, **24**, 2688 and refs. therein.

7 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.

8 G. A. Carriedo, J. A. K. Howard, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1984, 2545.

9 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

10 S. J. Davies, J. A. K. Howard, M. U. Pilotti, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1989, 2289.

11 G. Becker, G. Gresser, and W. Uhl, *Z. Naturforsch., Teil B*, 1981, **36**, 16; W. Rösch, U. Hees, and M. Regitz, *Chem. Ber.*, 1987, **120**, 1645.

12 F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.

13 M. R. Cook, P. Härter, P. L. Pauson, and J. Sraga, *J. Chem. Soc., Dalton Trans.*, 1987, 2757.

14 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-Ray system, revision 5.1, 1985.

15 P. Sherwood, BHGEN, a program for the calculation of idealised H-atom positions for a *nido*-icosahedral carbaborane fragment, Bristol University, 1986.

16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

*Received* 19*th December* 1989; *Paper* 9/05387E