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Reactions of $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$ with didentate phosphines and the synthesis and crystal structure of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-dppf-}P,P')AuB]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene]

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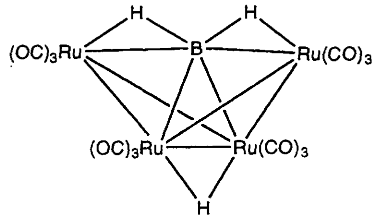
Ligand-substitution reactions of $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$ with the didentate phosphines dppf and dppa yielded compounds of the type $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(L\text{-}P)BH]$ [L = 1,1′-bis(diphenylphosphino)-ferrocene (dppf) or bis(diphenylphosphino)acetylene (dppa)] with the *P*-donor ligand replacing one CO ligand in a butterfly wingtip site. Spectroscopic data indicate that a redistribution of cluster hydrogen atoms occurs during CO ligand substitution. Subsequent reaction of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\text{dppf-}P)BH]$ with $[N(PPh_3)_2]Cl$ and $[Au_2Cl_2(\text{dppf})]$ yielded $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-dppf-}P,P')AuB]$, but there was a competitive intramolecular substitution reaction to give $[RhRu_3H_3(\eta^5\text{-}C_5Me_5)(CO)_7(\mu\text{-dppf-}P,P')B]$. The gold cluster has been characterised by single-crystal X-ray crystallography. The $RhRu_3B$ core is straddled by a {Au(dppf)} unit which co-ordinates to a wingtip ruthenium atom through a phosphorus atom whilst the gold centre bridges the ruthenium–boron edge. Possible routes to the formation of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-dppf-}P,P')AuB]$ have been investigated.

We recently reported phosphine and phosphite substitution reactions of the homometallic boride cluster $[Ru_4H(CO)_{12}BH_2]$ **1** and showed that the first site of substitution for a monodentate ligand PR_3 or $P(OR)_3$ is at a wingtip ruthenium atom, specifically in an equatorial position.[1] Substitution patterns with a range of bis(phosphine) ligands are dependent both on the phosphine and on the reaction conditions. 1,2-Bis(diphenylphosphino)ethane (dppe) favours an $Ru_{wingtip}$–Ru_{hinge} edge-bridging mode but there is some competition for the formation of the linked species $[\{Ru_4H(CO)_{11}BH_2\}_2(\mu\text{-dppe-}P,P')]$. Increasing the carbon backbone by one CH_2 unit favours products in which the ligand is pendant (attached to $Ru_{wingtip}$) or chelating (at $Ru_{wingtip}$), and the 1,1′-bis(diphenylphosphino)ferrocene (dppf) ligand behaves similarly. For ligands $Ph_2P(CH_2)_nPPh_2$ (n = 4 or 6) or $Ph_2PC{\equiv}CPPh_2$, products in which the ligand is pendant or linking between two clusters are observed.[1] We have extended these investigations to the heterometallic cluster $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$ **2** which is structurally related to **1**, and report here reactions between **2** and dppf and bis(diphenylphosphino)acetylene (dppa) and the subsequent reaction of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\text{dppf-}P)BH]$ with $[N(PPh_3)_2]Cl$ and $[Au_2Cl_2(\text{dppf})]$.



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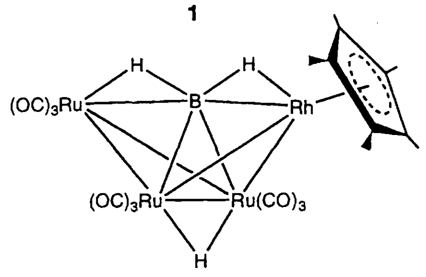

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Experimental

General data

Fourier-transform NMR spectra were recorded on a Bruker WM 250 or AM 400 spectrometer; ^1H shifts are reported with respect to δ 0 for $SiMe_4$; ^{11}B with respect to δ 0 for $F_3B{\cdot}OEt_2$ and ^{31}P with respect to δ 0 for H_3PO_4. All downfield chemical shifts are positive. Infrared spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer, FAB (fast atom bombardment) and FIB (fast ion bombardment) on Kratos instruments with 3-nitrobenzyl alcohol as matrix.

All reactions were carried out under argon by using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N_2 before use. Separations were carried out by thin-layer plate chromatography with Kieselgel 60-PF-254 (Merck). The reagents $[N(PPh_3)_2]Cl$ and dppf (Aldrich) and dppa (Strem) were used as received. The compounds $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$,[2] $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(PPh_3)BH]$[2] and $[Au_2Cl_2(\text{dppf})]$[3] were prepared according to published methods. Yields are with respect to the starting cluster **2** for the preparations of **3** and **4**, or with respect to the appropriate derivative cluster for the preparations of **5** and **6**.

Reactions of $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$ 2 with dppf and dppa

In a typical reaction, $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$[2] (81 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (10 cm^3) to give a red solution and 1 equivalent of dppf (55 mg, 0.1 mmol) was added. The solution became brown and, after stirring for 1 h at room temperature, solvent was removed *in vacuo* and the products separated by TLC, eluting with hexane–CH$_2$Cl$_2$ (2:1). A single brown band (R_f 0.5) identified as [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(dppf-*P*)BH] **3** (≈80% yield) separated from the brown baseline. The compound [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(dppa-*P*)BH] **4** was prepared similarly and was the only product collected (R_f 0.5; yield ⩾80%) in a series of reactions.

Compound **3**: NMR (CDCl$_3$, 298 K): ^{1}H (400 MHz), δ 7.7–7.4 (m, Ph, 20 H), 4.23 (br, C$_5$H$_4$, 4 H), 3.97 (br, C$_5$H$_4$, 4 H), 2.07 (s, Me, 15 H), −5.0 (br, Ru–H–B), −14.14 (d, J_{PH} 14 Hz, Ru–H–Ru) and −20.81 (s, Ru–H–Ru); ^{11}B (128 MHz), δ 149; ^{31}P (162 MHz), δ 24.0 (s, 1 P) and −18.7 (s, 1 P); IR (CH$_2$Cl$_2$, cm^{-1}), ν_{CO} 2055s, 2021vs, 1992s, 1967m and 1789w; FAB mass spectrum, *m/z* 1277 (M^+ − 2CO) with 7 CO losses (calc. for ^{12}C$_{52}$^{1}H$_{46}$^{11}B^{56}Fe^{16}O$_8$^{31}P$_2$^{103}Rh^{101}Ru$_3$ 1333).

Compound **4**: NMR (CDCl$_3$, 298 K): ^{1}H (400 MHz), δ 7.8–7.2 (m, Ph, 20 H), 2.07 (s, Me, 15 H), −5.1 (br, Ru–H–B), −14.4 (d, J_{PH} 14 Hz, Ru–H–Ru) and −20.5 (s, Ru–H–Ru); ^{11}B (128 MHz), δ 151; ^{31}P (162 MHz), δ 5.3 (s, 1 P) and −33.6 (s, 1 P); IR (CH$_2$Cl$_2$, cm^{-1}), ν_{CO} 2085s, 2024vs, 2001m, 1969m and 1790w; FAB mass spectrum; *m/z* 1033 (M^+ − 5CO) (calc. for ^{12}C$_{44}$^{1}H$_{38}$^{11}B^{16}O$_8$^{31}P$_2$^{103}Rh^{101}Ru$_3$ 1173).

Reaction of [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(dppf-*P*)BH] 3 with [N(PPh$_3$)$_2$]Cl and [Au$_2$Cl$_2$(dppf)]

A CH$_2$Cl$_2$ solution (5 cm^3) of [N(PPh$_3$)$_2$]Cl (57 mg, 0.1 mmol) was added to a CH$_2$Cl$_2$ (5 cm^3) solution of compound **3** (66 mg, 0.05 mmol). The brown solution was stirred and any reaction was monitored by IR spectroscopy, but after 1 h no changes had been observed. A solution of [Au$_2$Cl$_2$(dppf)] (51 mg, 0.05 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added and the solution stirred for 1 h. Solvent was removed *in vacuo* and the products separated by TLC, eluting first with hexane–CH$_2$Cl$_2$ (2:1) and then with hexane–CH$_2$Cl$_2$ (2:3). The first fraction (R_f 0.7, red-brown, ≈50% yield) was identified as [RhRu$_3$H$_3$(η^5-C$_5$Me$_5$)(CO)$_7$(μ-dppf-*P*,*P*′)B] **5**. The second fraction (R_f 0.5, red-brown, ≈20% yield) was identified as [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(μ-dppf-*P*,*P*′)AuB] **6**. A third fraction (R_f 0.2, brown, ≈10%) eluded full characterisation.

Compound **5**: NMR (CDCl$_3$, 298 K) ^{1}H (400 MHz), δ 7.7–7.4 (m, Ph, 20 H), 4.4–3.6 (m, C$_5$H$_4$, 8 H), 1.97 (s, Me, 15 H), −14.1 (d, J_{PH} 12.5, Ru–H–Ru, see text), −15.4 (dd, J_{PH} 10, 18, Ru–H–Ru) and −20.8 (d, J_{PH} 5.5 Hz, Ru–H–Ru); ^{11}B (128 MHz), δ 180 (vbr, $w_{\frac{1}{2}}$ 1550 Hz); ^{31}P (162 MHz), δ 25.3 (s, 1 P) and 24.0 (s, 1 P); IR (CH$_2$Cl$_2$, cm^{-1}) ν_{CO} 2028m, 2007vs, 2000m (sh), 1963m and 1786w; FAB mass spectrum; *m/z* 1306 (P^+) (calc. for ^{12}C$_{51}$^{1}H$_{46}$^{11}B^{56}Fe^{16}O$_7$^{31}P$_2$^{103}Rh^{101}Ru$_3$ 1305) with 6 CO losses.

Compound **6**: NMR (CDCl$_3$, 298 K) ^{1}H (400 MHz), δ 7.7–7.4 (m, Ph, 20 H), 4.4–3.2 (m, C$_5$H$_4$, 8 H), 2.07 (s, Me, 15 H), −13.6 (d, J_{PH} 14 Hz, Ru–H–Ru), and −20.0 (s, Ru–H–Ru); ^{11}B (128 MHz), δ 170; ^{31}P (162 MHz), δ 57.9 (s, 1 P) and 32.0 (s, 1 P); IR (CH$_2$Cl$_2$, cm^{-1}), ν_{CO} 2040s, 2008vs, 1969m, 1952m and 1772w; FAB mass spectrum; *m/z* 1529 (P^+) (calc. for ^{12}C$_{52}$^{1}H$_{45}$^{197}Au^{11}B^{56}Fe^{16}O$_8$^{31}P$_2$^{103}Rh^{101}Ru$_3$ 1529) with 9 CO losses.

Reaction of complex 3 with [N(PPh$_3$)$_2$]Cl and [AuCl(PPh$_3$)]

A CH$_2$Cl$_2$ solution (5 cm^3) of [N(PPh$_3$)$_2$]Cl (57 mg, 0.1 mmol) was added to a CH$_2$Cl$_2$ (5 cm^3) solution of compound **3** (66 mg, 0.05 mmol). The solution was stirred and after 15 min IR spectroscopy showed that no apparent reaction had occurred. A solution of [AuCl(PPh$_3$)] (30 mg, 0.06 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added and the solution was stirred for 20 min. Solvent was removed *in vacuo* and the products were separated by TLC, eluting with hexane–CH$_2$Cl$_2$ (2:1). Two fractions were collected and identified as compounds **5** (30) and **6** (40%).

Reaction of [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(PPh$_3$)BH] with [N(PPh$_3$)$_2$]Cl and [Au$_2$Cl$_2$(dppf)]

A CH$_2$Cl$_2$ solution (5 cm^3) of [N(PPh$_3$)$_2$]Cl (57 mg, 0.1 mmol) was added to a CH$_2$Cl$_2$ (5 cm^3) solution of the compound [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(PPh$_3$)BH][2] (52 mg, 0.05 mmol). The solution was stirred and after 15 min, IR spectroscopy showed that there had been no apparent reaction. A solution of [Au$_2$Cl$_2$(dppf)] (30 mg, 0.03 mmol) was added and the mixture stirred for 20 min. The solvent was removed *in vacuo* and the products were separated by TLC, eluting with hexane–CH$_2$Cl$_2$ (2:1). Starting cluster was recovered in ≈50% yield while the remainder of the material formed an intractable baseline on the TLC plate. No gold-containing products could be isolated from the reaction.

Crystallography

Crystallographic data for compound **6** are collected in Table 1. Black block crystals were photographically characterised and determined to belong to the triclinic crystal system. The centrosymmetric space group alternative was initially chosen by its frequency of occurrence and the distribution of *E* values; the choice was confirmed by subsequent refinement behaviour. An empirical correction for absorption was applied to the data. The structure was solved by direct methods, completed from Fourier-difference maps, and refined with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in idealised locations. All computations used SHELXTL 4.2 software.[4]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/103.

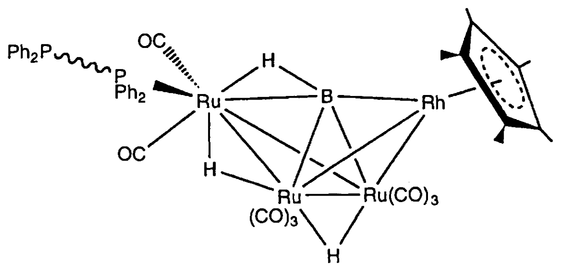
Results and Discussion

Reactions of [RhRu$_3$H(η^5-C$_5$Me$_5$)(CO)$_9$BH$_2$] with didentate bis(diphenylphosphine) ligands

We have previously reported[2] that the reaction of [RhRu$_3$H(η^5-C$_5$Me$_5$)(CO)$_9$BH$_2$] **2** with PPh$_3$ leads to the formation of [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(PPh$_3$)BH]. Substitution by the phosphine ligand occurs at a wingtip equatorial carbonyl and is accompanied by the migration of a Rh–H–B bridging hydrogen atom to a Ru$_{\text{hinge}}$–Ru$_{\text{wingtip}}$ bridging site, the wingtip site being that containing the PPh$_3$ ligand. The position of substitution mimics that of one PPh$_3$ ligand in [Ru$_4$H(CO)$_{12}$BH$_2$] **1**, but here there is no cluster-hydrogen migration.[1] Didentate ligands react with **1** to give edge-bridging, chelating, pendant-monodentate or cluster-linking modes of attachment (see Introduction), and in each case the product is formed without rearrangement of the cluster hydrogen atoms.[1] In the first part of this paper we report the results of the reactions of compound **2** with the didentate phosphines dppf and dppa, two compounds which possess very different degrees of flexibility.

The reaction at room temperature of compound **2** with dppf produces a single product **3**. The ^{11}B and ^{1}H NMR spectroscopic characteristics of **3** are similar to those of [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(PPh$_3$)BH], the structure of which has been crystallographically confirmed.[2] Additional signals in the ^{1}H NMR spectrum of **3** compared to that of [RhRu$_3$H$_2$(η^5-C$_5$Me$_5$)(CO)$_8$(PPh$_3$)BH] can be assigned to the protons in the η^5-C$_5$H$_4$ rings of the dppf ligand (see below).

The ^{31}P NMR spectrum of compound **3** exhibits two signals (relative integrals 1:1) and the chemical shifts of δ +24.0 and −18.7 indicate the presence of one ruthenium-bound PPh$_2$ group and one non-co-ordinated PPh$_2$ group respectively. For



Ph2P∿∿PPh2

3 dppf

4 dppa

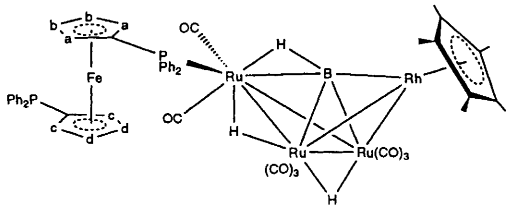
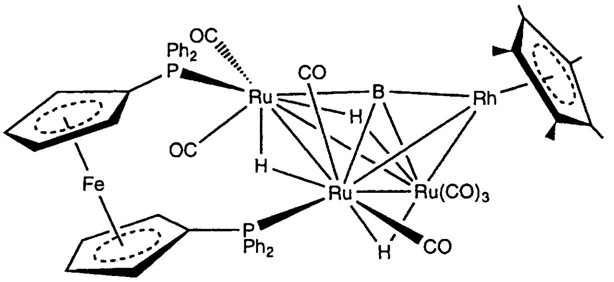


Fig. 1 Proposed structure of compound **3** indicating four environments for the ring protons of the dppf ligand (see text)



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free dppf the ${}^{31}P$ NMR signal is δ −21.5, and for $[Ru_4H(CO)_{12}(dppf\text{-}P)BH_2]$, in which the dppf ligand is in a pendant mode,[1] the ${}^{31}P$ NMR spectrum exhibits signals at δ 33.4 (co-ordinated P) and −20.1 (non-co-ordinated P). We therefore propose the structure shown for **3** with the site of substitution mimicking that in $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(PPh_3)BH]$. Allowing for rotational motion of the two $\eta^5\text{-}C_5H_4$ rings of the dppf ligand, the proposed structure possesses (a minimum) of four $\eta^5\text{-}C_5H_4$ proton environments as is shown in Fig. 1, but only two broad signals at δ 4.23 and 3.97 (relative integrals 1 : 1) were observed. These data may be rationalised by overlapping of signals assigned to protons a and c, and b and d. Representative proton NMR spectroscopic data for pendant dppf ligands include those for $[M(CO)_5(dppf\text{-}P)]$ (M = Cr, Mo or W);[5] for M = Cr, overlapping of the $\eta^5\text{-}C_5H_4$ resonances is also observed, reducing the number of signals to three. Three signals have also been reported for the $\eta^5\text{-}C_5H_4$ protons of $[Au(C_6F_5)_3(dppf\text{-}P)]$ although, two signals were assigned to the co-ordinated $\eta^5\text{-}C_5H_4PPh_2$ unit and one to the four protons of the pendant ring.[6]

Significantly, phosphine-for-carbonyl substitution is effected more readily in the heterometallic cluster **2** than in the homometallic cluster **1**. Compound **1** reacts only slowly with phosphines at room temperature when the reagents are stirred in CH_2Cl_2 solution, and even under conditions of photolysis periods of approximately 17 h are required.[1]

The reaction of compound **2** with dppa leads to a single product **4** in ≈80% yield. A comparison of the spectroscopic characteristics of compound **4** with those of **3** indicate that they are structurally related. The pendant mode of the dppa ligand is adequately confirmed by the ${}^{31}P$ NMR spectroscopic data. Signals at δ 5.3 and −33.6 (relative integrals 1 : 1) are assigned to the ruthenium-bound and non-co-ordinated PPh_2 groups; for free dppa, δ(${}^{31}P$) is −32.0.

Reaction of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(dppf\text{-}P)BH]$ 3 with $[N(PPh_3)_2]Cl$ and $[Au_2Cl_2(dppf)]$

The formation of compound **3** in high yield offered us the opportunity to study its reactivity patterns. We have been interested in cluster-expansion reactions about the semi-interstitial boron atom in butterfly clusters[7,8] and also in the reactions of the anions $[Ru_4H(CO)_{12}BH]^-$ and $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH]^-$ with gold(I) phosphines.[7-9] In many of these reactions the preliminary synthetic step is deprotonation of the respective neutral cluster, and this may be effected by combining a methanolic solution of $[N(PPh_3)_2]Cl$ with a CH_2Cl_2 solution of the parent cluster, with or without the presence of sodium carbonate, or in some cases by stirring a CH_2Cl_2 solution containing the cluster and $[N(PPh_3)_2]Cl$.

The addition of a two-fold excess of $[N(PPh_3)_2]Cl$ to compound **3** in CH_2Cl_2 solution gave no reaction as indicated by IR spectroscopic data. However, when 1 equivalent of $[Au_2Cl_2(dppf)]$ was added changes in the IR spectrum of the mixture indicated that a reaction had occurred. Three compounds were isolated after chromatographic separation, but only two could be characterised. The ${}^{11}B$ NMR spectrum of the first red-brown compound **5** exhibits a broad signal at δ +180 and the shift to lower field with respect to the resonance for compound **3** suggests an increase in the degree of direct boron–metal interaction.[10,11] The parent ion in the mass spectrum of **5** corresponds to the retention of the $RhRu_3B$ core and thus the increase in M–B direct bonding can only arise if the Ru–H–B hydrogen atom in **3** is no longer present in **5**. This is supported in the ${}^1H$ NMR spectrum of cluster **5**; in addition to signals assigned to Ph and $\eta^5\text{-}C_5H_4$ protons, there are three sharp high-field resonances (δ −14.1, −15.4 and −20.8, relative integrals 1 : 1 : 1) assigned to M–H–M bridges and no signal that may be attributed to an M–H–B bridging hydrogen atom. In contrast to the ${}^{31}P$ NMR spectrum of compound **3**, that of **5** exhibits two resonances of similar chemical shift (δ 25.3 and 24.0) which indicate that both P-donor atoms of the dppf ligand are co-ordinated. The mass spectrum supports the fact that the conversion of compound **3** into **5** involves intramolecular substitution of one CO ligand for the initially pendant PPh_2 group and that the formulation of **5** is $[RhRu_3H_3(\eta^5\text{-}C_5Me_5)(CO)_7(\mu\text{-}dppf\text{-}P,P')B]$. We propose that the dppf ligand in **5** is edge bridging and a comparison with published data for $[Ru_4H(CO)_{10}(\mu\text{-}dppe\text{-}P,P')BH_2]$[1] allows us to say that it adopts a $Ru_{wingtip}$(equatorial)–Ru_{hinge}(equatorial) mode as shown. The coupling patterns observed in the ${}^1H$ NMR spectrum of **5** are consistent with one hydride bridging the Ru_{hinge}–Ru_{hinge} edge [δ −20.8, doublet, J_{PH}(*cis*) 5.5 Hz], and one the same Ru–Ru edge that is bridged by the dppf ligand [δ −15.4, doublet of doublets, J_{PH}(*cis*) 10 and 18 Hz]. The third hydride ligand may bridge the $Ru_{wingtip}$–Ru_{hinge} edge as indicated although this demands a *trans* ${}^{31}P$–${}^1H$ coupling and the observed value of 12.5 Hz appears to be rather small. Alternatively, it may bridge the Rh–Ru_{hinge}(unsubstituted) edge and the observed coupling is then assigned to J_{RhH}. Despite the small coupling, we favour the Ru–Ru bridging mode since there is precedence for the migration of boron-associated cluster hydrogens to ruthenium atoms at which phosphine ligands have been introduced.[2,12]

The second red-brown compound **6** also displays a signal in its ${}^{11}B$ NMR spectrum that is further downfield (δ +170) than for the precursor **3**, implying an increase in the number of direct metal–boron interactions. The ${}^1H$ NMR spectrum indicates the presence of two metal-bound hydrogen atoms (relative integrals 1 : 1) in contrast to that of compound **5**, and the mass spectrum of **6** is consistent with the incorporation of a gold atom and a

Table 1 Crystallographic data for $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-}dppf\text{-}P,P')AuB]$ **6**

Formula	$C_{52}H_{45}AuBFeO_8P_2RhRu_3$
M	1529.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a, b, c/Å	11.577(2), 12.742(3), 20.025(5)
α, β, γ/°	76.46(2), 89.76(2), 75.72(2)
U/Å^3	2778.8(10)
Z	2
D_c/g cm^{-3}	1.826
μ(Mo-Kα)/cm^{-1}	40.7
T/K	296
Diffractometer	Siemens P4 (graphite monochromator)
Radiation	Mo-Kα (λ = 0.710 73 Å)
2θ Range/°	4–53 ($\pm h$, $\pm k$, $+l$)
Reflections (collected, independent, observed)	11 852, 11 509, 7338 ($>4\sigma F_o$)
R, R'*	0.0624, 0.0686
Goodness of fit	1.29
N_o/N_v	11.5

* $R = \Sigma\Delta/\Sigma(F_o)$; $R' = \Sigma(\Delta w^{\frac{1}{2}})/(F_o w^{\frac{1}{2}})$; $\Delta = |F_o - F_c|$; $w^{-1} = \sigma^2(F_o) + gF_o^2$.

Table 2 Selected bond distances (Å) and (°) for $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-}dppf\text{-}P,P')AuB]$ **6**

Ru(1)–Ru(2)	2.864(1)	Ru(1)–Ru(3)	2.974(2)
Ru(2)–Ru(3)	2.889(2)	Ru(3)–Rh	2.704(2)
Ru(2)–Rh	2.783(2)	Ru(1)–Au	2.702(1)
Au–P(1)	2.36(1)	Ru(1)–P(2)	2.364(3)
Rh–B	2.06(1)	Ru(1)–B	2.09(1)
Ru(2)–B	2.26(2)	Ru(3)–B	2.23(2)
Fe–cent(1,5)	1.65(1)	Fe–cent(6,10)	1.64(1)
Rh–cent(11,15)	1.91(1)		
Ru(3)–Rh–Ru(2)	63.5(1)	Ru(3)–Ru(1)–Ru(2)	59.3(1)
Rh–Ru(2)–Ru(1)	92.3(1)	Rh–Ru(3)–Ru(1)	91.6(1)
Rh–B–Ru(1)	158.5(9)	Ru(2)–B–Ru(3)	80.0(5)
B–Au–P(1)	162.0(4)	P(1)–Au–Ru(1)	146.7(1)
P(2)–Ru(1)–Au	87.2(1)	B–Au–Ru(1)	49.4(4)
cent(1,5)–Fe–cent(6,10)	176.0(3)	cent(11,15)–Rh–Ru(2)	142.5(3)
cent(11,15)–Rh–Ru(3)	153.9(4)	cent(11,15)–Rh–C(28)	120.1(4)
cent(11,15)–Rh–B	135.1(4)		

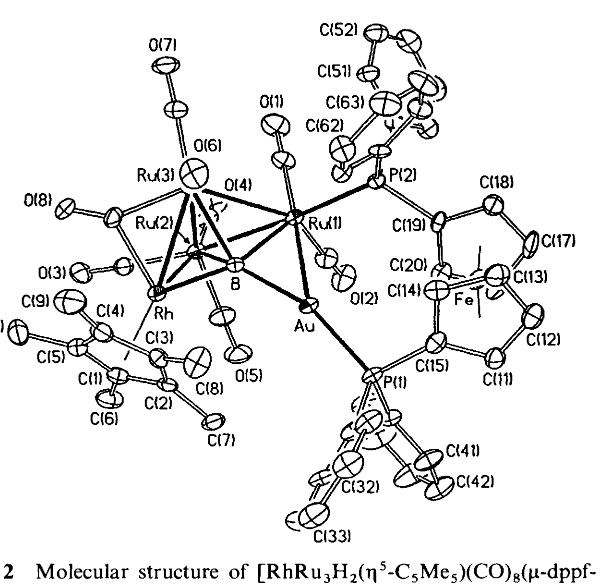


Fig. 2 Molecular structure of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-}dppf\text{-}P,P')AuB]$ **6**. The CO carbon atoms are numbered as 20 more than the corresponding labelled oxygen atom

formulation $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(dppf)AuB]$. Signals in the ^{31}P NMR spectrum at δ 57.9 and 32.0 (singlets, relative integrals 1 : 1) indicate that both phosphorus atoms of the dppf ligand are metal-bound, and we assign the more downfield signal to a $Au\text{-}PPh_2$ group and the second to a $Ru\text{-}PPh_2$ group, suggesting that the dppf ligand bridges between the gold(I) centre and a ruthenium atom in the cluster. This in turn implies that a Au–P bond in the precursor $[Au_2Cl_2(dppf)]$ has been cleaved during the reaction. We have determined the crystal structure of compound **6** in order to confirm its identity.

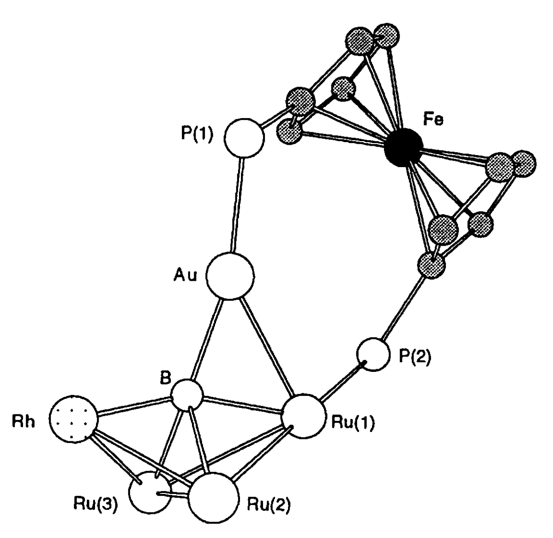


Fig. 3 Structure of the core of compound **6** which also shows that the carbon atoms two $\eta^5\text{-}C_5H_4$ rings are eclipsed

Crystal structure of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-}dppf\text{-}P,P')AuB]$ 6

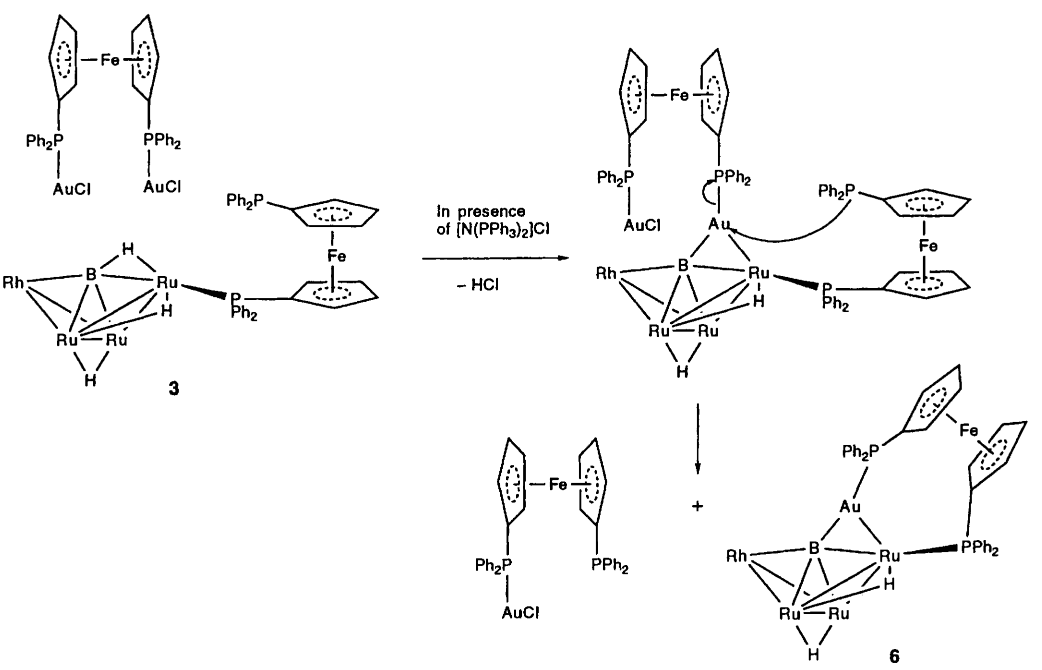
Crystals of compound **6** suitable for single-crystal X-ray diffraction were grown at −25 °C from a CH_2Cl_2 solution layered with hexane. The molecular structure is shown in Fig. 2 and selected bond distances and angles are listed in Table 2; the core structure of **6** is shown in Fig. 3. The $RhRu_3$ core of the cluster possesses a butterfly geometry, with the $Rh(\eta^5\text{-}C_5Me_5)$ moiety maintaining a wingtip site as in compound **2**. The $Ru_{wingtip}\text{–}B$ edge is bridged by a gold atom and the boron atom is within bonding distance of all five metal atoms with Rh–B 2.06(1), Ru–B in the range 2.09(1)–2.26(2), and Au–B 2.15(2) Å. The boron–gold bond length is relatively short compared to related distances of 2.29(2) Å in $[Ru_4H(CO)_{12}(dppf\text{-}P,P')Au_2B]$[13] and 2.47(2) Å in $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9\{(dppf\text{-}P,P')Au_2\}(AuCl)B]$.[9] The internal dihedral angle of the butterfly framework is 113.5° and the boron atom lies 0.38 Å above the wingtip–wingtip axis of the butterfly. The two phosphorus atoms are in different environments; P(1) is attached to the gold atom whilst P(2) occupies an equatorial site on the wingtip atom Ru(1).

The ferrocene unit lies above the cluster oriented such that the carbon atoms of the C_5 rings are eclipsed (Fig. 3). The rings are mutually twisted so that the P–C vectors subtend an angle of 66.5°. All carbonyl ligands are terminally attached except for C(28)O(8) which bridges the edge Rh–Ru(3) [Rh–C(28) 2.10(2) and Ru(3)–C(28) 1.99(1) Å]. An absorption in the IR spectrum of **6** at 1772 cm^{-1} is consistent with the persistence of this co-ordination mode in solution.

The two cluster hydrogen atoms were not directly located but inspection of the orientations of the carbonyl ligands attached to Ru(1), Ru(2) and Ru(3) combined with ^1H NMR spectroscopic data indicates that the edges Ru(2)–Ru(3) [δ (^1H) −20.0, s] and Ru(1)–Ru(3) [δ (^1H) −13.6, d, $J_{PH}(cis)$ 14 Hz] are each bridged by a hydrogen atom.

Possible pathways to the formation of compound 6

A number of examples of compounds containing a M–Au bond (M = Rh, Ir[14,15] or Fe[16–18]) bridged by the dppm ligand



Scheme 1 Possible route to the formation of $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\mu\text{-dppf-}P,P')AuB]$ **6**

$(Ph_2PCH_2PPh_2)$ have been reported, and are derived by a general strategy of adding electrophilic gold reagents to a mononuclear organometallic anion containing a monodentate dppm-*P* ligand. In these cases the proposed initial step is attack at the gold centre by the pendant PPh_2 group, followed by M–Au bond formation. The close proximity in which the two metal atoms are held by the dppm ligand must be a crucial feature of the reaction. In related work, Braunstein *et al.*[19] have prepared $[(OC)_2(\eta^5\text{-}C_5H_4Me)Mn(\mu\text{-dppm-}P,P')AuBr]$ from the reaction of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(\text{dppm-}P)]$ with [AuBr(tht)] (tht = tetrahydrothiophene) but in this heterometallic compound the metal centres are not within bonding contact.

A cluster-bound {Au–P–P} unit has been structurally confirmed in the compound $[\{Os_4H(CO)_{12}Au(\text{dppa-}P)\}_2]$. It contains two $Os_4H(CO)_{12}$ tetrahedra linked by two bridging $Au\text{–}PPh_2C{\equiv}CPPh_2$ units and is derived from the reaction of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ with $[Au_2Cl_2(\text{dppa})]$ under reflux.[20]

The reaction of compound **3** with $[Au_2Cl_2(\text{dppf})]$ to yield **6** raises questions concerning possible mechanistic pathways, and in particular whether the dppf moiety present in **6** originates from $[Au_2Cl_2(\text{dppf})]$ or cluster **3**. In order to gain some insight into the pathway two reactions were carried out. The first involved the reaction of **3** with $[AuCl(PPh_3)]$ and $[N(PPh_3)_2]Cl$ and this generated **6** in good yield. In the second a CH_2Cl_2 solution containing $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(PPh_3)BH]$[2] and $[N(PPh_3)_2]Cl$ was combined with $[Au_2Cl_2(\text{dppf})]$ but *no* gold-containing cluster compounds could be isolated. These two results suggest that the formation of **6** requires the presence of a pendant dppf ligand in the cluster precursor and we propose that nucleophilic attack by the pendant PPh_2 group in **3** occurs at one gold centre in $[Au_2Cl_2(\text{dppf})]$. Related to this is the work of Lin *et al.*[21] who have reported equilibria involving $[AuCl(\text{dppm-}P)]$, $[ClAu(\mu\text{-dppm-}P,P')AuCl(\text{dppm-}P)]$ and $[ClAu(\mu\text{-dppm-}P,P')_2AuCl]$ which arise from intramolecular PPh_2 attack at a gold centre. Our data do not indicate whether such a step occurs before or after the gold unit has become attached to the cluster. However, we consider it likely that an intermediate compound of the type $[RhRu_3H_2(\eta^5\text{-}C_5Me_5)(CO)_8(\text{dppf-}P)B\{Au(\text{dppf-}P,P')AuCl\}]$ is produced which then undergoes intramolecular nucleophilic attack by the ruthenium-bound pendant dppf ligand in a manner represented in Scheme 1.

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