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Towards linked clusters: reactions of $[Ru_6(CO)_{17}B]^-$ with dppm and $[ClAu(L-L)AuCl]$ (L–L = bis(diphenylphosphino)-alkanes, -ethene and -ethyne, and the crystal structure of $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$ (dppm = bis(diphenylphosphino)methane)[1]

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Abstract

The reaction between $[(PPh_3)_2N][Ru_6(CO)_{17}B]$ and bis(diphenylphosphino)methane (dppm) followed by protonation gives $[HRu_6(CO)_{15}(P,P'\text{-dppm})]$ in high yield; its structure has been established by single crystal X-ray diffraction methods and confirms an edge-bridging site for the dppm ligand. Reactions of $[Ru_6(CO)_{17}B]^-$ with six gold(I) derivatives [ClAu(L–L)AuCl] (L–L = bisphosphine) have been studied; ligands L–L have been chosen to illustrate the effects of backbones with varying degrees of flexibility. The products are generally of three types: $[\{Ru_6(CO)_{17}B\}_2(\mu\text{-Au(L–L)Au})]$, $[\{Ru_6(CO)_{17}B\}(Au(L–L)AuCl)]$ and $[\{Ru_6(CO)_{17}B\}_2Au]^-$; the relative yields of these products depend upon the nature of L–L. For L–L = (*Z*)-bis(diphenylphosphino)ethene, ((*Z*)-dppet), the conformation of the ligand facilitates the formation of $[Ru_6(CO)_{16}BAu((Z)\text{-dppet})]$; spectroscopic data indicate that (*Z*)-dppet is bonded to the cluster both via the gold(I) centre and one phosphorus-donor atom. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: X-ray diffraction; Biphosphine ligands; Boride clusters

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1. Introduction

As part of our studies of the reactivities of clusters containing interstitial and semi-interstitial boron atoms, we have reported substitution patterns of $[HRu_4(CO)_{12}BH_2]$ with a range of bisphosphine ligands [1]. The ligands studied included $Ph_2P(CH_2)_nPPh_2$ ($n =$ 1–4, 6), 1,1′-bis(diphenylphosphino)ferrocene and bis(diphenylphosphino)ethyne, and four different bonding modes were observed for these ligands: pendant, chelating, Ru–Ru edge-bridging, and cluster linking. Within a series of ligands with common terminal PPh_2 donor groups, clearly, the preferred bonding mode of a particular ligand is influenced by the flexibility of the ligand backbone. It is well recognized, for example, that dppm favours M–M bridging modes in clusters [2], and this follows from the large number of dinuclear complexes that are known (e.g. A-frame complexes) in which the metal centres are bridged by dppm. More flexible ligands have the ability to link two metal clusters together, although relatively few such compounds have been reported to date; examples include $[\{HRu_4(CO)_{11}BH_2\}_2(\mu\text{-L–L})]$ (L–L = dppe, dppp, dppb, dpph, dppf and dppa; dppp = bis(diphenylphosphino)propane, dpph = bis(diphenylphosphino)hexane) [1], $[\{Os_3(CO)_{10}\}(\mu\text{-dppa})_2]$ [3], and $[\{Os_3(CO)_{11}\}_2(\mu\text{-}$

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[1] This paper is dedicated to Michael Bruce on the occasion of his 60th birthday.

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dppa)] [3]. Although, as we have noted [1], several products are often formed, reactions of bis(phosphines) with clusters can be controlled to varying extents by careful choice of ligand backbones.

The use of the reagents [ClAu(L–L)AuCl] where L–L is a bisphosphine ligand has received some attention as a method of linking clusters. In our own studies, we have reported [$\{HRu_4(CO)_{12}BHAu\}_2(\mu$-dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) [4], [$\{HRhRu_3(\eta^5$ - $C_5Me_5)(CO)_9B(AuCl)Au_2\}_2(\mu$ - dppa)$_2$] [5], while other related species have included [$\{FeAu_2\}(\mu$-dppe)$_2$] [6], [$\{Mo_2H(\mu$-dppm)$(CO)_8Au\}_2\{\mu$-L-L)] (L–L = dppm, dppe, dppp) [7], [$\{PtW(CC_6H_4Me$-4)$(CO)_2$(cod)$(\eta^5$-$C_2Me_2B_9H_9)Au\}_2(\mu$-L–L)] (L–L = dppe, dppp, dppb) [8], [$\{Fe_2(CO)_7(\mu$-PhC = CHPh)Au$\}_2\{\mu$-L–L)] (L–L = dppm, dppe, dppp) [9], $\{H_3Ru_4(CO)_{12}Au\}_2(\mu$-dppm) [10]. In the present study, an advantage of using [ClAu(L–L)AuCl] as a reagent for cluster linkage is that the cluster precursor, a monoanion, has only one potential site for attachment of a gold(I) centre, leaving the cluster-bound Au(L–L)AuCl-chain free to attack a second cluster anion.

In this paper, we first describe the reaction of $[Ru_6(CO)_{17}B]^-$ with dppm, followed by protonation (to give neutral products which are more easily separated than their conjugate bases). Secondly, we report reactions of $[Ru_6(CO)_{17}B]^-$ with several gold(I) derivatives [ClAu(L–L)AuCl] in which the ligands L–L have been chosen to illustrate the effects of backbones with varying degrees of flexibility. Although our aims are to ultimately optimize conditions for homo- or heterocluster-linkage, this preliminary study focuses attention upon the range of possible products with a given [ClAu(L–L)AuCl] derivative.

2. Experimental section

2.1. General data

Fourier-transform NMR spectra were recorded on a Bruker WM 250 spectrometer; ^{1}H shifts are reported with respect to δ 0 for Me_4Si, ^{11}B-NMR with respect to δ 0 for $F_3B.OEt_2$, and ^{31}P-NMR with respect to δ 0 for 85% H_3PO_4; downfield chemical shifts are positive. Solution infrared spectra were recorded on a Perkin–Elmer FT 1710 spectrophotometer, and fast ion bombardment (FIB) mass spectra using Kratos instruments (3-NBA matrix = 3-nitrobenzyl alcohol). Good agreement was obtained between observed and simulated isotopic patterns for all mass envelopes quoted.

All reactions were carried out under argon by using standard Schlenk methods. Solvents were pre-dried and distilled under N_2. Separations were achieved by using thin layer plate chromatography with Kieselgel 60-PF-254 (Merck). Bisphosphine ligands were used as received (Aldrich or Strem); the synthesis of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ was as reported [11], and the preparations of [ClAu(L–L)AuCl] were prepared according to or based on published methods [12]. Typical yields are quoted.

Ligand abbreviations: dppm = bis(diphenylphosphino)methane, dppa = bis(diphenylphosphino)ethyne, (*Z*) - dppet = (*Z*) - bis(diphenylphosphino)ethene, (*E*) - dppet = (*E*)-bis(diphenylphosphino)ethene, dppe = bis (diphenylphosphino)ethane, dppb = bis(diphenylphosphino)butane.

2.2. Preparation of [$HRu_6(CO)_{15}$(*P,P′*-dppm)B]

$[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (33 mg, 0.02 mmol) was dissolved in CH_2Cl_2 (5 ml), and to this was added dppm (8 mg, 0.02 mmol). The solution was stirred at r.t. and the reaction monitored by spot TLC; after 1 h, $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ had been consumed. CF_3CO_2H (5 µl) was added to the reaction mixture and the solution stirred for 5 min. Solvent was removed in vacuo, and the products separated by TLC (2:1 hexane: CH_2Cl_2). One brown fraction eluted, identified as [$HRu_6(CO)_{15}$(*P,P′*-dppm)B] ($\approx$90%). ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.1–7.5 (m, Ph, 20H), 3.2 (t, CH_2, 2H), -17.4 (d, J_{PH} 5 Hz, Ru–H–Ru); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.7; ^{31}P{^{1}H}-NMR ($CDCl_3$, 298 K): δ 22.9. IR (CH_2Cl_2) ν(CO) 2073 m, 2032 vs, 2021 s, 2008 m, 1974 w cm^{-1}. MS (positive FIB): 1424 (P^+) with 12 CO losses.

2.3. Reaction of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ with [ClAu(dppm)AuCl]

[ClAu(dppm)AuCl] (34 mg, 0.04 mmol) and $TlPF_6$ (4 mg, 0.01 mmol) were dissolved in CH_2Cl_2 (5 ml) and the solution added dropwise over a period of 1 h to a constantly stirring solution of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (35 mg, 0.02 mmol) in CH_2Cl_2 (5 ml). The solution became red–brown in colour. Solvent was removed in vacuo, and the products separated by TLC (1:1 hexane: CH_2Cl_2). One fraction (red–brown) was collected, and was reseparated by TLC (1:2 hexane: CH_2Cl_2) to give three fractions, the first of which was in low yield and could not be fully characterized (see text). The second fraction was identified as [$\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppm)Au)] (orange, $\approx$10%) and the third as $[(Ph_3P)_2N][\{Ru_6(CO)_{17}B\}_2Au]$ (red–brown, 70%).

[$\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppm)Au)]: ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.3–7.8 (m, Ph, 20H), 3.1 (t, J_{PH} 11 Hz, CH_2, 2H); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.4; ^{31}P{^{1}H}-NMR ($CDCl_3$, 298 K): δ 67.0. IR (CH_2Cl_2) ν(CO) 2072 m, 2053 vs, 2036 m, 2016 m, 1991 m, 1849 w cm^{-1}. MS (negative FIB): 1263 (fragment $Ru_6(CO)_{16}BAu$), 1094 (fragment $Ru_6(CO)_{17}B$) with 5 CO losses.

$[(Ph_3P)_2N][\{Ru_6(CO)_{17}B\}_2Au]$: ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.4–7.8 (m, Ph); ^{11}B-NMR ($CDCl_3$, 298 K): δ 193.4; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 21.0 (cation). IR (CH_2Cl_2) ν(CO) 2072 m, 2053 vs, 2036 m, 2016 m, 1991 m, 1849 w cm^{-1}. MS (negative FIB): 2385 (P^-).

2.4. Reaction of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ with [ClAu(dppe)AuCl]

$[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (35 mg, 0.02 mmol) was dissolved in CH_2Cl_2 (5 ml), and to this was added [ClAu(dppe)AuCl] (35 mg, 0.04 mmol) and $TlPF_6$ (4 mg, 0.01 mmol). The solution was stirred for 30 min, solvent removed in vacuo, and products separated by TLC (1:2 hexane: CH_2Cl_2). The first fraction was present in very low yield and could not be sufficiently well characterized. Two further fractions were collected; the first was $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppe)Au)] (orange, ≈40%), and the second was $[\{Ru_6(CO)_{17}B\}(\mu$-Au(dppe)AuCl)] contaminated with $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppe)Au)]. On standing, the ratio of these components altered, with $[\{Ru_6(CO)_{17}B\}(\mu$-Au(dppe)AuCl)] converting into $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppe)Au)].

$[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppe)Au)]: ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.4–7.8 (m, Ph, 20H), 2.9 (CH_2, 4H); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.5; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 71.5. IR (CH_2Cl_2) ν(CO) 2087 w, 2055 vs, 2039 vs, 1991 m, 1868 w, 1836 w cm^{-1}. MS (negative FIB): 2951 (P^-–CO), 1094 (fragment $Ru_6(CO)_{17}$ B).$[\{Ru_6(CO)_{17}B\}(\mu$-Au(dppe)AuCl)]: a pure sample could not be obtained, and spectroscopic data are deduced from mixtures of $[\{Ru_6(CO)_{17}B\}(\mu$-Au(dppe)AuCl)] and $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppe)Au)]. ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.4–7.8 (m, Ph), 2.6 (CH_2), 2.9 (CH_2); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.5; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 70.0 (d, $J_{PP'}$ 60 Hz, 1P), 30.8 (d, $J_{PP'}$ 60 Hz, 1P).

2.5. Reaction of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ with [ClAu(dppb)AuCl]

$[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (35 mg, 0.02 mmol) was dissolved in CH_2Cl_2 (5 ml), and to this stirring solution was added dropwise a solution (in CH_2Cl_2, 5ml) of [ClAu(dppb)AuCl] (36 mg, 0.04 mmol) and $TlPF_6$ (4 mg, 0.01 mmol). The period of addition was 1 h, after which the solvent removed in vacuo, and products separated by TLC (1:2 hexane: CH_2Cl_2). The first fraction was $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppb)Au)] (orange, ≈ 70%), and the third was $[(Ph_3P)_2N][\{Ru_6(CO)_{17}B\}_2Au]$ (trace amount). The middle fraction was formed in low yield and, on standing, rapidly converted to $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppb)Au)].

$[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppb)Au)]: ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.4–7.8 (m, Ph, 20H), 2.2 (m, CH_2, 4H), 2.7 (m, CH_2, 4H); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.4; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 70.5. IR (CH_2Cl_2) ν(CO) 2086 w, 2055 vs, 2038 vs, 1991 m, 1867 w, 1836 w cm^{-1}. MS (positive FIB): 3009 (P^+).

2.6. Reaction of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ with [ClAu(dppa)AuCl]

$[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (24 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (5 ml), and to this was added [ClAu(dppa)AuCl] (13 mg, 0.015 mmol) and $TlPF_6$ (4 mg, 0.01 mmol). The solution was stirred for 30 min, solvent removed in vacuo, and products separated by TLC (1:1 hexane: CH_2Cl_2). Only one product was collected and was identified as $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au(dppa)Au)] (orange–red, ≈50%). $[\{Ru_6(CO)_{17}B\}_2$ (μ-Au(dppa)Au)]: ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.5–7.8 (m, Ph); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.6; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 47.1. IR (CH_2Cl_2) ν(CO) 2088 w, 2056 vs, 2039 vs, 1990 m cm^{-1}. MS (negative FIB): 2939 (P^-–CO), 1263 (fragment $Ru_6(CO)_{16}BAu$) with 3 CO losses, 1094 (fragment $Ru_6(CO)_{17}B$) with 1 CO loss.

2.7. Reaction of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ with [ClAu((E)-dppet)AuCl]

[ClAu((*E*)-dppet)AuCl] (22 mg, 0.025 mmol) and $TlPF_6$ (4 mg, 0.01 mmol) were added to a solution of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (41 mg, 0.025 mmol) in CH_2Cl_2 (5 ml). The solution was stirred for 30 min, solvent was removed in vacuo, and the products separated by TLC (1:1 hexane: CH_2Cl_2). Three fractions were eluted, the first (orange) was non-boron containing. The third fraction was $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au((*E*)-dppet)Au)] (red, ≈20%); it was not possible to obtain a pure sample of the second fraction, due to its ready conversion into $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au((*E*)-dppet)Au)] (see text).

$[\{Ru_6(CO)_{17}B\}_2(\mu$-Au((*E*)-dppet)Au)]: ^{1}H-NMR ($CDCl_3$, 298 K): δ 7.5–7.7 (m, Ph, 20H), 7.21 (m, CH, 2H); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.5; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 70.1. IR (CH_2Cl_2) ν(CO) 2087 m, 2055 s, 2038 vs, 1831 w cm^{-1}. MS (positive FIB): 2976 (P^+).

2.8. Reaction of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ with [ClAu((Z)-dppet)AuCl]

[ClAu((*Z*)-dppet)AuCl] (17 mg, 0.02 mmol) and $TlPF_6$ (4 mg, 0.01 mmol) were added to a solution of $[(Ph_3P)_2N][Ru_6(CO)_{17}B]$ (35 mg, 0.02 mmol) in CH_2Cl_2 (5 ml). The solution was stirred for 30 min, solvent was removed in vacuo, and the products separated by TLC (1:1 hexane: CH_2Cl_2). Three fractions were eluted; the first was $[\{Ru_6(CO)_{17}B\}_2(\mu$-Au((*Z*)-dppet)Au)] (orange, 10%), the second was identified as $[Ru_6(CO)_{16}B(Au((Z)\text{-dppet})]$ (brown–green, ≈20%), and the fraction with lowest retention value was $[(Ph_3P)_2N][\{Ru_6(CO)_{17}B\}_2Au]$ (≈60%).

$[\{Ru_6(CO)_{17}B\}_2(\mu\text{-}Au((Z)\text{-dppet})Au)]$: ^1H-NMR ($CDCl_3$, 298 K): δ 7.5–7.7 (m, Ph, 20H), 7.2 (m, CH, 2H); ^{11}B-NMR ($CDCl_3$, 298 K): δ 194.5; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 69.8. IR (CH_2Cl_2) ν(CO) 2087 m, 2055 s, 2038 vs cm^{-1}. MS (positive FIB): 2978 (P^+).

$[Ru_6(CO)_{16}B(Au((Z)\text{-dppet})]$: ^1H-NMR ($CDCl_3$, 298 K): δ 7.3–7.7 (m, Ph, 20H), 7.2–7.1 (unresolved m, CH, 2H); ^{11}B-NMR ($CDCl_3$, 298 K): δ 195.3; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 50.4 (d, $J_{PP'}$ 62 Hz, 1P), 22.5 (d, $J_{PP'}$ 62 Hz, 1P). IR (CH_2Cl_2) ν(CO) 2073 m, 2043 vs, 2024 vs, 1978 w, 1855 w, 1820 w cm^{-1}. MS (positive FIB): 1661 (P^+) with 14 CO losses.

2.9. Crystal structure determination of $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$

Crystals suitable for X-ray diffraction were grown from a concentrated CH_2Cl_2 solution layered with hexane. Crystallographic data for $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$ are collected in Table 1 and atomic coordinates in Table 2. Dark red plates were photographically characterized and determined to belong to the triclinic system. The centrosymmetric 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 difference Fourier maps, and refined with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in idealized locations. All computations used SHELXTL 4.2 software [13].

Table 1
Crystal data for $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$

Formula	$C_{40}H_{23}BO_{15}P_2Ru_6$
Formula weight	1422.8
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.122(7)
b (Å)	11.544(5)
c (Å)	18.543(7)
α (°)	71.71(4)
β (°)	87.65(5)
γ (°)	79.11(4)
Volume (Å^3)	2219(2)
Z	2
D_{calc} (g cm^{-3})	2.129
μ(Mo–K$_\alpha$) (cm^{-1})	21.3
Temperature (K)	238
Diffractometer	Siemens P4 (graphite monochromator)
2θ range (°)	4–45 ($\pm h$, $\pm k$, $\pm l$)
Reflections (collected, indpt)	5859, 5657, 4464
$R(F)$, $R(wF^2)$[a] (%)	5.37, 7.22
GOF	1.52
N_o/N_v	7.7
Max. peak (eÅ^{-3})	1.45

[a] Quantity minimized = $R(F) = \Sigma\Delta/\Sigma(F_o)$; $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$ $\Delta = |F_o - F_c|$.

3. Results and discussion

3.1. Preparation of $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$

We have previously observed that substitution reactions of $[Ru_6(CO)_{17}B]^-$ with PPh_3 followed by protonation yielded $[HRu_6(CO)_{16}(PPh_3)B]$; the yield depended upon reaction conditions, but no conditions were found under which to facilitate di- or higher substitution [14]. The reaction of $[Ru_6(CO)_{17}B]^-$ with a didentate phosphine was therefore of interest; if monosubstitution continued to be the preferred trend for this cluster, use of didentate ligands could provide a route into linked cluster-systems. On the other hand, the presence of the second donor atom in close proximity to the cluster core may encourage further substitution. The ligand chosen for the initial study was dppm, and reaction with $[Ru_6(CO)_{17}B]^-$, followed by protonation, proceeded smoothly to give one product in high yield. Spectroscopic and mass spectrometric data were in agreement with the formation of the disubstituted product $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$. In the $^{31}P\{^1H\}$-NMR spectrum, a singlet (δ 22.9) indicated the presence of equivalent phosphorus atoms. In the ^1H-NMR spectrum, in addition to resonances for the dppm ligand, a high field signal (δ −17.4) indicated the presence of a ruthenium-bound hydride ligand; the shift is typical for an Ru–H–Ru bridging mode, and the doublet nature of the signal ($J_{PH} = 5$ Hz) suggested a *cis*-H–Ru–P arrangement. The signal in the ^{11}B-NMR spectrum at δ 194.7 was as expected for a boron atom, interstitial in an octahedral Ru_6-cage [15].

The structure of $[HRu_6(CO)_{15}(P,P'\text{-dppm})B]$ was confirmed by the results of a single crystal X-ray diffraction study. The molecular structure is shown in Fig. 1 and selected bond distances and angles are listed in Table 3. The structure is similar to that reported for $[Ru_6(CO)_{15}(P,P'\text{-dppm})C]$ [16]; in the Ru_6-cage, the Ru–Ru distances lie in the range from 2.840 to 3.054(1) Å, with the longest edge being that bridged by the dppm ligand. This relatively undistorted octahedral cage contrasts with the rather severe distortion of the core in $[Ru_6(CO)_{15}(P,P'\text{-dppf})C]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) [17]. The

Table 2
Atomic coordinates ($\times 10^4$) for [$HRu_6(CO)_{15}$(*P*,*P*′-dppm)B]

	x	*y*	*z*
Ru(1)	431.1(7)	6769.1(7)	263.3(5)
Ru(2)	3130.2(7)	6547.3(7)	2211.1(4)
Ru(3)	148.2(8)	4985.6(8)	1877.6(5)
Ru(4)	130.9(7)	7258.5(8)	1044.7(5)
Ru(5)	2749.4(8)	4758.4(8)	1451(5)
Ru(6)	2012.6(8)	4236.2(7)	3019.7(5)
P(1)	724(2)	8359(2)	3090(2)
P(2)	3324(2)	8364(2)	2483(2)
B	1640(11)	5799(11)	2063(7)
O(1)	−2119(8)	8154(9)	2022(6)
O(2)	−691(8)	5522(8)	4115(5)
O(3)	4543(9)	4905(8)	3648(5)
O(4)	5450(8)	6712(8)	1303(5)
O(5)	−545(10)	6712(8)	1303(5)
O(6)	−2402(9)	5174(9)	2499(6)
O(7)	345(8)	2468(9)	3074(5)
O(8)	−71(10)	9912(8)	906(5)
O(9)	2225(8)	8022(8)	−556(5)
O(10)	−1231(8)	7077(9)	332(5)
O(11)	2169(9)	2263(8)	1494(6)
O(12)	3442(12)	5336(11)	−216(6)
O(13)	5428(7)	3666(8)	1920(5)
O(14)	3905(10)	1872(8)	3316(6)
O(15)	1481(9)	3383(9)	4710(5)
C(1)	−1167(11)	7638(11)	2251(6)
C(2)	−193(10)	5966(10)	3573(7)
C(3)	3932(9)	5436(10)	3128(6)
C(4)	4589(10)	6618(10)	1653(6)
C(5)	−284(11)	4115(12)	1243(7)
C(6)	−1457(11)	5159(11)	2254(7)
C(7)	679(11)	3404(10)	2815(7)
C(8)	360(11)	8915(12)	971(7)
C(9)	1793(10)	7719(10)	33(8)
C(10)	−373(12)	6922(12)	687(7)
C(11)	2333(11)	3252(12)	1452(7)
C(12)	3164(11)	3252(12)	1452(7)
C(13)	4423(11)	4072(10)	1758(7)
C(14)	3180(10)	2767(11)	3198(7)
C(15)	1722(10)	3731(10)	4072(7)
C(16)	1822(9)	9306(9)	2560(6)
C(21)	−1588(10)	9160(10)	3557(6)
C(22)	−2697(10)	9987(11)	3523(7)
C(23)	−2875(10)	11142(10)	3018(6)
C(24)	−1992(10)	11470(10)	2499(7)
C(25)	−884(9)	10684(9)	2518(6)
C(26)	−678(9)	9507(9)	3049(6)
C(31)	1931(11)	6762(10)	4432(6)
C(32)	2399(12)	6483(12)	5167(7)
C(33)	2110(13)	7320(15)	5563(7)
C(34)	1429(12)	8456(15)	5227(8)
C(35)	992(10)	8754(12)	4486(7)
C(36)	1228(9)	7914(9)	4071(6)
C(41)	3840(11)	8838(12)	3835(6)
C(42)	4490(13)	8638(14)	4505(7)
C(43)	5558(13)	7781(14)	4642(7)
C(44)	5999(11)	7157(11)	4137(7)
C(45)	5335(10)	7359(10)	3481(7)
C(46)	4221(9)	8175(10)	3329(6)
C(51)	3526(11)	9916(10)	1005(6)
C(52)	3988(10)	10841(10)	436(6)
C(53)	4876(11)	11375(11)	607(7)
C(54)	5373(11)	10981(12)	1334(7)
C(55)	4918(10)	10055(11)	1905(6)
C(56)	4011(9)	9517(8)	1739(5)

boron atom in [$HRu_6(CO)_{15}$(*P*,*P*′-dppm)B] is fully interstitial (consistent with the ^{11}B-NMR spectrum, see above). The cluster-bound hydrogen atom was not located, but an inspection of the carbonyl ligand orientations leads to the conclusion that it bridges the edge Ru(2)–Ru(4); carbonyl ligands C(3)–O(3) and C(10)–O(10) lean back, consistent with the placement of a H atom along edge Ru(2)–Ru(4), *trans* to each of these carbonyls. Each of C(3)–O(3) and C(10)–O(10) is in a semi-bridging mode across edges Ru(2)–Ru(5) and Ru(4)–Ru(3) respectively. Carbonyl ligand C(7)–O(7) is fully bridging: Ru(3)–C(7) = 2.09(1) and Ru(6)–C(7) = 2.02(1) Å. The placement of the H atom along edge Ru(2)–Ru(4) renders the two phosphorus atoms inequivalent; the observation of only one ^{31}P-NMR signal and the presence of a doublet in the ^{1}H-NMR ($J_{PH} = 5$Hz) may be rationalized in terms of a static hydride and coincidental ^{31}P-NMR signals.

The preference for dppm to coordinate in an edge-bridging mode was not unexpected, but test reactions with the more flexible dppf ligand also showed that attachment to a single cluster core in a *P*,*P*′-mode was favoured; we did not fully characterise the product of this reaction, and did not distinguish between a chelating mode at one metal centre or an edge-bridging mode; the latter has been crystallographically established for [$Ru_6(CO)_{15}$(*P*,*P*′-dppf)C] [17]. Since our aim was to explore ways to link Ru_6B-cores, we turned our attention to a different strategy, that of using gold(I) bisphosphine derivatives.

3.2. Reactions between [$Ru_6(CO)_{17}B$]$^-$ and [ClAu(L–L)AuCl] with L–L having a saturated backbone

As we have already stated, the linkage of cluster units is one aim of the present work. However, in this study, we also wished to investigate the formation of [cluster]Au(L–L)AuCl species, with a view to using them to link different cluster species. The reactions between [$Ru_6(CO)_{17}B$]$^-$ and [ClAu(L–L)AuCl] (L–L = dppm, dppe and dppb) were carried out with a 2-fold excess of gold(I) bisphosphine.

The reaction of [$Ru_6(CO)_{17}B$]$^-$ with a 2-fold excess [ClAu(dppm)AuCl] yielded two main products. The highest mass peak in the FIB mass spectrum of the minor product corresponded to the fragment {$Ru_6(CO)_{16}$BAu} and a dominant peak corresponding to the fragment {$Ru_6(CO)_{17}$B} was also observed; no parent ion was detected, a problem that we have often encountered when dealing with linked cluster species. Evidence for cluster linkage came from the observation of one signal in the ^{31}P{^{1}H}-NMR spectrum (δ 67.0), downfield from that of the starting compound [ClAu(dppm)AuCl] (δ 25.4). In the ^{1}H-NMR spectrum, in addition to signals due to the Ph protons, a triplet at δ 3.1 was assigned to the dppm CH_2 protons. In the ^{11}B-NMR spectrum, one signal at δ 194.4 signified the

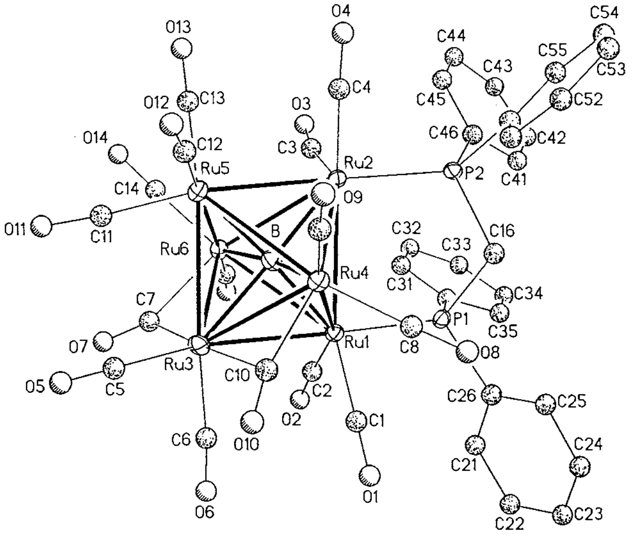


Fig. 1. The molecular structure of [$HRu_6(CO)_{15}$(*P*,*P*′-dppm)B]; the cluster H atom was not located; other H atoms are omitted for clarity.

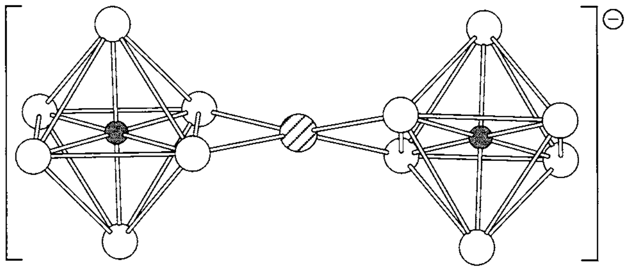


Fig. 2. The proposed structure of [{$Ru_6(CO)_{17}B$}$_2$Au]$^-$.

retention of an Ru_6B-interstitial site. The product was proposed as [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(dppm)Au)]. The major product of the reaction, was the fused cluster [{$Ru_6(CO)_{17}B$}$_2$Au]$^-$, isolated as the [$(Ph_3P)_2N$]$^+$ salt. We have previously reported the fusion product [{$HRu_4(CO)_{12}BH$}$_2$Au]$^-$, formed in reactions of [$HRu_4(CO)_{12}BH$]$^-$ with gold(I) phosphines [18] and fusion through gold(I) has been structurally confirmed in [{$HFe_4(CO)_{12}BH$}$_2$Au]$^-$ [18]. The FIB mass spectrum of [$(Ph_3P)_2N$][{$Ru_6(CO)_{17}B$}$_2$Au] showed a peak at *m*/*z* 2385 with an isotopic distribution consistent with that expected for [{$Ru_6(CO)_{17}B$}$_2$Au]$^-$. The ^{31}P-NMR spectrum exhibited one signal due to [$(Ph_3P)_2N$]$^+$, and the absence of dppm was further supported by the absence in the ^{1}H-NMR spectrum of a resonance due to the CH_2 protons. In the ^{11}B-NMR spectrum, a signal at δ 193.4 confirmed the retention of the Ru_6B-core. The fusion of octahedral carbide clusters has previously been observed through thallium [19] and mercury [20] centres, and the anions [{$Ru_6(CO)_{16}C$}$_2$Tl]$^-$ and [{$Ru_6(CO)_{16}C$}$_2$Hg]$^{2-}$ provide structural precedent for [{$Ru_6(CO)_{17}B$}$_2$Au]$^-$ for which we propose the structure shown in Fig. 2. By comparisons with related fused species, it is unlikely that the environment at the gold(I) centre would be planar in the solid state. A further example of cluster fusion of this type has been confirmed crystallographically in [{$HOs_3(CO)_{10}$}$_2$Au]$^-$ [21].

Table 3
Selected bond distances and angles for [$HRu_6(CO)_{15}$(*P*,*P*′-dppm)B]

Bond distances (Å)			
Ru(1)–Ru(2)	3.054(1)	Ru(1)–Ru(3)	2.897(2)
Ru(1)–Ru(4)	2.923(1)	Ru(1)–Ru(6)	3.000(1)
Ru(2)–Ru(4)	2.982(1)	Ru(2)–Ru(5)	2.939(2)
Ru(2)–Ru(6)	3.082(1)	Ru(3)–Ru(4)	2.978(1)
Ru(3)–Ru(5)	2.953(1)	Ru(3)–Ru(6)	2.840(1)
Ru(4)–Ru(5)	2.987(1)	Ru(5)–Ru(6)	2.896(1)
Ru(1)–B	2.06(1)	Ru(2)–B	2.07(1)
Ru(3)–B	2.14(1)	Ru(4)–B	2.11(1)
Ru(5)–B	2.11(1)	Ru(6)–B	2.08(1)
Ru(1)–P(1)	2.327(3)	Ru(2)–P(2)	2.355(3)
P(1)–C(16)	1.84(1)	P(2)–C(16)	1.84(1)
Bond angles (°)			
Ru(1)–B–Ru(5)	175.2(7)	Ru(2)–B–Ru(3)	177.5(7)
Ru(4)–B–Ru(6)	173.0(8)	Ru(2)–Ru(1)–P(1)	86.4(1)
Ru(3)–Ru(1)–P(1)	172.7(1)	Ru(4)–Ru(1)–P(1)	111.2(1)
Ru(6)–Ru(1)–P(1)	125.5(1)	Ru(1)–Ru(2)–P(2)	93.1(1)
Ru(4)–Ru(2)–P(2)	107.0(1)	Ru(5)–Ru(2)–P(2)	164.3(1)
Ru(6)–Ru(2)–P(2)	135.3(1)	Ru(2)–P(2)–C(16)	111.8(4)
Ru(1)–P(1)–C(16)	115.1(4)	P(1)–C(16)–P(2)	112.5(5)

In the reaction of [$Ru_6(CO)_{17}B$]$^-$ with [ClAu(dppe)AuCl], no [{$Ru_6(CO)_{17}B$}$_2$Au]$^-$ was formed, and with [ClAu(dppb)AuCl], a trace quantity was obtained. In both these reactions, the favoured products were [{$Ru_6(CO)_{17}B$}(μ-Au(L–L)AuCl)] and [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(L–L)Au)], L–L = dppe or dppb; for L–L = dppe, the initial yields of each compound were approximately equal, but for dppb, [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(dppb)Au)] was greatly favoured over [{$Ru_6(CO)_{17}B$}(μ-Au(dppb)AuCl)]. In each case, the chloro-derivative was found to convert to the linked species on standing in solution, and pure samples of [{$Ru_6(CO)_{17}B$}(μ-Au(L–L)AuCl)] could not be obtained. [{$Ru_6(CO)_{17}B$}(μ-Au(dppe)AuCl)] was characterized by multinuclear NMR spectroscopies by comparing spectra of the mixtures with spectra of pure [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(dppe)Au)]. Assignment of [{$Ru_6(CO)_{17}B$}(μ-Au(dppb)AuCl)] was tentative, because of rapid conversion to [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(dppb)Au)].

The formulation of the linked product [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(dppb)Au)] was supported by the appearance in the FIB mass spectrum of a parent ion at *m*/*z* 3009 with the expected isotopic distribution. Both the ^{1}H- and ^{31}P-NMR spectra were in accord with a symmetrical species, and the ^{11}B-NMR spectrum confirmed a μ_6-B environment. The mass spectrum of the proposed [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(dppe)Au)] did not show a parent ion (see experimental). The ^{31}P- and

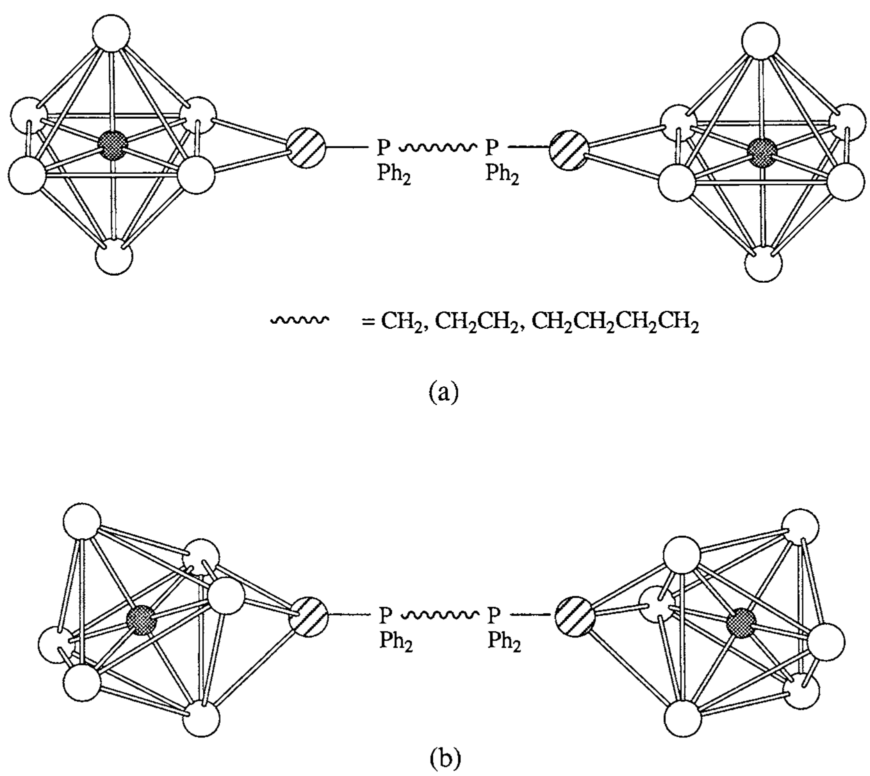


Fig. 3. Proposed structures for [$\{Ru_6(CO)_{17}BAu\}_2$(μ-L–L)] (L–L = dppm, dppe or dppb) with an (a) edge-bridging or (b) face-capping gold(I) centre.

^{1}H-NMR spectra were consistent with a symmetrical species. Fig. 3 shows proposed structures for [$\{Ru_6(CO)_{17}B\}_2$(μ-Au(L–L)Au)] (L = dppm, dppe or dppb); either edge-bridging or face-capping AuL units are possible; in the closest analogue that has been crystallographically characterized, [$Ru_6(CO)_{17}B$\{AuP(C_6H_4-2-Me)$_3$\}], the AuP(C_6H_4-2-Me)$_3$ group bridges an Ru–Ru edge [11].

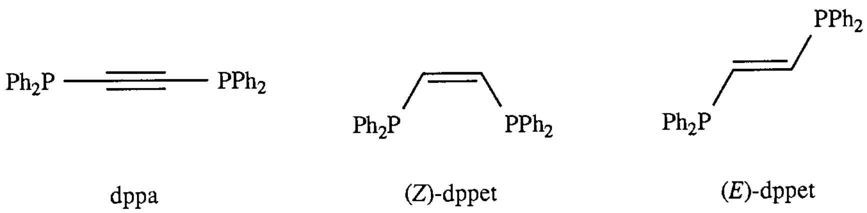
The formation of [$\{Ru_6(CO)_{17}B\}$(μ-Au(dppe)AuCl)] is based on two pieces of evidence: (i) its asymmetric nature is apparent in its ^{1}H- and ^{31}P-NMR spectra, and (ii) the compound converts to [$\{Ru_6(CO)_{17}B\}_2$(μ-Au(dppe)Au)]. In the ^{31}P-NMR spectrum, two doublets (1:1 relative integrals, $J_{PP'} = 60$ Hz) are observed at δ 70.0 and 30.8. While the latter signal has a chemical shift close to that of [ClAu(dppe)AuCl] (δ 31.2), the former shift is indicative of Cl^- loss and attachment to the ruthenium cluster. The compound [$\{Ru_6(CO)_{17}B\}$(Au(dppe)AuCl)] has potential use for linking the $\{Ru_6(CO)_{17}B\}$ moiety to another cluster, but it is clear that competition with conversion to [$\{Ru_6(CO)_{17}B\}_2$(μ-Au(dppe)Au)] is a major problem.

3.3. Reactions between [$Ru_6(CO)_{17}B]^-$ and [ClAu(L–L)AuCl] with L–L having an unsaturated backbone

An investigation of the reactivity of [$Ru_6(CO)_{17}B]^-$ towards [ClAu(L–L)AuCl] with L–L having an unsaturated backbone included the ligands dppa, (*Z*)-dppet and (*E*)-dppet (Scheme 1). Reactions were carried out with a 1:1 ratio cluster:[ClAu(L–L)AuCl] in order to encourage the formation of [$\{Ru_6(CO)_{17}B\}$(Au(L–L)AuCl)].

The reaction of [$Ru_6(CO)_{17}B]^-$ with [ClAu(dppa)AuCl] gave one product having mass spectrometric data indicative of [$\{Ru_6(CO)_{17}B\}_2$(μ-Au(dppa)Au)]. The ^{31}P-NMR spectrum exhibited a singlet (δ 47.1), at a chemical shift downfield of [ClAu(dppa)AuCl] (δ + 3.0). Thus, even with a 1:1 stoichiometry, it appears to be more favourable to form the linked cluster product rather than [$\{Ru_6(CO)_{17}B\}$(Au(dppa)AuCl)].

Like [ClAu(dppa)AuCl], [ClAu((*E*)-dppet)AuCl] also has a rigid, backbone. The reaction between [$Ru_6(CO)_{17}B]^-$ and [ClAu((*E*)-dppet)AuCl] gave [$\{Ru_6(CO)_{17}B\}$(Au((*E*)-dppet)AuCl)] and [$\{Ru_6(CO)_{17}B\}_2$(μ-Au((*E*)-dppet)Au)]. In addition to signals due to Ph protons, the ^{1}H-NMR spectrum showed one signal (δ 7.21) assigned to the alkene protons; in the ^{31}P\{^{1}H\}-NMR spectrum, one resonance at δ 70.1 (downfield from that for [ClAu((*E*)-dppet)AuCl], δ 27.5) indicated the formation of a symmetrical molecule. These, and the ^{11}B-NMR spectrum, were consistent with the formation of the proposed linked system. Characterization of the second fraction from the TLC separation of the products of the reaction of [$Ru_6(CO)_{17}B]^-$ and [ClAu((*E*)-



Scheme 1.

dppet)AuCl] proved difficult; during chromatography and in solution, it readily converted to [{$Ru_6(CO)_{17}B$}$_2$(μ-Au((*E*)-dppet)Au)]. By comparison of its behaviour with that of [{$Ru_6(CO)_{17}B$}(Au((*E*)-dppe)AuCl)], we propose that this product is [{$Ru_6(CO)_{17}B$}(Au((*E*)-dppet)AuCl)] but we were unable to fully characterize it by IR and NMR spectroscopies and mass spectrometry. Thus, for both [ClAu(dppa)AuCl] and [ClAu((*E*)-dppet)AuCl)], the driving force for the formation of the linked species [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(L–L)Au)] appears to be too great to easily isolate the proposed intermediate compounds [{$Ru_6(CO)_{17}B$}$_2$(μ-Au(L–L)AuCl)].

The reaction of $[Ru_6(CO)_{17}B]^-$ with [ClAu((*Z*)-dppet)AuCl] gave different results, as might be expected from the conformation of the P–C = C–P backbone. The major product was $[\{Ru_6(CO)_{17}B\}_2Au]^-$ (Fig. 2). The lowest yield product was [{$Ru_6(CO)_{17}B$}$_2$(μ-Au((*Z*)-dppet)Au)]; a singlet in the $^{31}P\{^1H\}$-NMR spectrum (δ 69.8, compared to δ 10.6 for [ClAu((*Z*)-dppet)AuCl]) was in accord with a symmetrical product containing cluster-bound gold(I) centres. The symmetrical nature of the compound was also evident from the presence of one resonance due to the olefinic CH protons.

Mass spectrometric data for the final product indicated the formation of [$Ru_6(CO)_{16}B$(Au((*Z*)-dppet)]. Two, equal intensity doublets ($J_{PP'} = 62$ Hz) at δ 50.4 and 22.5 were observed in the $^{31}P\{^1H\}$-NMR spectrum, and these were assigned, respectively, to gold(I)- and ruthenium-bound phosphorus atoms. The region of the ^1H-NMR spectrum for the olefinic protons contained an unresolved multiplet (δ 7.2–7.1). The proposed structure of the product is shown in Fig. 4. Such a coordination mode has been crystallographically confirmed for the {Au(dppf)}unit in [$H_2RhRu_3(\eta^5$-$C_5Me_5)(CO)_8$(dppf)AuB] [22], and the dppm ligand has previously been used to bring together gold and hetero-metal centres in a controlled manner [23]. A related mode has been observed in [{$HOs_4(CO)_{12}$Au(dppa)}$_2$], a dimer supported by two bridging dppa ligands, one phosphorus attached directly to an osmium atom of one Os_4-core, and the other bonded through gold(I) to the second Os_4-core; this species was prepared from $[H_3Os_4(CO)_{12}]^-$ and [ClAu(dppa)AuCl] [3].

The pathway to [$Ru_6(CO)_{16}B$(Au((*Z*)-dppet)] must clearly involve Au–P bond cleavage at some point. We favour as the first step in the reaction, the formation of [$Ru_6(CO)_{17}B$(Au((*Z*)-dppet)AuCl]. The major product of the reaction is $[\{Ru_6(CO)_{17}BAu\}_2]^-$, and, assuming that this originates from an intermediate [$Ru_6(CO)_{17}B$(Au((*Z*)-dppet)AuCl], then its formation should involve the loss of (*Z*)-dppet)AuCl. This molecule has the potential to (i) undergo phosphine substitution at ruthenium in $[Ru_6(CO)_{17}B]^-$, and/or (ii) undergo addition of $[(Z)\text{-dppet)Au}]^+$ to $[Ru_6(CO)_{17}B]^-$ (Scheme 2). Step (i) would leave a pendant –AuCl unit that could attack the cluster by an intramolecular process to give the observed product [$Ru_6(CO)_{16}B$(Au((*Z*)-dppet)], while step (ii) would give a pendant $-PPh_2$ donor that could undergo an intramolecular substitution reaction. In either case, the conformation of the PCCP-backbone in (*Z*)-dppet is vital as a driving force for the final ring-closing process.

We now return to the reaction of $[Ru_6(CO)_{17}B]^-$ with dppm, in which we observed the formation in low yield of a product which we were not able to fully characterize. Since this reaction also produced $[\{Ru_6(CO)_{17}BAu\}_2]^-$ as the major product and since dppm has a propensity for bridging dimetal units, we suggest that a pathway similar to that shown in Scheme 2 may be reasonably expected to operate. Thus, the last product of the reaction may tentatively be proposed as [$Ru_6(CO)_{16}B$(Au(dppm)].

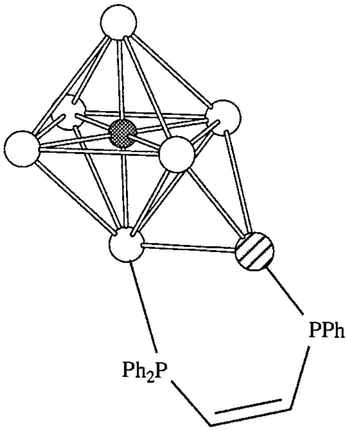
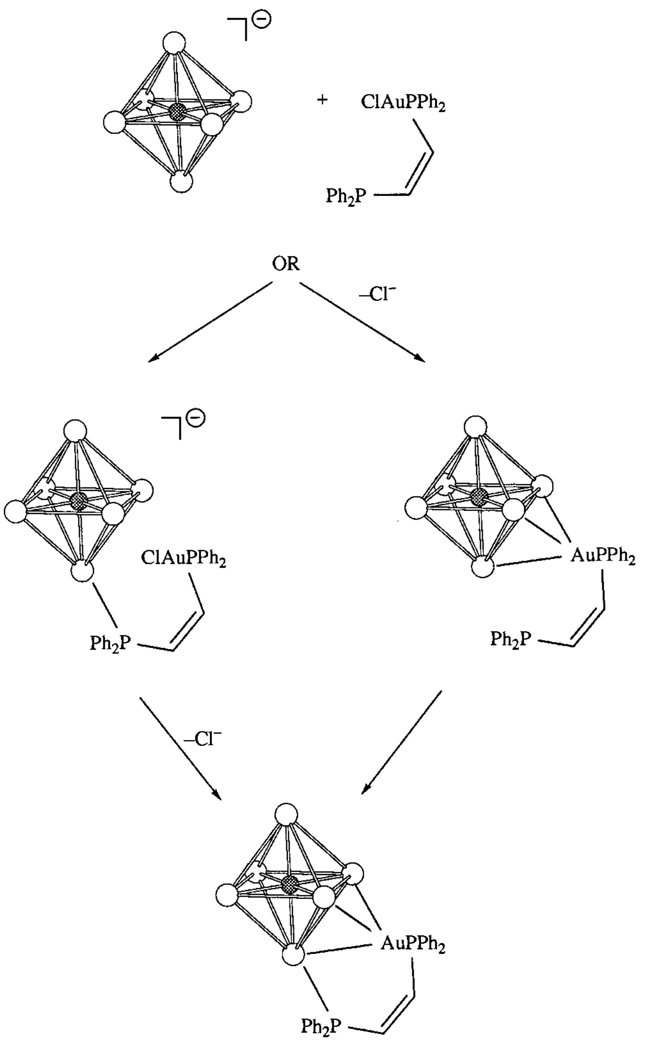


Fig. 4. Proposed structure of [$Ru_6(CO)_{16}B$(Au((*Z*)-dppet)].



Scheme 2.

4. Conclusions

In this paper, we have shown that the substitution reaction of $[Ru_6(CO)_{17}B]^-$ with dppm, followed by protonation gives $[HRu_6(CO)_{15}B(P,P'\text{-dppm})]$. The close proximity of the two P-donors apparent overcomes the problems we faced earlier [14] when attempting to perform disubstitution reactions using PPh_3. We have also described a series of reactions of $[Ru_6(CO)_{17}B]^-$ with [ClAu(L–L)AuCl] in which the ligands L–L are of two families: dppm, dppe and dppb have saturated backbones, while dppa, (*E*)-dppet and (*Z*)-dppet have unsaturated backbones. This exploratory study has illustrated the range of possible products obtained when $[Ru_6(CO)_{17}B]^-$ reacts with these [ClAu(L–L)AuCl] derivatives. Along the series dppm, dppe, and dppb, we observed an increased tendency for the formation of the linked-cluster species $[\{Ru_6(CO)_{17}B\}_2(\mu\text{-Au(L–L)Au})]$. For the rigid dppa and (*E*)-dppet ligands, cluster linkage was again favoured. For the conformationally restricted (*Z*)-dppet ligand, the formation of the fused cluster anion $[\{Ru_6(CO)_{17}BAu\}_2]^-$ was the major pathway. In this reaction, $[Ru_6(CO)_{16}B(Au((Z)\text{-dppet})]$ was also formed, and possible pathways have been proposed.

Acknowledgements

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