



Preparation and molecular structures of the decanuclear diyne-ruthenium-silver and -copper complexes $[M_6\{\mu_3-C\equiv C\equiv C[Ru(dppe)Cp^*]\}_4(\mu-dppm)_2](BF_4)_2$ ($M = Ag, Cu$)

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ARTICLE INFO

Article history:

Received 19 August 2009

Received in revised form 11 March 2010

Accepted 11 March 2010

Available online 16 March 2010

Keywords:

Cluster
Diyne
Copper
Silver
Ruthenium
Structure

ABSTRACT

Reactions between $[M_2(dppm)_2(NCMe)_2]X_2$ [$M = Ag, X = ClO_4$; $M = Cu, X = BF_4$] and $Ru(C\equiv C\equiv CM)(dppe)Cp^*$ [$M = Ag, Cu$; generated in situ from $Ru(C\equiv C\equiv CH)(dppe)Cp^*$ and $AgNO_3$ or $CuCl(PPh_3)$, respectively] afford the cationic mixed-metal cluster diyne complexes $[M_6\{\mu_3-C\equiv C\equiv C[Ru(dppe)Cp^*]\}_4(\mu-dppm)_2]X_2$, of which the structures were determined by single-crystal XRD studies. Electrochemical studies indicate that there is no interaction between the ruthenium centres. Reactions between $[M_2(\mu-dppm)_2(NCMe)_2](BF_4)_2$ and $Ru(C\equiv C\equiv CM')(dppe)Cp^*$ ($M, M' = Cu, Ag$) afforded a mixture of $Ag_{6-n}Cu_n$ clusters, as shown by ES-MS and crystallographic studies. Preliminary studies suggest that extensive disproportionation occurs in solution.

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1. Introduction

The formation of trinuclear copper(I) clusters in which the Cu–Cu vectors are bridged by dppm ligands, and bearing a variety of alkynyl groups capping the Cu_3 clusters, has been known for over a decade, the compounds $[Cu_3(\mu-dppm)_3(\mu_3-C\equiv CR)_n](X)_{3-n}$ having been described by the groups of Gimeno and co-workers [1] and Yam and co-workers [2]. Since that time, many other examples have been described, including diyne derivatives [3], extensive studies resulting from the demonstration that some show unusual luminescent behaviour. Some years later, Yam and coworkers described analogous clusters containing silver(I) [4]. Tetranuclear complexes $Cu_4(\mu_3-C\equiv CR)_4(PR'_3)_4$ have also been described [5], as well as $[Cu_4(\mu_4-C\equiv C)(\mu-dppm)_4](BF_4)_2$ [6].

Trinuclear alkynyl derivatives of Group 11 metals in which the alkynyl is end-capped by other metal-ligand fragments have also been described. For example, the reactions between $[M_2(\mu-$

$dppm)_2(NCMe)_2]X_2$ ($[2-M]X_2$; $M = Cu, Ag$; $X = BF_4, PF_6$) with $Re(C\equiv C\equiv C_6H_2R_2C\equiv CH-4)(NN)(CO)_3$ ($R = H, Me$; $NN = bpy, Me_2bpy, Bu^t_2bpy$) afforded complexes $[M_3\{\mu_3-C\equiv C\equiv C_6H_2R_2C\equiv C[Re(NN)(CO)_3]\}_2(\mu-dppm)_3]X_2$ [7] while similar complexes containing diyne spacers have also been described [8]. Under different reaction conditions, hexanuclear diyne complexes $[Ag_6\{\mu_3-C\equiv C\equiv C[Re(NN)(CO)_3]\}_4(\mu-dppm)_4](PF_6)_2$ could be obtained [9]. This communication describes some related systems containing ruthenium.

2. Results and discussion

The reaction of $Ru(C\equiv C\equiv CH)(dppe)Cp^*$ ($Cp^* = \eta-C_5Me_5$) with $AgNO_3$, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) as base, affords a yellow insoluble, apparently non-explosive and presumably polymeric material of composition $Ru(C\equiv C\equiv CAg)(dppe)Cp^*$ **1-Ag**. The similar copper(I) analogue **1-Cu** can be obtained from the reaction between $Ru(C\equiv C\equiv CH)(dppe)Cp^*$ and $CuCl(PPh_3)$ in the presence of NaOMe. Both materials were characterised only on the basis of their microanalyses and limited IR spectral data, the latter having weak $\nu(C\equiv C)$ bands between 2025 and 2075 cm^{-1} . The ES-MS of **1-Ag** contains ions at m/z ca 1400 corresponding to $\{[Cp^*(dppe)$

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$\text{RuC}_4)_2]^+$ and $[\{\text{Cp}^*(\text{dppe})\text{RuC}_4)_2 + \text{Ag}\}]^+$, possibly arising from impurities, together with some 3+ ions at m/z ca 7000, indicating very high mass aggregates. Further studies of these systems are necessary for full characterisation.

Nevertheless, we have used both compounds as sources of the diyne-ruthenium fragment in their reactions with $[\text{M}_2(\mu\text{-dppm})_2(\text{NCMe})_2]^{2+}$ ($\text{M} = \text{Cu}, \text{Ag}$) (Scheme 1). The reaction between $\text{Ru}(\text{C}\equiv\text{C}\equiv\text{C}\text{Ag})(\text{dppe})\text{Cp}^*$ **1-Ag** and $[\text{Ag}_2(\mu\text{-dppm})_2(\text{NCMe})_2](\text{ClO}_4)_2$ **[2-Ag](ClO₄)₂** was carried out in $\text{CH}_2\text{Cl}_2/\text{MeOH}$. Upon work-up, crystalline $[\text{Ag}_6\{\mu_3\text{-C}\equiv\text{C}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\mu\text{-dppm})_2](\text{ClO}_4)_2$ **[3-Ag](ClO₄)₂** was obtained in 76% yield (Scheme 1). The analogous Cu_6Ru_4 derivative **[3-Cu](BF₄)₂** was obtained as a red crystalline solid in 80% yield from the reaction between $\text{Ru}(\text{C}\equiv\text{C}\equiv\text{Cu})(\text{dppe})\text{Cp}^*$ **1-Cu** and $[\text{Cu}_2(\mu\text{-dppm})_2(\text{NCMe})_2](\text{BF}_4)_2$ **[2-Cu](BF₄)₂**.

The IR spectra of **[3-Ag](ClO₄)₂** and **[3-Cu](BF₄)₂** contain medium intensity $\nu(\text{C}\equiv\text{C})$ bands at 2039 (sh), 2003 (br) (Ag) or 2004 (sh), 1985 (br) cm^{-1} (Cu), while NMR spectra contain appropriate resonances for the Cp^* , dppe and dppm ligands. In particular, the ^{31}P NMR spectra contain single resonances for the dppe ligands at δ_{P} 80.5 (Ag) or 79.3 (Cu), together with broad multiplets at δ_{P} 6.5 (Ag) or $-6.6, -11.0$ (Cu) for the dppm ligands. The electrospray mass spectra (ES-MS), discussed further below, contain the parent dications $[\text{M}]^{2+}$ at m/z 2073.5 (Ag) or 1941 (Cu), together with weak, presently unassigned, 3+ and 4+ ions and, for **[3-Cu]**²⁺, weak peaks at lower mass corresponding to $[\{\text{Cp}^*(\text{dppe})\text{RuC}_4)_2]^+$ and $[\{\text{Cp}^*(\text{dppe})\text{RuC}_4)_2 + \text{Cu}\}]^+$.

A cyclic voltammetric study of **[3-Ag](ClO₄)₂** showed only a single quasi-reversible oxidation process at +1.29 V, with a second irreversible wave at +2.02 V. This result is consistent with there being no electronic communication between the four ruthenium centres in **[3-Ag]**²⁺. Thus, insertion of the Ag_6 unit into the $\text{Ru-C}_4\text{-C}_4\text{-Ru}$ fragment destroys the interaction found previously for related $\text{Ru-C}_8\text{-Ru}$ systems [10].

The CV of **[3-Cu](BF₄)₂** was dominated by a large, irreversible anodic process from ca +0.38 V. The oxidation was accompanied by significant fouling of the electrode, consistent with degradation of the cluster core. The chemical stability of the redox products was not enhanced at sub-ambient temperatures, and the process

remained electrochemically and chemically irreversible at scan rates up to 800 mV s^{-1} . Attempts to probe further the nature of the oxidation processes were hampered by the instability of the redox products on the longer timescale of spectro-electrochemical experiments.

2.1. Molecular structures

Crystals of the 9MeCN-solvate of **[3-Ag](ClO₄)₂** were obtained from MeCN/diethyl ether, while a mixed $\text{CHCl}_3\text{-C}_6\text{H}_6$ solvate of **[3-Cu](BF₄)₂** was isolated from a mixture of these solvents. Both crystals proved suitable for XRD structure determinations. Fig. 1 is a plot of the cation **[3-Ag]**⁺, the copper analogue being similar. Pertinent structural parameters are collected in Tables 1 and 2.

In the cation **[3-Ag]**²⁺, the core is a centrosymmetric distorted octahedral Ag_6 cluster (Fig. 2). Atom sets $\text{Ag}(1)\text{Ag}(3\text{a})$ and $\text{Ag}(1\text{a})\text{Ag}(3)$ are each bridged by one dppm ligand [$\text{Ag}(1)\text{-P}(5)$ and $\text{Ag}(3)\text{-P}(6')$ separations of 2.404(2), 2.411(2) Å, respectively] leading to long $\text{Ag}\cdots\text{Ag}$ distances [3.5334(6) Å]. All other $\text{Ag}\cdots\text{Ag}$ separations are in the range of 2.8104(8)–3.0056(9) Å, which are shorter than the sum of van der Waals radii for Ag (3.4 Å) and are thus suggestive of significant argentophilic interactions [11]. For **[3-Cu]**²⁺, a similar arrangement is found, with $\text{Cu}(1)\text{-P}(5)$ and $\text{Cu}(3)\text{-P}(6)$ separations of 2.194(2), 2.222(2) Å, respectively, and $\text{Cu}\cdots\text{Cu}$ distances between 2.446(1) and 3.301(2) Å.

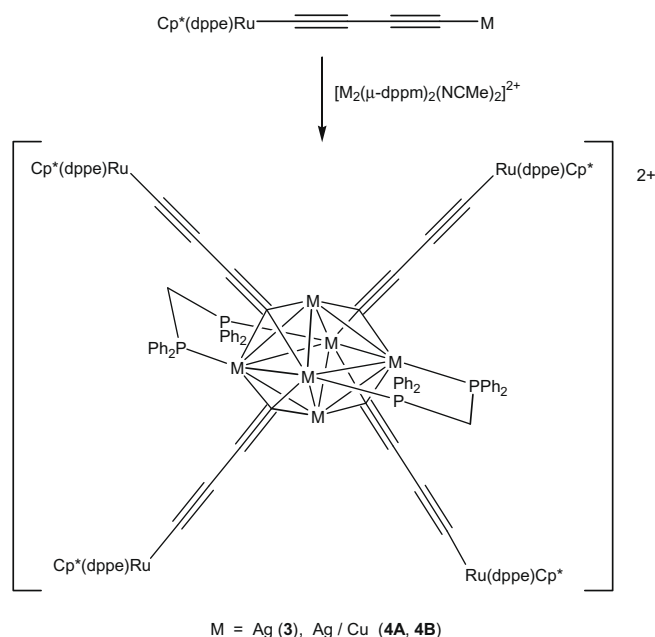
Four of the triangular faces of the M_6 octahedron are capped by atoms C(4), C(4'), C(8), C(8') (where the prime refers to the centrosymmetrically related atom) of the butadiynyl-ruthenium group in an asymmetric μ_3, η^1 -bridging mode [$\text{Ag}(1,2,3)\text{-C}(4)$ 2.359(6), 2.075(6), 2.330(6); $\text{Ag}(1,2,3)\text{-C}(8, \text{ or } 8')$ 2.303(6), 2.109(6), 2.389(6); $\text{Cu}(1,2,3)\text{-C}(4)$ 2.093(6), 1.900(6), 2.110(6); $\text{Cu}(1,2,3)\text{-C}(8, \text{ or } 8')$ 2.075(6), 1.937(6), 2.043(6) Å]. The diyne nature of the carbon chain is shown by the short-long-short CC bond sequences [ranges 1.226(8)–1.240(8), 1.360(9), 1.365(8) (Ag), 1.224–1.231(8), 1.369(9), 1.372(9) (Cu)] which indicate that the alternating $\text{C}\equiv\text{C}$ and C-C bonds are preserved in the chain. Angles at C(1), C(2), C(3), and C(5), C(6), C(7) are close to linear [range 171.1(6)–179.8(7)°].

The geometries of the $\text{Ru}(\text{dppe})\text{Cp}^*$ end-caps are similar to those found in many related derivatives, with distances Ru-P [2.269(2)–2.278(2) Å], $\text{Ru-C}(\text{Cp}^*)$ [2.228(7)–2.310(7) Å] and $\text{Ru-C}(\text{diynyl})$ [1.965(6)–1.981(6) Å] and angles P-Ru-P [83.60(8)–84.78(2)°] and $\text{P-Ru-C}(\text{diynyl})$ [82.0(2)–88.4(2)°], respectively. These values may be compared to those found in $\text{Ru}(\text{C}\equiv\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ [12]. There is no obvious contact between the four ruthenium centres, except that provided through the Ag_6 cluster via the diyne links.

Overall, the structure has some features in common with those found for $[\text{Ag}_6(\mu\text{-dppm})_4\{\mu_3\text{-C}\equiv\text{C}\equiv\text{C}[\text{Re}(\text{NN})(\text{CO})_3]\}_4](\text{PF}_6)_2$ ($\text{NN} = \text{Me}_2\text{bpy}, \text{Br}_2\text{phen}$) [9], in which the central Ag_6 unit has $\text{Ag}\cdots\text{Ag}$ separations between 2.940(3)–3.007(3) and 3.0206(11)–3.0415(10) Å, respectively. However, there are only two bridging dppm ligands in **[3-Ag]**²⁺ and **[3-Cu]**²⁺. The extents of $\text{M}\cdots\text{M}$ interactions are not obvious from the structural determinations and would require computational studies to establish.

2.2. Mixed Ag/Cu complexes

In an effort to describe the reaction in more detail, we then studied the reactions between the $\text{Ru}(\text{C}\equiv\text{C}\equiv\text{CM}')(\text{dppe})\text{Cp}^*$ precursors **1-M'** and $[\text{M}_2(\mu\text{-dppm})_2(\text{NCMe})_2](\text{BF}_4)_2$ **[2-M](BF₄)₂** ($\text{M}, \text{M}' = \text{Cu}, \text{Ag}$) using a stoichiometry that generated equal amounts of M and M' in solution. From these reactions, we obtained pale yellow solids **[4A]**²⁺ (from **[1-Cu]**²⁺ + **[2-Ag]**²⁺) and **[4B]**²⁺ (from **[1-Ag]**²⁺ + **[2-Cu]**²⁺) as the BF_4 salts, each of which afforded crystals



Scheme 1. Synthesis of $[\text{M}_6\{\mu_3\text{-C}\equiv\text{C}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\mu\text{-dppm})_2]^{2+}$.

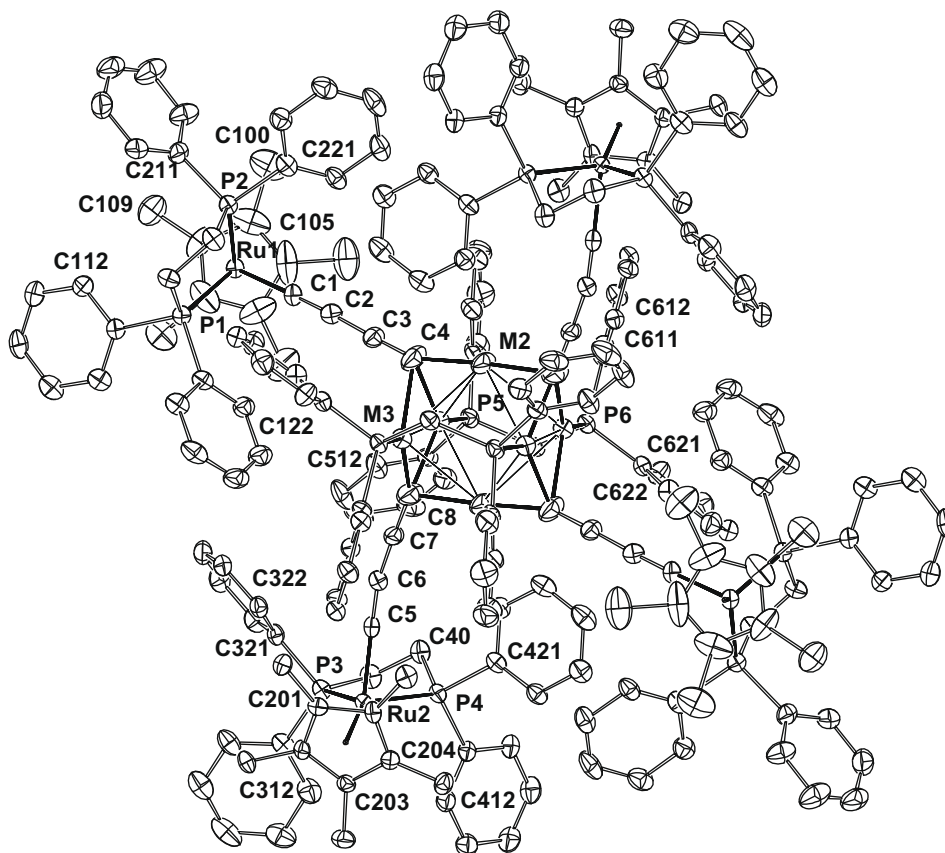


Fig. 3. Plot of the cation in $[(\text{Cu}/\text{Ag})_6\{\text{C}\equiv\text{CC}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\text{dppm})_2](\text{BF}_4)_2$ [**4A**](BF_4)₂.

The Ag/Cu atoms are not statistically placed at each of the sites in the cluster core, rather the refinements for the products from **1-Ag** and **1-Cu** converge with the fraction of Ag at the M(1,2,3) sites being 0.403(6), 0.287(7), 0.721(6) in [**4A**]²⁺, and 0.287(1), 0.713(1), 0.577(1) in [**4B**]²⁺, corresponding to compositions $\text{Ag}_{2.8}\text{Cu}_{3.2}$ ([**4A**]²⁺) and $\text{Ag}_{3.1}\text{Cu}_{2.9}$ ([**4B**]²⁺). Strangely, the chemically equivalent dppm-bridged equatorial sites M(1) and M(3) have very unequal occupancy values in each case (0.403/0.721 and 0.287/0.577, respectively), while the unique apical site M(2) has the lowest Ag contribution for [**4A**]²⁺ (0.287) but the largest for [**4B**]²⁺ (0.713). The overall composition deduced from the site occupancy factors is supported by the M–M bond distances, with average values gradually decreasing from [**3-Ag**]²⁺ to [**4B**]²⁺ to [**4A**]²⁺ and finally, to [**3-Cu**]²⁺, as the fraction of the larger Ag decreases at the expense of increasing Cu (Table 1), with longer bonds to comparable sites of higher Ag contribution.

Electrospray mass spectra of solutions of [**4A**](BF_4)₂ and [**4B**](BF_4)₂ in MeOH revealed that in each case, a mixture of complexes containing $\text{Ag}_{6-n}\text{Cu}_n$ ($n = 1 - 6$) cores was present. Virtually identical mass spectra were found for both [**4A**]²⁺ and [**4B**]²⁺ (Fig. 4). The highest mass ions of significance correspond to $[\text{M}]^{2+}$ and are found between m/z 1940 and 2030, corresponding to complexes with $\text{Cu}_{6-n}\text{Ag}_n$ ($n = 1 - 6$) cores. However, the distribution is not the statistical one expected from an equal Cu/Ag ratio. The measured ratios are 0.03:0.34:1.00:0.80:0.14:0:0 for $n = 0 - 6$, respectively, corresponding to an overall composition $\text{Cu}_{3.7}\text{Ag}_{2.3}$ for the products from each of the reactions. Clearly there is a bias towards the inclusion of more Cu than expected on a purely statistical basis, irrespective of whether it is added as diyne **1-Cu** or the dppm-bridged dimer **2-Cu**. Further, the overall compositions calculated from the ion relative intensities differ significantly from those obtained from the X-ray studies, namely $\text{Ag}_{2.8}\text{Cu}_{3.2}$ ([**4A**]²⁺)

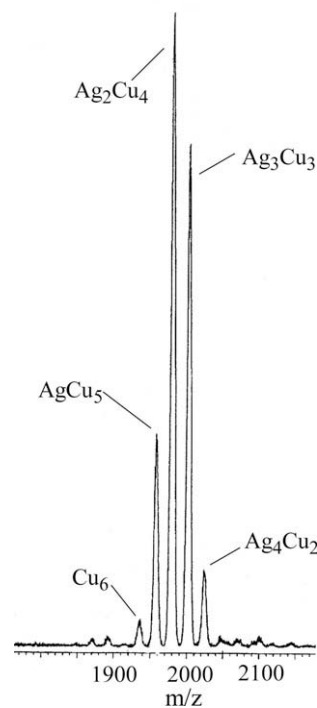


Fig. 4. ES mass spectrum (m/z 1900–2100) of [**4A**]²⁺ shows the distribution of core compositions for the $[(\text{Ag}_n\text{Cu}_{6-n})\{\text{C}_4\text{Ru}(\text{dppe})\text{Cp}^*\}_4(\text{dppm})_2]^{2+}$ ions. The mass spectrum of [**4B**]²⁺ shows essentially the same relative intensities.

and $\text{Ag}_{3.1}\text{Cu}_{2.9}$ ([**4B**]²⁺). From the stoichiometry of the reaction mixture, an Ag_3Cu_3 ratio might have been expected.

A possible explanation for the discrepancy is the occurrence of redistribution reactions in solution. Further studies of the ES-MS in MeCN as a function of time have given the following results:

- Within the time of mixing, solutions of a mixture of $[3\text{-Ag}]^{2+}$ and $[3\text{-Cu}]^{2+}$ contain cluster ions corresponding to Cu_6 , AgCu_5 , Ag_2Cu_4 and Ag_3Cu_3 , the concentrations of the silver-rich ions increasing on standing. However, no Ag_4Cu_2 ions are present after ten minutes, although this species would have been expected to form statistically.
- A solution of pre-prepared Ag_4Cu_2 cluster contains Ag_5Cu and Ag_4Cu_2 , with lesser amounts of Ag_3Cu_3 and Ag_6 . After ten minutes, the spectra were more complex.

These data suggest that these clusters are labile in solution, with complex disproportionation reactions occurring, and in turn provide an explanation for the broad resonances found in the ^{31}P NMR spectra. The differing compositions of materials studied by XRD methods and ES-MS presumably reflect differing stoichiometries of the isolated materials that were used in the separate experiments.

3. Conclusions

Reactions between the Group 11 cations $[\text{M}_2(\mu\text{-dppm})_2(\text{NCMe})_2]^{2+}$ ($\text{M} = \text{Ag}, \text{Cu}$) and the Ag and Cu derivatives of the diyne $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ have given a series of polynuclear complexes in which four $\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ fragments and two dppm ligands are attached to a hexanuclear Group 11 metal core. The stoichiometry requires addition of four Ag-diyne fragments to the disilver cation. Formation of the hexanuclear cation may be envisaged as involving formation of the Ag_6 assembly by argentophilic combination of the precursor reagents **1** and **2**, followed by migration of the dppm ligands and capping of four Ag_3 faces by the diyne fragments.

Differing compositions of solid materials isolated from mixed-metal reactions, together with extended ES-MS studies, suggest that rapid disproportionation of the complexes is occurring in solution. In this study, it has not been possible to determine how these reactions occur, but scrambling processes of the ligands about the central core may account for the almost identical compositions of the two products obtained in the mixed-metal reactions. This process may involve migration of the dppm ligands between Group 11 metal centres, or migration of the face-capping diyne ligands, or both.

4. Experimental

4.1. General experimental conditions

All reactions were carried out under dry nitrogen using standard Schlenk techniques, although normally no special precautions to exclude air were taken during subsequent workup. Common solvents were dried, distilled under nitrogen, and degassed before use.

4.2. Instruments

Infrared spectra: Bruker IFS28 FT-IR spectrometer. IR spectra were obtained from samples in Nujol mulls mounted between NaCl discs. NMR spectra: Varian ACP300 instrument (^1H at 300.13 MHz, ^{31}P at 121.503 MHz) at 298 K. Unless otherwise stated, samples were dissolved in acetone- d_6 (Aldrich) contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H spectra and external H_3PO_4 for ^{31}P NMR spec-

tra. Electrospray mass spectra (ES-MS; positive-ion mode): Fisons VG Platform II spectrometer. Solutions in MeOH were injected via a 10 ml injection loop; nitrogen was used as the drying and nebulising gas. Ions listed are the most intense peaks in the isotopic envelope. CVs were recorded from solutions in CH_2Cl_2 ca 10^{-4} M in analyte also containing 10^{-1} M $[\text{NBu}_4]\text{BF}_4$ in a gas-tight single-compartment three-electrode cell equipped with platinum working, coiled platinum wire auxiliary and platinum wire pseudo-reference electrodes at scan rates of 50–800 mV s^{-1} . All redox potentials are reported vs SCE, with the $\text{FeCp}^*_{2+}/[\text{FeCp}^*_{2+}]^+$ redox couple (-0.07 V vs. SCE) used as internal reference. Data were collected using a computer-interfaced EcoChemie PGSTAT-30 potentiostat. Elemental analyses were performed by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

4.3. Reagents

The compounds $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CR})(\text{dppe})\text{Cp}^*$ ($\text{R} = \text{H}, \text{SiMe}_3$) [12], $[\text{Cu}_2(\text{dppm})_2(\text{NCMe})_2](\text{BF}_4)_2$ [13], $[\text{Ag}_2(\text{dppm})_2(\text{NCMe})_2](\text{ClO}_4)_2$ [14] and $\text{CuCl}(\text{PPh}_3)$ [15] were made by the cited methods.

4.4. Preparation of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CAG})(\text{dppe})\text{Cp}^*$ **1-Ag**

To a solution of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ (68.4 mg, 0.1 mmol) in MeCN (15 mL) was added dbu (0.06 mL, 0.4 mmol), followed by solid AgNO_3 (34 mg, 0.2 mmol). The resulting suspension was stirred overnight at r.t. before being filtered on a sintered glass funnel and washed with MeCN (2 mL) to give yellow $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CAG})(\text{dppe})\text{Cp}^*$ **1-Ag** which was dried under vacuum (59 mg, 75%). IR/ cm^{-1} : $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 2075m, 2045m. Anal. Calcd. ($\text{C}_{40}\text{H}_{39}\text{AgP}_2\text{Ru}$): C, 60.76; H, 4.94; Ag, 13.67. Found: C, 60.29; H, 5.01; Ag, 13.14%.

4.5. Preparation of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CCu})(\text{dppe})\text{Cp}^*$ **1-Cu**

To a suspension of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$ (76 mg, 0.1 mmol) and $\text{CuCl}(\text{PPh}_3)$ (36 mg, 0.1 mmol) in THF (10 mL) was added NaOMe (from 30 mg Na dissolved in 1 mL MeOH) to give a deep red solution. The reaction mixture was stirred overnight at r.t. The resulting light yellow precipitate was filtered under nitrogen, washed thoroughly with MeOH (2 mL) and dried under vacuum to give $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CCu})(\text{dppe})\text{Cp}^*$ **1-Cu** (55 mg, 73%). IR/ cm^{-1} : $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 2044w, 2025 w. Anal. Calcd. ($\text{C}_{40}\text{H}_{39}\text{CuP}_2\text{Ru}$): C, 64.38; H, 5.27. Found: C, 64.09; H, 5.43%.

4.6. Preparation of $[\text{Ag}_6\{\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}\}_4(\text{dppm})_2](\text{ClO}_4)_2$ **[3-Ag]** $(\text{ClO}_4)_2$

CAUTION: Appropriate care should be taken with reactions involving perchlorates and poly-yenes.

$\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CAG})(\text{dppe})\text{Cp}^*$ (80 mg, 0.1 mmol) was added slowly to $[\text{Ag}_2(\text{dppm})_2(\text{MeCN})_2](\text{ClO}_4)_2$ (32 mg, 0.025 mmol) dissolved in $\text{CH}_2\text{Cl}_2\text{-MeOH}$ (1/1) (15 mL). After stirring overnight with exclusion of light a clear deep red solution resulted. After evaporation to dryness, the solid residue was extracted with MeCN and subsequent diffusion of Et_2O vapour into the concentrated solution resulted in the formation of yellow crystals of $[\text{Ag}_6\{\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}\}_4(\text{dppm})_2](\text{ClO}_4)_2 \cdot 9\text{MeCN}$ **[3-Ag]** $(\text{ClO}_4)_2 \cdot 9\text{MeCN}$ (90 mg, 76%). Anal. Calcd. ($\text{C}_{210}\text{H}_{200}\text{Ag}_6\text{Cl}_2\text{O}_8\text{P}_{12}\text{Ru}_4 \cdot 9\text{MeCN}$): C, 58.08; H, 4.85; N, 2.67; M (cation), 4147. Found: C, 58.05; H, 4.68; N, 2.31%. IR/ cm^{-1} : $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 2039 (sh), 2003m (br). ^1H NMR: δ 1.53 (s, 60H, Cp*), 2.11 (s, 27H, MeCN), 3.48–3.68 (m, 4H, $\text{CH}_2\text{-dppm}$), 2.09, 3.03 (16H, $\text{CH}_2\text{-dppe}$), 7.07–7.84 (m, 120H, Ph); ^{31}P NMR: δ 80.5 (br s, dppe), 6.5 (br m, dppm). ES-MS/ m/z : 2073.5, $[\text{Ag}_6(\text{dppm})_2\{\text{Ru}(\text{dppe})\text{Cp}^*\}_4]^{2+}$.

4.7. Preparation of $[\text{Cu}_6\{\text{C}\equiv\text{CCvC}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\text{dppm})_2](\text{BF}_4)_2$ [**3-Cu**](BF_4)₂

A similar reaction used $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CCu})(\text{dppe})\text{Cp}^*$ (74 mg, 0.1 mmol) and $[\text{Cu}_2(\text{dppm})_2(\text{MeCN})_2](\text{BF}_4)_2$ (30 mg, 0.05 mmol). After stirring overnight, solvent was removed from the clear dark red solution and the residue was crystallized from CH_2Cl_2 to give red $[\text{Cu}_6\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\text{dppm})_2](\text{BF}_4)_2$ [**3-Cu**](BF_4)₂ (81 mg, 77%). Anal. Calcd. ($\text{C}_{210}\text{H}_{200}\text{B}_2\text{Cu}_6\text{F}_8\text{P}_{12}\text{Ru}_4$): C, 62.21; H, 4.97; M (cation), 3882. Found: C, 61.81; H, 5.01%. IR/ cm^{-1} : $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 2004 (sh), 1985m (br); $\nu(\text{BF})$ 1092m. ^1H NMR: δ 1.57 (s, 60H, Cp*), 3.66 (m, 4H, CH_2 -dppm), 2.10, 2.84 (2 \times m, 16H, CH_2 -dppe), 6.94–8.00 (m, 120H, Ph); ^{31}P NMR: δ 79.3 (br s, dppe), –6.6, –11.0 (2 \times m, dppm). ES-MS/ m/z : 1941, $[\text{Cu}_6(\text{dppm})_2[\text{Ru}(\text{dppe})\text{Cp}^*]_4]^{2+}$. X-ray quality crystals were grown from $\text{CHCl}_3/\text{C}_6\text{H}_6$.

4.8. Preparation of $[(\text{Ag}/\text{Cu})_6\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\text{dppm})_2](\text{BF}_4)_2$ [**4A** and **4B**]

These mixed-metal compounds were made in reactions similar to that used for **2**, using either $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CCu})(\text{dppe})\text{Cp}^*$ and $[\text{Ag}_2(\text{dppm})_2(\text{MeCN})_2](\text{BF}_4)_2$ [to give [**4A**](BF_4)₂] or $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CAg})(\text{dppe})\text{Cp}^*$ and $[\text{Cu}_2(\text{dppm})_2(\text{MeCN})_2](\text{BF}_4)_2$ [to give [**4B**](BF_4)₂]. Both products formed yellow solids. Anal. for **4B** only. Calcd. ($\text{C}_{210}\text{H}_{200}\text{Ag}_{3.1}\text{B}_2\text{Cu}_{2.9}\text{F}_8\text{P}_{12}\text{Ru}_4$): C, 60.09; H, 4.77. Found: C, 59.91; H, 4.99%. IR/ cm^{-1} : $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 1989w. ^1H NMR: δ 1.46 (s, 60H, Cp*), 2.05, 2.81 (16H, CH_2 -dppe), 3.4–3.7 (m, 4H, CH_2 -dppm), 6.90–7.75 (m, 120H, Ph). ^{31}P NMR: for **4A** δ 80.2 (br s, dppe), –2.8, –10.9 (2 \times m, dppm); for **4B** δ 79.8 (s, 8P, dppe) (dppm P not detected). ES-MS/ m/z : 1985, $[\text{Ag}_2\text{Cu}_4(\text{dppm})_2[\text{Ru}(\text{dppe})\text{Cp}^*]_4]^{2+}$; 1963, $[\text{AgCu}_5(\text{dppm})_2[\text{Ru}(\text{dppe})\text{Cp}^*]_4]^{2+}$; 2029, $[\text{Ag}_4\text{Cu}_2(\text{dppm})_2[\text{Ru}(\text{dppe})\text{Cp}^*]_4]^{2+}$; 2007, $[\text{Ag}_3\text{Cu}_3(\text{dppm})_2[\text{Ru}(\text{dppe})\text{Cp}^*]_4]^{2+}$.

4.9. Structure determinations

Diffraction data were measured using an Oxford Diffraction Xcalibur ([**3-Ag**](ClO_4)₂, [**4A**](BF_4)₂, [**4B**](BF_4)₂; Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) or Gemini ([**3-Cu**](BF_4)₂; Cu $K\alpha$ radiation, $\lambda = 1.54178$ vÅ) CCD diffractometers at 100(2) K. N_{tot} reflections were merged to N unique (R_{int} cited) after multi-scan or analytical

absorption corrections with N_o having $I > 2\sigma(I)$. Following solution by direct methods, the structures were refined against F^2 . Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})_H being included following a riding model. Neutral atom complex scattering factors were used; computation used the SHELXL-97 program [16]. Pertinent results are given in the Figures and in Tables 1–3.

5. Variata

[**3-Ag**](ClO_4)₂. Ph ring (62n) was found to be disordered over two sets of sites with both components assigned occupancy factors of 0.5 after trial refinement. Refinement of ring C42n with anisotropic displacement factors gave unacceptable ellipsoids. A disordered model gave two components with sof 0.85 and 1 – 0.85 with some of the atoms of the minor component unacceptably close to solvent atoms. The atoms of this ring were therefore refined with isotropic parameters. The site occupancy of solvent MeCN(5) was set at 0.5 after trial refinement. Atoms of disordered groups were refined with isotropic displacement parameters, with both rings being refined as rigid bodies.

[**3-Cu**](BF_4)₂. One $\text{Ru}(\text{dppe})\text{Cp}^*$ group is disordered over two sets of sites with occupancies refined to 0.578(2) and its complement (with the exception of one Ph group which is common to both components). One Ph ring of the minor component was modeled as being further disordered over two sets of sites and refined with isotropic displacement parameters and with occupancies set equal after trial refinement. The BF_4 anion and solvent CHCl_3 molecule were similarly disordered. The solvent C_6H_6 molecule was refined with occupancies set at 0.5 after trial refinement, with C atoms refined with isotropic displacement parameters. Residual electron density not modeled as either solvent was effectively removed by use of the program SQUEEZE [17], resulting in a significant decrease in the R -factor.

[**4A**](BF_4)₂. Site occupancy factors for the Ag atoms at the mixed Ag/Cu sites 1, 2 and 3 were found to be 0.403(6), 0.287(6) and 0.721(6), respectively, with the occupancies for the Cu atoms being the complements.

[**4B**](BF_4)₂. Site occupancy factors for the Ag atoms at the mixed Ag/Cu sites 1, 2 and 3 were found to be 0.287(1), 0.713(1) and

Table 3
Crystal data and refinement details.

Complex	[3-Ag](ClO_4) ₂ ·9MeCN	[3-Cu](BF_4) ₂ ·2CHCl ₃ ·C ₆ H ₆	[4A](BF_4) ₂ ·8CH ₂ Cl ₂	[4B](BF_4) ₂ ·10MeCN
Formula	$\text{C}_{210}\text{H}_{200}\text{Ag}_6\text{P}_{12}\text{Ru}_4$ ·2ClO ₄ ·9C ₂ H ₃ N	$\text{C}_{210}\text{H}_{200}\text{Cu}_6\text{P}_{12}\text{Ru}_4$ ·2BF ₄ ·2CHCl ₃ ·C ₆ H ₆	$\text{C}_{210}\text{H}_{200}(\text{Ag}_{2.82}\text{Cu}_{3.18})\text{P}_{12}\text{Ru}_4$ ·2BF ₄ ·8CH ₂ Cl ₂	$\text{C}_{210}\text{H}_{200}(\text{Ag}_{3.15}\text{Cu}_{2.85})\text{P}_{12}\text{Ru}_4$ ·2BF ₄ ·10C ₂ H ₃ N
Formula weight	4715.23	4371.32	4859.11	4604.84
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.2375(9)	16.4015(8)	16.3895(5)	16.4269(5)
b (Å)	18.0414(8)	17.4036(7)	17.6167(4)	17.4036(4)
c (Å)	19.3672(6)	20.7303(6)	21.3267(7)	20.8055(4)
α (°)	105.794(3)	79.070(3)	94.304(2)	78.167(2)
β (°)	92.668(3)	89.119(3)	107.006(3)	88.749(2)
γ (°)	113.674(5)	66.041(4)	113.817(2)	65.372(2)
Volume (Å ³)	5224	5297	5254	5278
Z	1	1	1	1
ρ_c (Mg m ⁻³)	1.499	1.370	1.536	1.449
Crystal size (mm ³)	0.21 \times 0.17 \times 0.16	0.12 \times 0.04 \times 0.02	0.29 \times 0.26 \times 0.05	0.26 \times 0.20 \times 0.13
μ (Mo $K\alpha$) (mm ⁻¹)	1.007	4.883 (Cu- $K\alpha$)	1.205	0.997
$F(0\ 0\ 0)$	2394	2230	2459	2349
$T_{\text{min/max}}$	0.90	0.75/0.91	0.75	0.94
N_{tot}	35 274	55 190	66 926	80 412
N (R_{int})	17 766 (0.050)	18 764 (0.1092)	31 695 (0.043)	33 579 (0.045)
N_o	9282	10 942	20 825	18 043
R_1, wR_2 [$I > 2\sigma(I)$]	0.0471, 0.1036	0.0612, 0.1568	0.0622, 0.1624	0.0478, 0.1030
R_1, wR_2 (all data)	0.0922, 0.1138	0.1142, 0.1791	0.1003, 0.1777	0.0981, 0.1166
T (K)	100(2)	100(2)	100(2)	100 (2)

0.557(1), respectively, with the occupancies for the Cu atoms being the complements.

Acknowledgements

PJL holds an EPSRC Leadership Fellowship. We thank the Australian Research Council for support of this work and Johnson Matthey plc, Reading, UK, for a generous loan of RuCl₃.nH₂O.

Appendix A. Supplementary material

CCDC 734433 [3-Ag](ClO₄)₂, 768209 [3-Cu](BF₄)₂, 734434 [4A](BF₄)₂ and 734432 [4B](BF₄)₂ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.016.

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