

Alkynylphosphanes as supports for mixed-metal Co_4M ($\text{M} = \text{Ru}$, Os) fluoride complexes: Syntheses, structures and thermolysis studies

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Abstract

Treatment of the tetrameric group eight fluoride complexes $[\text{MF}(\mu\text{-F})(\text{CO})_3]_4$ [$\text{M} = \text{Ru}$ (**1a**), Os (**1b**)] with the alkynylphosphane, $\text{Ph}_2\text{PC}\equiv\text{CPh}$, results in fluoride-bridge cleavage and the formation of the air-sensitive monomeric octahedral complexes $[\text{MF}_2(\text{CO})_2(\text{PPh}_2\text{CCPh})_2]$ [$\text{M} = \text{Ru}$ (**2a**), Os (**2b**)] in high yield. The molecular structure of **2b** reveals a *cis, cis, trans* configuration for each pair of ligands, respectively. The free alkyne moieties in **2** can be readily complexed to hexacarbonyldicobalt fragments by treatment with dicobalt octacarbonyl to afford $[\text{MF}_2(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]$ [$\text{M} = \text{Ru}$ (**3a**), Os (**3b**)]. Evidence for an intramolecular non-bonded contact between a bound fluoride and a cobalt carbonyl carbon atom is seen in the molecular structure of **3a**. Thermolysis of **3a** at 50 °C results in fluoride dissociation to give $[\text{RuF}(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]^+$ (**4**), while no reaction occurred with the osmium analogue. Prolonged thermolysis at 120 °C in a sealed vessel of both **3a** and **3b** gave only insoluble decomposition products.

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1. Introduction

The application of alkynylphosphanes ($\text{PR}_2\text{C}\equiv\text{CR}$, $\text{R} = \text{hydrocarbyl}$) in organometallic chemistry has been the subject of considerable research activities over the last three decades which can, in part, be attributed to their polyfunctional nature [1,2] and also to their capacity to undergo coupling/insertion reactions with other coordinated groups [3–7]. These coupling reactions can occur with the intact ligand [3,4] or with units derived from fragmentation of the alkynylphosphane (e.g., phosphide and acetylide) [5–7]. In addition, their use to promote the formation of homo- and hetero-metallic clusters has been documented [8].

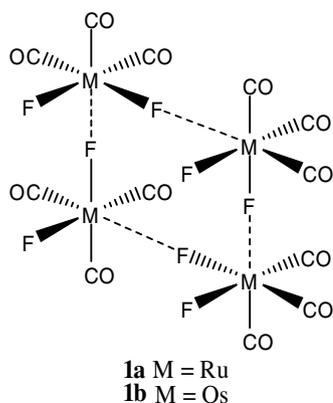
Interest in low valent transition metal fluorides continues to grow, particularly for their roles in coordination chemistry and fluoroorganic synthesis [9]. We have been

interested in exploring the reactivity of the tetrameric group 8 fluoride complexes $[\text{MF}(\mu\text{-F})(\text{CO})_3]_4$ ($\text{M} = \text{Ru}$, **1a**; Os , **1b**; Fig. 1) towards two electron donors and have found that with simple monodentate phosphanes scission of divalent metal complex **1** occurs to give monomeric species of the type *cis, cis, trans*- $[\text{MF}_2(\text{CO})_2(\text{PR}_3)_2]$ [**2**; $\text{M} = \text{Ru}$, Os ; $\text{PR}_3 = \text{PPh}_3$, PEt_2Ph , $\text{P}(\text{C}_6\text{H}_{11})_3$] [10]. Notably, as the steric bulk of the phosphane increases reactivity is inhibited with only products resulting from decomposition of **1** being observed [11].

In this paper, we are concerned with exploiting the bifunctional nature of the alkynylphosphane, $\text{Ph}_2\text{PC}\equiv\text{CPh}$ [12], to prepare more sterically bulky examples of complexes of type **2**. Specifically, polymetallic Co_4M (Ru , Os) difluoride species are being targeted with a view to probing their potential thermolytically initiated fragmentation/coupling chemistry. This program has been further fuelled by reports of P–F coupling reactions [13] and fluoroacyl formation [10b,14] in related late transition metal fluoride complexes.

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Fig. 1. Tetrameric $[\text{MF}(\mu\text{-F})(\text{CO})_3]$ (**1**).

2. Results and discussion

Interaction of $[\text{MF}(\mu\text{-F})(\text{CO})_3]_4$ [$\text{M} = \text{Ru}$ (**1a**), Os (**1b**)] [15] with eight equivalents of $\text{Ph}_2\text{PC}\equiv\text{CPh}$ in tetrahydrofuran at ambient temperature afforded *cis,cis,trans*- $[\text{MF}_2(\text{CO})_2(\text{Ph}_2\text{PCCPh})_2]$ [$\text{M} = \text{Ru}$ (**2a**), Os (**2b**)] in good yield (Scheme 1). Both complexes have been characterised by IR, ^1H , ^{19}F and ^{31}P NMR spectroscopy and gave satisfactory microanalyses (see Table 1 and Section 4). In addition, **2b** has been the subject of a single crystal X-ray diffraction study.

Crystals of **2b** suitable for the X-ray determination were grown by slow vapour diffusion of hexane into a saturated dichloromethane solution containing the complex at room temperature. The molecular structure of

2b is shown in Fig. 2; selected bond lengths and angles are presented in Table 2. The structure consists of a single osmium atom bound by two fluorides, two carbonyl ligands and two alkynylphosphane ligands to complete a distorted octahedral geometry. The pairs of fluoride and carbonyl ligands are disposed mutually *cis* while the alkynylphosphanes are *trans* [$\text{P}(1)\text{-Os}(1)\text{-P}(2)$ $173.44(5)^\circ$] to one another, a relative disposition also seen in *trans*- $[\text{Ru}(\text{acac})_2(\text{Ph}_2\text{PCCR})_2]$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$) [16]. Each alkynic unit points in a similar direction to a carbonyl ligand which is likely stabilised through hydrogen bonding interactions involving an *ortho*-hydrogen atom on one alkynic phenyl group and a carbonyl oxygen atom [$\text{O}(2)\cdots\text{H}(30)$ 3.105 \AA , $\text{O}(1)\cdots\text{H}(6)$ 2.713 \AA]. The C–O and Os–F bond lengths are similar to those reported for the structurally related complex *cis,cis,trans*- $[\text{OsF}_2(\text{CO})_2(\text{PPh}_3)_2]$ [10a]. No significant intermolecular interactions are apparent.

Two $\nu(\text{CO})$ bands are seen in the IR spectra for both **2a** and **2b**, the stretching frequencies in osmium **2b** being ca. 20 cm^{-1} less than those for ruthenium **2a** and resembling the trend seen for the structurally related complexes $[\text{MX}_2(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) [10a]. In the mass spectra of **2a** and **2b**, fragmentation peaks are evident corresponding to the loss of fluoride and carbonyl ligands from their molecular ions. Their ^{19}F NMR spectra reveal resonances at $\delta -336.7$ (**2a**) and $\delta -315.6$ (**2b**) for the fluoride ligands that take the form of triplets with the phosphorus–fluorine coupling constants [24 Hz (**2a**), 33 Hz (**2b**)] comparable to those seen in $[\text{MF}_2(\text{CO})_2(\text{PPh}_3)_2]$ [20 Hz (Ru), 30 Hz (Os)] [10a].

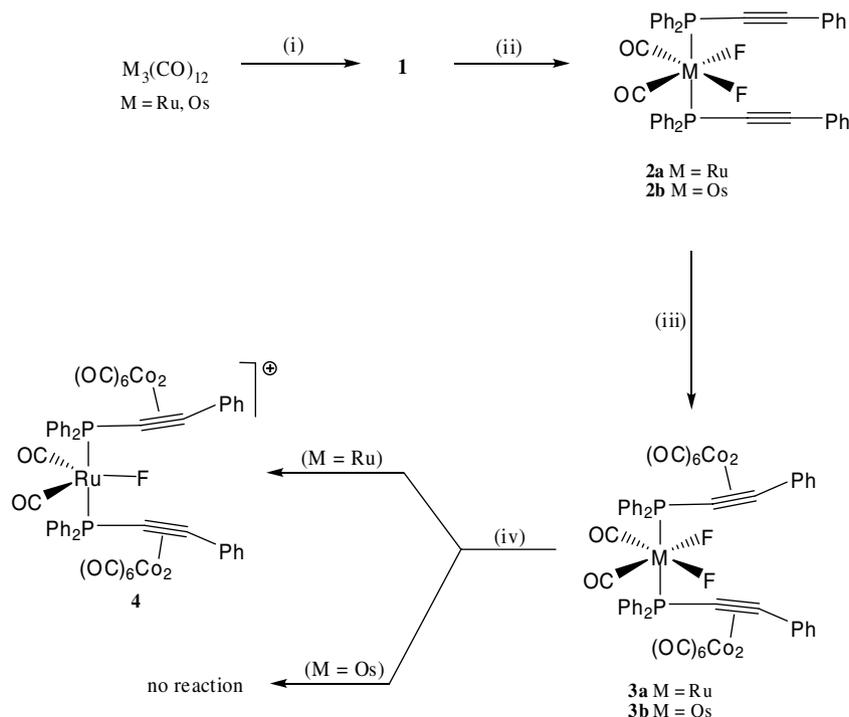
Scheme 1. Reagents and conditions: (i) F_2 , anhydrous HF [15]; (ii) Ph_2PCCPh , THF, 12 h; (iii) $\text{Co}_2(\text{CO})_8$, CH_2Cl_2 , 24 h; (iv) 50°C , CDCl_3 , 20 h.

Table 1
Spectroscopic and analytical data for the new complexes

Complex	$\nu(\text{CO})$ (cm^{-1}) ^a	¹ H NMR (δ) ^b	¹⁹ F NMR (δ) ^c	³¹ P NMR (δ) ^d	Microanalysis (%) ^e	
					C	H
2a	2039(s), 1966(s)	8.20–8.12 (m, 20H, Ar-H), 7.55–7.30 (m, 10H, Ar-H)	–336.7 (t, ² J _{PF} 24, Ru–F)	–5.5 (t, ² J _{PF} 24, Ru–P)	65.60 (65.71)	3.85 (3.91)
2b	2020(s), 1937(s)	8.10, 7.60–7.30 (m, 30H, Ar-H)	–315.6 (t, ² J _{PF} 33, Os–F)	–23.1 (t, ² J _{PF} 33, Os–P)	59.04 (58.74)	3.39 (3.50)
3a	2092(s), 2072(s), 2062(s), 2030(br), 2018(br), 1995(br), 1958(br)	8.15, 7.80, 7.40–7.20 (m, 30H, Ar-H)	–306.2 (t, ² J _{PF} 26, Ru–F)	29.0 (t, ² J _{PF} 26, Ru–P)	48.36 (48.39)	2.20 (2.24)
3b	2093(s), 2071(br), 2062(br), 2036(br), 2014(br), 1996(br), 1936(br)	7.90–7.00 (m, 30H, Ar-H)	–285.3 (t, ² J _{PF} 34, Os–F)	10.6 (t, ² J _{PF} 34, Os–P)	45.25 (45.19)	1.90 (1.94)

^a Recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer on solid samples.

^b Recorded in CDCl₃ at 293 K, chemical shifts in ppm relative to SiMe₄ (0.0 ppm).

^c Recorded in CDCl₃ at 293 K, chemical shifts in ppm relative to CFCl₃ (0.0 ppm), coupling constants in Hz.

^d Recorded in CDCl₃ at 293 K, chemical shifts in ppm relative to 85% H₃PO₄ (0.0 ppm), coupling constants in Hz.

^e Calculated values shown in parentheses.

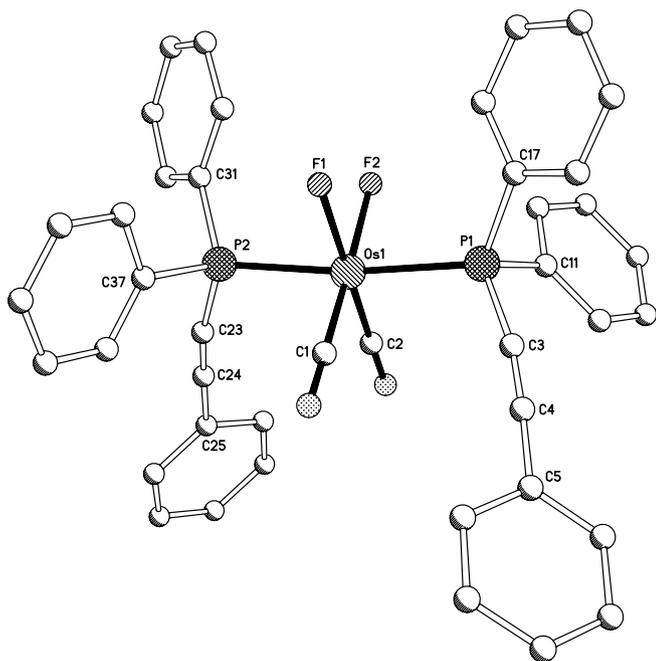


Fig. 2. Molecular structure of **2b** with partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

With the intent of increasing the steric properties of the two P-coordinated alkynylphosphanes in **2**, the reactivity of the free alkynic units towards dicobalt octacarbonyl was examined. Hence, interaction of **2** with two equivalents of [Co₂(CO)₈] at room temperature gave, on work-up, [MF₂(CO)₂(μ-η¹:η²-PPh₂CCPh)₂{Co₂(CO)₆}₂] [M = Ru (**3a**), Os (**3b**)] in high yield (Scheme 1). Both complexes have been characterised by IR, ¹H, ¹⁹F and ³¹P NMR spectroscopy and gave satisfactory microanalyses (see Table 1 and Section 4). In addition, **3a** has been the subject of a single crystal X-ray diffraction study.

Crystals of **3a** suitable for the X-ray determination were grown by prolonged standing of a hexane–dichlorometh-

Table 2
Selected bond distances (Å) and angles (°) for **2b**

Bond lengths (Å)			
Os(1)–F(1)	2.023(3)	P(1)–C(11)	1.826(5)
Os(2)–F(2)	2.023(3)	P(1)–C(3)	1.746(5)
Os(1)–C(1)	1.872(5)	C(3)–C(4)	1.211(7)
Os(1)–C(2)	1.868(5)	P(2)–C(31)	1.797(5)
Os(1)–P(1)	2.3795(13)	P(2)–C(37)	1.818(5)
Os(1)–P(2)	2.3797(14)	P(2)–C(23)	1.756(5)
P(1)–C(17)	1.816(5)	C(23)–C(24)	1.188(7)
Bond angles (°)			
F(1)–Os(1)–F(2)	83.47(11)	F(2)–Os(1)–P(1)	86.53(9)
F(1)–Os(1)–C(1)	92.53(18)	F(2)–Os(1)–P(2)	88.00(9)
F(1)–Os(1)–C(2)	177.11(18)	P(1)–Os(1)–P(2)	173.44(5)
F(1)–Os(1)–P(1)	89.62(9)	Os(1)–P(1)–C(3)	111.07(18)
F(1)–Os(1)–P(2)	86.15(9)	P(1)–C(3)–C(4)	170.7(5)
F(2)–Os(1)–C(1)	93.95(17)	Os(1)–P(2)–C(23)	111.61(18)
F(2)–Os(1)–C(2)	93.95(17)	P(2)–C(23)–C(24)	169.4(5)

ane mixture containing the complex. The complex crystallises with two discrete independent molecules (A and B in Table 3) within its asymmetric unit. The molecular structure of **3a** (molecule A) is shown in Fig. 3; selected bond distances and angles for bond A and B are listed in Table 3. The main difference between the two molecules derives from the relative inclination of the phenyl groups. The molecular structure of **3a** consists of a single octahedral ruthenium centre bound by two *cis*-fluorides, two *cis*-carbonyls and two *trans*-phosphanes in a manner similar to that seen for **2b** and [RuF₂(CO)₂(PPh₂Et)₂] [10a]. Unlike in **2b**, however, the alkynic moieties within the phosphanes are additionally bound by η²:η²-Co₂(CO)₆ units; the geometric parameters of the pseudo-tetrahedral Co₂C₂ cores are unexceptional. In comparison to [RuF₂(CO)₂(PPh₂Et)₂] [10a], it is apparent that the presence of coordinated Co₂(CO)₆ units in **3a** has little effect on the Ru–F, Ru–P and Ru–C bond distances. As with **2b** one *ortho*-hydrogen atom per alkynyl phenyl group undergoes a

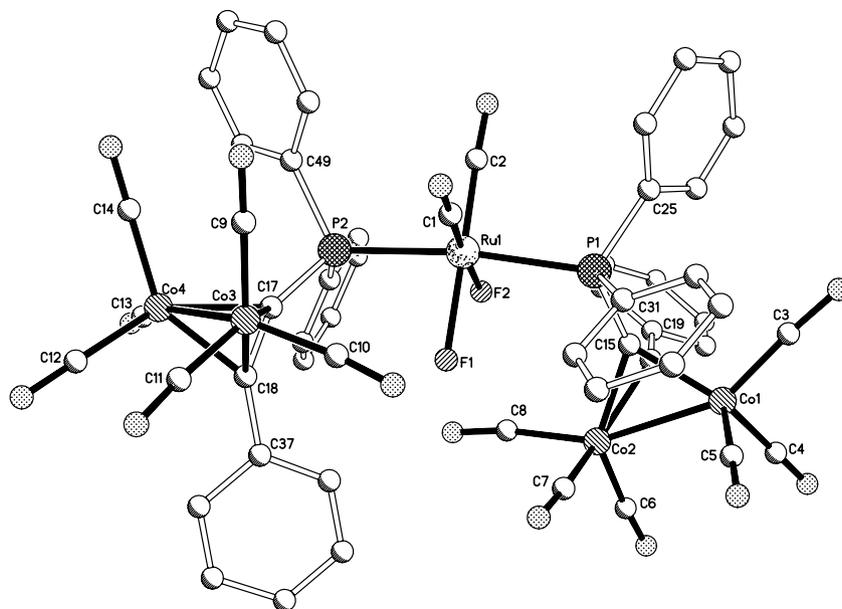


Fig. 3. Molecular structure of **3a** with partial atom labeling scheme; all hydrogen atoms have been omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for **3a**

	Molecule A	Molecule B
<i>Bond lengths (Å)</i>		
Ru(1)–F(1)	2.017(6)	2.017(6)
Ru(2)–F(2)	1.989(6)	1.993(6)
Ru(1)–C(1)	1.843(12)	1.814(12)
Ru(1)–C(2)	1.833(12)	1.840(10)
Ru(1)–P(1)	2.392(3)	2.404(3)
Ru(1)–P(2)	2.417(3)	2.398(3)
P(1)–C(25)	1.805(10)	1.793(11)
P(1)–C(31)	1.821(10)	1.822(10)
P(2)–C(49)	1.823(11)	1.806(10)
P(2)–C(43)	1.806(10)	1.803(10)
Co–C(carbonyl)	1.764(15)–1.819(15)	1.784(16)–1.849(14)
C–O(carbonyl)	1.114(13)–1.206(11)	1.112(12)–1.185(12)
Co–C(alkyne)	1.949(9)–1.993(11)	1.946(12)–1.962(10)
C(18)–C(37)	1.470(15)	1.515(14)
C(16)–C(19)	1.476(13)	1.483(15)
Co(1)–Co(2)	2.4552(19)	2.461(2)
Co(3)–Co(4)	2.454(2)	2.4519(19)
<i>Bond angles (°)</i>		
F(1)–Ru(1)–F(2)	86.0(2)	85.6(2)
F(1)–Ru(1)–C(1)	92.9(4)	94.4(4)
F(1)–Ru(1)–C(2)	175.6(4)	174.3(3)
F(1)–Ru(1)–P(1)	87.79(18)	86.02(18)
F(1)–Ru(1)–P(2)	86.56(18)	88.67(18)
F(2)–Ru(1)–C(1)	176.4(4)	178.4(3)
F(2)–Ru(1)–C(2)	89.8(4)	89.0(4)
F(2)–Ru(1)–P(1)	86.03(18)	86.30(17)
F(2)–Ru(1)–P(2)	87.18(18)	86.30(17)
P(1)–Ru(1)–P(2)	171.44(10)	171.55(10)
Ru(1)–P(1)–C(15)	113.7(3)	117.1(4)
P(1)–C(15)–C(16)	143.0(8)	146.6(9)
C(19)–C(16)–C(15)	142.8(9)	141.4(11)
Ru(1)–P(2)–C(17)	115.3(4)	113.1(3)
P(2)–C(17)–C(18)	146.1(9)	145.4(8)
C(17)–C(18)–C(37)	144.2(11)	140.6(9)

hydrogen bonding interaction, in this case, however, with a fluoride [C(24)H···F(2) 2.142 Å, C(38)H···F(1) 2.150 Å] rather than with a carbonyl oxygen atom. In addition, an intramolecular non-bonded contact is evident between F(2) and cobalt carbonyl C(8) [2.664 Å]. This type of F···C_{CO} interaction is not unprecedented, but is usually only observed intermolecularly between ‘superelectrophilic’ metal carbonyl cations and fluoro-anions of either anti-mony or boron [17]. No significant intermolecular interactions are apparent.

The spectroscopic data for **3** are consistent with the solid state properties being maintained in solution. In the ¹⁹F NMR spectra, triplets are seen for the equivalent fluoride ligands in **3a** and **3b** with chemical shifts and phosphorus-fluorine coupling constants similar to those seen for **2a** and **2b**, respectively. The IR spectra show a series of ν(CO) bands in a pattern characteristic of other Co₂(CO)₆-alkyne complexes [18] along with lower wavenumber ν(CO) bands that can be attributed to the group eight metal carbonyl groups. The ³¹P NMR spectra of **3a** and **3b** reveal triplet resonances for the equivalent phosphorus atoms shifted ca. 30 ppm downfield with regard to **2a** and **2b**, consistent with the loss of the alkyne π-system on coordination [8c,19].

In order to probe the capacity of **3** to undergo fragmentation reactions (e.g., P–C bond cleavage, fluoride migration), a spectroscopic study on the thermolysis of **3a** and **3b** was undertaken. Separate NMR tubes were charged with solutions of **3** in CDCl₃ and sealed. Osmium complex **3b** remained unaffected by heating in CDCl₃ at 50 °C, with no decomposition or formation of any other species being apparent. Prolonged heating of **3b** in toluene-*d*₈ at 120 °C resulted in the formation of intractable decomposition products.

However, after heating a CDCl_3 solution of ruthenium complex **3a** at 50 °C for 4 h, both the ^{31}P and ^{19}F NMR data supported the formation of a new complex. In the ^{31}P NMR spectrum, a signal corresponding to the starting material was flanked by a new doublet at δ 26.6, while in the ^{19}F NMR spectrum the additional fluorine signal took the form of a mutually coupled triplet ($^2J_{\text{PF}}$ 27 Hz) at δ –348.4. After heating at 50 °C for a further 16 h the transformation was complete. In the resultant ^{19}F NMR spectrum, the mutually coupled triplet at δ –348.4 was accompanied by two small singlets at δ –113.1 and δ –139.6. The spectroscopic data indicate that thermolysis of **3a** causes the formation of a single fluorine- and phosphane-containing cation $[\text{RuF}(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]^+$ (**4**) (Scheme 1). The triplet in the ^{19}F NMR spectrum of **4** is substantially upfield shifted when compared to that for the parent complex **3a** and falls in the range found for previously reported related mono-fluoro ruthenium cationic complexes [20]. The singlets at δ –113.1 and δ –139.6 observed in the ^{19}F NMR spectrum during the transformation of **3a** to **4** are most likely due to varying degrees of solvent fluorination [21], suggesting that thermolysis of **3a** (and formation of **4**) involves fluoride dissociation from the metal. It is uncertain as to the precise nature of the anion in **4** but a chloride ion (or a Cl-containing species), generated during fluorination of the chlorinated NMR solvent, would seem likely. Heating a toluene- d_8 solution of **3a** to 120 °C resulted in the formation of intractable decomposition products.

Unfortunately, attempts to fill the vacant coordination site in **4** with CO or acetonitrile failed with the corresponding NMR spectra revealing only the presence of unreacted starting material. This may be rooted in steric protection of the metal centre in **4**, or intramolecular stabilisation interactions between the ruthenium centre and the pendant carbonyl groups of the $(\mu\text{-}\eta^1\text{:}\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2$ fragments. Unfortunately, all attempts to isolate **4** were unsuccessful, and it was characterised solely by NMR spectroscopy.

3. Conclusions

In this study, we have shown that $\text{Ph}_2\text{PC}\equiv\text{CPh}$ can be readily introduced into the coordination sphere of a group 8 ($M = \text{Ru}, \text{Os}$) fluoride complex as a P-donor ligand to afford octahedral **2**. Complexation of the alkyne moieties within **2** with dicobalt hexacarbonyl groups preserves the MF_2 core by generating the mixed-metal Co_4M ($M = \text{Ru}, \text{Os}$) clusters **3**. Thermolysis of **3a** at 50 °C leads to the formation of another complex, which was spectroscopically characterised as $[\text{RuF}(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]^+$ (**4**), formed by dissociation of one of the fluoride ligands. Under similar conditions, no reaction of **3b** was observed, indicating an increased stability of the Os–F bond in **3b** when compared to the Ru–F bond of **3a**. Exposing either **3a** or **3b** to more forcing conditions led to the formation of intractable decomposition products.

4. Experimental

4.1. General procedures and materials

All reactions, unless otherwise stated, were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques or in a nitrogen purged dry box. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use [22]. The infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer on solid samples. The ES (electrospray) and the FAB mass spectra were recorded using a micromass Quattro LC mass spectrometer and a Kratos Concept spectrometer with methanol or 3-nitrobenzyl alcohol as the matrix, respectively. ^1H , ^{31}P , ^{19}F and ^{13}C NMR spectra were recorded on a Bruker spectrometer (ARX 250, AM 300 or DRX 400 MHz) at ambient temperature; chemical shifts (δ) for the ^1H and ^{13}C NMR spectra were referenced internally to TMS ($\delta = 0$) while ^{19}F and ^{31}P were referenced externally to CFCl_3 ($\delta = 0$) and 85% H_3PO_4 ($\delta = 0$), respectively. Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

The compounds, (tricarbonyl)rutheniumdifluoride tetramer (**1a**) [15], (tricarbonyl)osmiumdifluoride tetramer (**1b**) [15] and phenylethyndiphenylphosphane [12], were prepared according to previously reported procedures while dicobalt octacarbonyl was obtained from Aldrich Chemical Co. and used without further purification. All other chemicals were obtained commercially and used without further purification.

4.2. Synthesis of $[\text{MF}_2(\text{CO})_2(\text{PPh}_2\text{CCPh})_2]$ (**2**)

4.2.1. (i) $M = \text{Ru}$ (**2a**)

Under an atmosphere of nitrogen a Schlenk vessel was charged with **1a** (0.250 g, 0.280 mmol) and Ph_2PCCPh (0.657 g, 2.296 mmol) and freshly distilled tetrahydrofuran (40 mL) introduced. After stirring the reaction mixture at room temperature for 12 h under a partial vacuum, the volatiles were removed under reduced pressure and the residue washed with methanol (2×5 mL). Recrystallization from a mixture of tetrahydrofuran and hexane gave $[\text{RuF}_2(\text{CO})_2(\text{PPh}_2\text{CCPh})_2]$ (**2a**) as an air- and moisture-sensitive white powder. Yield: 0.515 g, 60%. IR (cm^{-1}): 3048 w, 2163 ($\text{C}\equiv\text{C}$), 2039s (CO), 1966s (CO), 1480m, 1435s, 1094m, 848s, 683s. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 195.3 (CO), 132.9, 131.1 (Ar-CH), 129.9 (Ar-C), 128.6 (Ar-CH), 112.3 (P– $\text{C}\equiv\text{C}$), 79.4 (P– $\text{C}\equiv\text{C}$). FAB mass spectrum, m/z 721 $[\text{MH}-\text{F}-\text{CO}]^+$, 701 $[\text{M}-2\text{F}-\text{CO}]^+$, 673 $[\text{M}-2\text{F}-2\text{CO}]^+$.

4.2.2. (ii) $M = \text{Os}$ (**2b**)

Using a similar procedure, **1b** (0.349 g, 0.280 mmol) and Ph_2PCCPh (0.657 g, 2.296 mmol) gave $[\text{OsF}_2(\text{CO})_2(\text{PPh}_2\text{CCPh})_2]$ (**2b**) as an air- and moisture-sensitive white

powder. Yield: 0.594 g, 62%. Crystals suitable for X-ray diffraction were grown by slow vapour diffusion of hexane into a saturated dichloromethane solution of **2b**. IR (cm^{-1}): 3048w, 2162 ($\text{C}\equiv\text{C}$), 2020s (CO), 1937s (CO), 1484s, 1434s, 850s, 688s. FAB mass spectrum, m/z 839 $[\text{M}-\text{F}]^+$, 811 $[\text{M}-\text{F}-\text{CO}]^+$, 783 $[\text{M}-\text{F}-2\text{CO}]^+$, 764 $[\text{M}-2\text{F}-2\text{CO}]^+$.

4.3. Synthesis of $[\text{MF}_2(\text{CO})_2(\mu-\eta^1:\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]$ (**3**)

4.3.1. (i) $M = \text{Ru}$ (**3a**)

Under an atmosphere of nitrogen a Schlenk tube was charged with **2a** (0.400 g, 0.522 mmol) and dicobaltoctacarbonyl (0.357 g, 1.043 mmol) and freshly distilled dichloromethane (10 mL) introduced. After stirring the red solution at room temperature for 24 h the volatiles were removed under reduced pressure to give a dark red solid. Recrystallisation of the solid from a mixture of dichloromethane and hexane gave **3a** as air- and moisture-sensitive deep red needles. Yield: 0.559 g, 80%. Crystals suitable for an X-ray diffraction study were grown by vapour diffusion of hexane into a saturated dichloromethane solution. IR (cm^{-1}): 3053w, 2092 (CO), 2072s (CO), 2062s (CO), 2030br (CO), 2018br (CO), 1995br (CO), 1958br (CO), 1480s, 1432s, 1094s, 695s. ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 198.3 (CO), 138.2 (Ar-C), 134.0 (Ar-C), 133.9 (Ar-CH), 131.5 (Ar-CH), 130.9 (Ar-CH), 128.5 (Ar-CH), 128.1 (Ar-CH), 105.8 (P-C \equiv C), 77.1 (P-C \equiv C). FAB mass spectrum, m/z 1227 $[\text{M}-4\text{CO}]^+$, 1199 $[\text{M}-5\text{CO}]^+$, 1115 $[\text{M}-8\text{CO}]^+$, 1087 $[\text{M}-9\text{CO}]^+$, 1059 $[\text{M}-10\text{CO}]^+$.

4.3.2. (ii) $M = \text{Os}$ (**3b**)

Using a similar procedure, **2b** (0.477 g, 0.522 mmol) and dicobaltoctacarbonyl (0.357 g, 1.043 mmol) gave $[\text{OsF}_2(\text{CO})_2(\mu-\eta^1:\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]$ (**3b**) as an air- and moisture-sensitive deep red powder. Yield: 0.447 g, 60%. IR (cm^{-1}): 3294br, 2093 (CO), 2071br (CO), 2062br (CO), 2036br (CO), 2014br (CO), 1996br (CO), 1936br (CO), 1561s, 1432s, 1094s, 688s. FAB mass spectrum, m/z 1289 $[\text{M}-5\text{CO}]^+$, 1205 $[\text{M}-8\text{CO}]^+$, 1117 $[\text{M}-9\text{CO}]^+$, 1149 $[\text{M}-10\text{CO}]^+$, 1121 $[\text{M}-11\text{CO}]^+$, 1093 $[\text{M}-12\text{CO}]^+$, 1065 $[\text{M}-14\text{CO}]^+$, 975 $[\text{M}-14\text{CO}-2\text{Co}]^+$.

4.4. Thermolysis of $[\text{MF}_2(\text{CO})_2(\mu-\eta^1:\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]$ (**3**)

4.4.1. (i) $M = \text{Ru}$ (**3a**)

Complex **3a** (0.050 g, 0.037 mmol) was dissolved in CDCl_3 (1 mL) in an NMR tube under a nitrogen atmosphere. The tube was sealed, and immersed in an oil bath which was held at 50 °C. After 20 h, the ^{19}F and ^{31}P NMR spectra revealed complete reaction of **3a**, with concomitant formation of $[\text{RuF}(\text{CO})_2(\mu-\eta^1:\eta^2\text{-PPh}_2\text{CCPh})_2\{\text{Co}_2(\text{CO})_6\}_2]^+$ (**4**). ^1H NMR (CDCl_3): δ 8.10, 7.75, 7.45–7.20 (m, 30H, Ar-H); ^{19}F $\{^1\text{H}\}$ NMR (CDCl_3): δ –348.4 (t, $^2J_{\text{PF}}$ 27, Ru-F); ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3): δ

26.6 (d, $^2J_{\text{PF}}$ 27, Ru-P). Heating a solution of **3a** in toluene- d_8 at 120 °C resulted in the formation of intractable decomposition products.

4.4.2. (ii) $M = \text{Os}$ (**3b**)

Using a similar protocol, **3b** (0.050 g, 0.035 mmol) and CDCl_3 (1 mL). After heating at 50 °C, **3b** could be recovered intact. Prolonged heating of **3b** in toluene- d_8 at 120 °C resulted in the formation of intractable decomposition products.

4.5. Crystallographic studies

Data for **2b** and **3a** were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Table 4. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement based on full-matrix least-squares on F^2 employed SHELXTL version 6.10 [23]. Hydrogen atoms were included in calculated positions (C–H = 0.96 Å) riding on the bonded atom with isotropic displacement parameters set to $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters.

Table 4
Crystallographic and data processing parameters for **2b** and **3a**

Complex	2b	3a
Formula	$\text{C}_{42}\text{H}_{30}\text{F}_2\text{O}_2\text{OsP}_2$	$\text{C}_{54}\text{H}_{30}\text{Co}_4\text{F}_2\text{O}_{14}\text{P}_2\text{Ru}$
Molecular weight	856.80	1339.51
Crystal size (mm^3)	$0.34 \times 0.07 \times 0.06$	$0.47 \times 0.10 \times 0.03$
Temperature (K)	150	150
Crystal system	trigonal	triclinic
Space group	$P\bar{3}1$	$P\bar{1}$
a (Å)	10.7451(13)	9.6526(11)
b (Å)	10.7451(13)	19.844(2)
c (Å)	26.256(5)	28.972(3)
α (°)	90	104.777(2)
β (°)	90	91.295(2)
γ (°)	120	90.072(2)
V (Å 3)	2625.3(7)	5364.5(11)
Z	3	4
D_{calc} (Mg m^{-3})	1.626	1.659
$F(000)$	1266	2664
μ (Mo $K\alpha$) (mm^{-1})	3.781	1.618
Reflections collected	22132	38792
Independent reflections	7546	18721
R_{int}	0.0549	0.0814
Restraints/parameters	1/442	0/1387
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0298$, $wR_2 = 0.0604$	$R_1 = 0.0842$, $wR_2 = 0.1899$
Final R indices (all data)	$R_1 = 0.0315$, $wR_2 = 0.0609$	$R_1 = 0.1392$, $wR_2 = 0.2181$
Goodness of fit on F^2 (all data)	1.024	0.928

Data in common: graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å; $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where a is a constant adjusted by the program; goodness of fit = $[\sum (F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

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Appendix A. Supplementary data

CCDC 656947 and 656946 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.2007.09.006](https://doi.org/10.1016/j.jorganchem.2007.09.006).

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