Investigation on the reactivity of tetranuclear Group 7/8 mixed-metal clusters toward triphenylphosphine

Md. Rassel Moni [a,b], Md. Jadu Mia [a], Shishir Ghosh [a,*], Derek A. Tocher [c], Shaikh M. Mobin [d], Tasneem A. Siddiquee [e], Shariff E. Kabir [a,*]

[a] *Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh*

[b] *Department of Chemistry, Comilla University, Comilla-3506, Bangladesh*

[c] *Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom*

[d] *Discipline of Chemistry, School of Basic Science, Indian Institute of Technology Indore, Khandwa Road, Indore 452 017, India*

[e] *Department of Chemistry, Tennessee State University, 3500 John A. Merritt Blvd., Nashville, TN 37209, USA*

*Corresponding authors.

E-mail addresses: sghosh_006@yahoo.com (S. Ghosh); skabir_ju@yahoo.com (S.E. Kabir)

Abstract

Reactions of the tetranuclear mixed-metal clusters $ReM_3(CO)_{13}(\mu_3\text{-thpymS})$ (**1**, M = Os; **2**, M = Ru; thpymSH = tetrahydropyrimidine-2-thiol) with PPh_3 are examined. At room temperature reaction between **1** and PPh_3 in the presence Me_3NO leads to the formation of mono- and bis-phosphine substituted clusters $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-thpymS})$ (**3**) and $ReOs_3(CO)_{11}(PPh_3)_2(\mu_3\text{-thpymS})$ (**4**). Cluster **3** also reacts with PPh_3 under similar conditions to give **4**. In contrast, a similar reaction between **2** and PPh_3 furnishes only the mono-phosphine substituted clusters $ReRu_3(CO)_{12}(PPh_3)(\mu_3\text{-thpymS})$ (**3**). All the new clusters have been characterized by analytical and spectroscopic data together with single crystal X-ray diffraction for **1**, **3** and **5**.

Keywords: Mixed-metal clusters; Tetrahydropyrimidine-2-thiol; Carbonyls; Triphenylphosphine; X-ray structures.

1. Introduction

Research on mixed-metal clusters has been spurred by the possible cooperative reactivity as a result of having two or more metal centers with different chemical properties in close proximity [1,2], which offer attractive perspective in stoichiometric and catalytic transformations [3-6]. Heterometallic systems may also combine the catalytic features of different metals to give novel reactivity that is inaccessible by homometallic systems [7]. We have reported systematic synthesis of a number of mixed-metal carbonyl clusters containing heterocyclic thiolate ligand(s) in the past few years [8-16]. For example, the Group 7/8 mixed-metal clusters of the general formula $MM'_3(CO)_{13}(\mu_3\text{-}L)$ [M = Mn, Re; M′ = Os, Ru; L-H = nitrogen containing heterocyclic thiol] can be readily obtained from the direct reaction between $M'_3(CO)_{10-x}(NCMe)_x$ (x = 0, 2) and $M_2(CO)_6(\mu\text{-}L)_2$ in moderate to good yield (Scheme 1). The metallic core of these mixed-metal clusters forms a butterfly skeleton where the Group 7 metal (Mn or Re) always occupies a wingtip position [10-16]. The heterocyclic thiolate ligand is facially located on the convex side of the butterfly core that contains the Group 7 metal, but recent studies showed that it can also be shifted to the other face of the convex side by heating as shown in Scheme 1 [16].
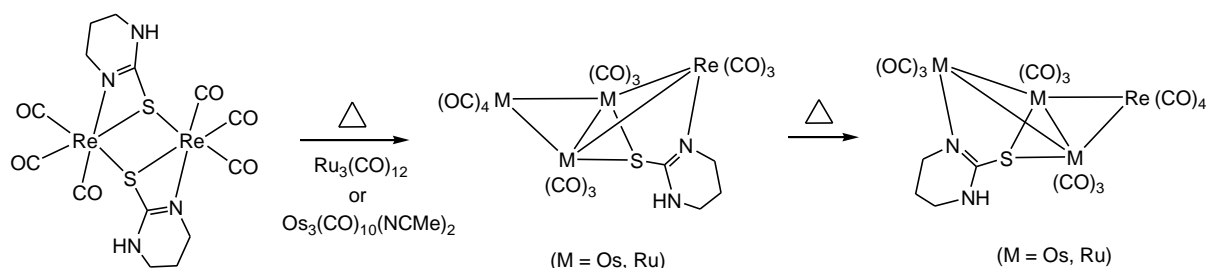
Scheme 1. Synthesis and thermally induced structural rearrangement of $ReM_3(CO)_{13}(\mu_3\text{-}thpymS)$ (M = Os, Ru).

Clusters having a butterfly arrangement of metal atoms are considered intermediate between tetrahedral and square-planar clusters [17,18] which have been studied as intermediates in homogeneous catalytic processes [18,19], and also considered as a model for chemisorption of small molecules [20]. Although the $MM'_3(CO)_{13}(\mu_3\text{-}L)$ type butterfly clusters are relatively easy to prepare, studies on their reactivity toward various substrates has been almost neglected [12,13]. Tertiary phosphines (PR_3) are an important class of ligands in

organometallic chemistry as their steric and electronic properties can easily be tuned in a systematic and predictable way over a very wide range by varying the R group(s) and they are also capable of stabilizing an exceptionally wide variety of metal complexes. Now we have investigated the reactions of two such mixed-metal clusters namely $ReOs_3(CO)_{13}(\mu_3\text{-thpymS})$ (**1**) and $ReRu_3(CO)_{13}(\mu_3\text{-thpymS})$ (**2**) with PPh_3, the results of which will be reported herein.

2. Experimental

2.1. General procedures

All the reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent-grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Clusters **1** and **2** were prepared according to the published procedures [16]. PPh_3 was purchased from Sigma-Aldrich and used without further purification. $Me_3NO \cdot 2H_2O$ was dried by azeotropic distillation using benzene with Dean–Stark distillation equipment. Products were separated in the air by TLC plates coated with 0.25 mm of silica gel (HF254-type 60, E. Merck, Germany). Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. NMR spectra were recorded on a Varian Unity 500 NMR spectrometer. All chemical shifts are reported in δ units and are referenced to the residual protons of the deuterated solvent (^1H) and external 85% H_3PO_4 (^{31}P) as appropriate. Elemental analyses were performed by the Microanalytical Laboratories of Wazed Miah Science Research Centre at Jahangirnagar University.

2.2. Reaction of $ReOs_3(CO)_{13}(\mu_3\text{-thpymS})$ (**1**) with PPh_3

Me_3NO (6 mg, 0.084 mmol) was added to a CH_2Cl_2 solution (20 mL) of **1** (50 mg, 0.040 mmol) and PPh_3 (21 mg, 0.080 mmol) and the reaction mixture was then stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3 v/v) developed four bands. The first and second bands were unconsumed PPh_3 (5 mg) and **1** (2 mg), respectively, whilst the third and fourth bands afforded $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-thpymS})$ (**3**) (15 mg, 25%)

and ReOs$_3$(CO)$_{11}$(PPh$_3$)$_2$(μ_3-thpymS) (**4**) (32 mg 46%) as red crystal after recrystalization from hexane/CH$_2$Cl$_2$ at 4 °C.

Data for **3**: Anal. Calcd for C$_{34}$H$_{22}$N$_2$O$_{12}$Os$_3$PReS: C, 27.77; H, 1.51; N, 1.91. Found: C, 28.16; H, 1.57; N, 1.98%. IR (ν_{CO}, CH$_2$Cl$_2$): 2073m, 2022vs, 1997s, 1943m, 1903w cm^{-1}. ^{1}H NMR(CDCl$_3$): δ 7.47 (m, 15H), 6.40 (s, br, 1H), 4.13 (t, J 5 Hz, 2H), 3.21 (m, 2H), 1.87 (m, 2H). ^{31}P\{^{1}H\} NMR (CDCl$_3$) : δ 7.0 (s).

Data for **4**: Anal. Calcd for C$_{51}$H$_{37}$N$_2$O$_{11}$Os$_3$P$_2$ReS: C, 35.93; H, 2.19; N, 1.64. Found: C, 36.34; H, 2.25; N, 1.69%. IR (ν_{CO}, CH$_2$Cl$_2$): 2052m, 2010vs, 2005sh, 1976s, 19655w, 1936m, 1913m cm^{-1}. ^{1}H NMR(CDCl$_3$): δ 7.44 (m, 4H), 7.34 (m, 26H), 6.34 (s, br, 1H), 4.19 (m, 2H), 3.30 (m, 2H), 1.95 (m, 2H). ^{31}P\{^{1}H\} NMR (CDCl$_3$): δ 10.0 (d, J 4 Hz, 1P), 6.5 (d, J 4 Hz, 1P).

2.3. Conversion of 3 to 4

A CH$_2$Cl$_2$ solution (10 mL) of **3** (20 mg, 0.014 mmol), Me$_3$NO (1 mg, 0.014 mmol) and PPh$_3$ (4 mg, 0.015 mmol) was stirred at room temperature for 2 h. A similar work up and chromatographic separation described above afforded **4** (16 mg, 69%) after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C.

2.4. Reaction of ReRu$_3$(CO)$_{13}$(μ_3-thpymS) (2) with PPh$_3$

A CH$_2$Cl$_2$ solution (20 mL) of **2** (40 mg, 0.041 mmol), PPh$_3$ (22 mg, 0.084 mmol) and Me$_3$NO (6 mg, 0.084 mmol) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/CH$_2$Cl$_2$ (7:3 v/v) developed six bands. The first and second bands were unconsumed PPh$_3$ and **2**, while the fourth band yielded ReRu$_3$(CO)$_{12}$(μ_3-thpymS)(PPh$_3$) (**5**) (28 mg, 56%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. The contents of the other three bands were too small for complete characterization.

Data for **5**: Anal. Calcd for C$_{34}$H$_{22}$N$_2$O$_{12}$PRu$_3$ReS: C, 33.94; H, 1.84; N, 2.33. Found: C, 34.48; H, 1.91; N, 2.36%. IR (ν_{CO}, CH$_2$Cl$_2$): 2069m, 2022vs, 1996s, 1949m,br, 1903 w,br cm^{-1}. ^{1}H NMR(CDCl$_3$): δ 7.49 (m, 15H), 6.51 (s,br, 1H), 4.03 (t, J 5.6 Hz, 2H), 3.36 (m, 2H), 1.94 (t, J 5.6 Hz, 2H). ^{31}P\{^{1}H\} NMR (CDCl$_3$): δ 32.6 (s).

2.5. X-ray crystallography

Single crystals suitable for single crystal X-ray diffraction analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **1**, **3** and **5** at 4 °C. Suitable single crystals of **1** were mounted on an Agilent Super Nova dual diffractometer (Agilent Technologies Inc., Santa Clara, CA) (for **1**) or Oxford Diffraction Super Nova diffractometer (for **3**) using a Nylon Loop and the diffraction data were collected at 150(1) K using Mo-Kα radiation (λ = 0.71073). Unit cell determination, data reduction, and absorption corrections were carried out using CrysAlisPro [21]. The structures were solved with the ShelXS [22] structure solution program by direct methods and refined with ShelXL [23] (for **1**) or XL [22] (for **3**) refinement package using least squares minimisation within the OLEX2 [24] graphical user interface. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included using a riding model. The selected crystal of **5** was attached to a MiTeGen loop by Apiezon H grease and mounted on a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073) at 293(2) K. Data collection and subsequent data processing were performed using the available diffractometer software Crystal Clear (Rigaku). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELX-97) [25] and expanded by Fourier techniques. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included using a riding model. Pertinent crystallographic parameters are given in Table 1.

3. Results and discussion

3.1. Solid-state structure of *1*

Few years ago, we have reported the butterfly clusters $ReOs_3(CO)_{13}(\mu_3\text{-thpymS})$ (**1**) and $ReRu_3(CO)_{13}(\mu_3\text{-thpymS})$ (**2**) synthesized from the reactions between $Re_2(CO)_6(\mu\text{-thpymS})_2$ and $Os_3(CO)_{10}(NCMe)_2$ or $Ru_3(CO)_{12}$ [16]. The solid-state molecular structure of **2** was also reported by us at that time, while we were unable to grow single crystals of **1** which was eventually characterized by elemental analysis and spectroscopic data only. Fortunately, we have obtained single crystals of **1** during the present study and carried out single crystal X-ray diffraction studies, the results of which are shown in Fig. 1. As expected, the molecule consists of a butterfly core of four metal atoms with the rhenium at a wingtip position. The

interplanar angle of the butterfly is 159.5° and the thpymS ligand is located on the convex side by making bonds with the hinge osmium atoms and rhenium. It coordinates with rhenium using one of the ring nitrogen while bridges the hinge osmium atoms using the sulfur. The Os–Os [Os(1)–Os(3) 2.8596(3), Os(1)–Os(2) 2.8650(3) and Os(2)–Os(3) 2.7626(4) Å], Os–Re [Re(1)–Os(3) 2.9249(3) and Re(1)–Os(2) 2.9307(3) Å], Re–N [2.181(5) Å] and Os–S [Os(2)–S(1) 2.4081(15) and Os(3)–S(1) 2.3979(16) Å] bond distances are within the expected range and similar to those reported for related clusters [12,13]. The and bond distances

3.2. Reactions of 1 and 2 with PPh$_3$: Synthesis of phosphine-substituted mixed-metal clusters

Me$_3$NO initiated reactions between **1** and PPh$_3$ at room temperature led to the isolation of mono- and bis-phosphine substituted clusters ReOs$_3$(CO)$_{11}$(μ-CO)(PPh$_3$)(μ_3-thpymS) (**3**) and ReOs$_3$(CO)$_{11}$(PPh$_3$)$_2$(μ_3-thpymS) (**5**) in 25 and 46% yield, respectively, after chromatographic separation and workup. In separate experiments, we also found that **3** converted in to **4** upon treatment with PPh$_3$ under similar conditions (Scheme 2).
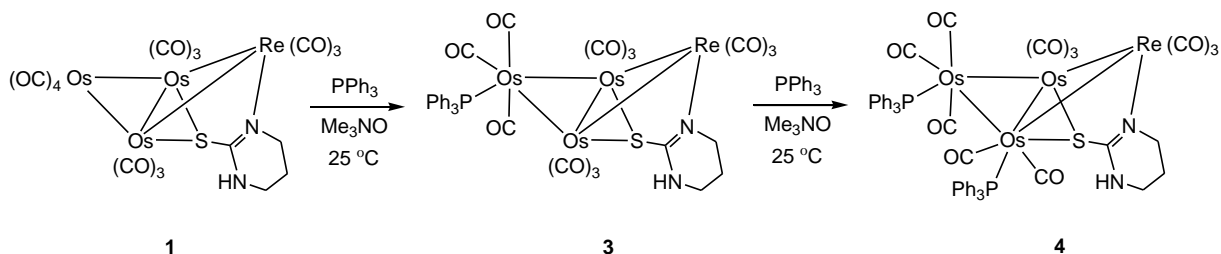
Scheme 2. Reaction of ReOs$_3$(CO)$_{13}$(μ_3-thpymS) (**1**) with PPh$_3$

The mono-phosphine substituted cluster **3** has been characterized structurally together with spectroscopic methods. The solid-state molecular structure of **3** is depicted in Fig. 2 with the captions containing selected bond lengths and angles. The cluster core is made up of four metal atoms, a rhenium and three osmium atoms, in its core making a butterfly skeleton where rhenium occupies a wingtip position. The thpymS ligand is facially located on its convex side in such a way that it is bonded to rhenium using one of the ring nitrogen atoms and bridges the hinge metal atoms through sulfur. The PPh$_3$ ligand occupies one of the equatorial positions of the wingtip osmium as observed in the analogous cluster ReOs$_3$(CO)$_{12}$(PPh$_3$)(μ_3-pyS) (pySH = 2-mercaptopyridine) [13]. The incoming phosphine

ligand usually occupies one of the equatorial positions in $M_3(CO)_{12}$ (M = Os, Ru, Fe) to avoid nonbonding interaction with the axial carbonyls bound to other metal centers at the same face. But in these butterfly clusters, the carbonyls axially bonded to the hinge metals on their convex side had been removed by the bridging sulfur ligand. This factor together with the butterfly arrangement of the metal core makes enough space in these clusters for a phosphine ligand to be axially bound to the wingtip Group 8 metal on their convex side as observed in $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-mbt})$ (mbtH = 2-mercatobenzothiazole) [12] (Chart 1). The triosmium wing of the butterfly in **3** [Os(1)–Os(3) 2.8807(4), Os(2)–Os(3) 2.9165(4), Os(1)–Os(2) 2.7618(3) Å] undergoes small expansion upon phosphine substitution as compared to **1** [Os(1)–Os(3) 2.8596(3), Os(1)–Os(2) 2.8650(3), Os(2)–Os(3) 2.7626(4) Å] due to both steric and electronic reasons as expected, while the rhenium containing wing remains almost unaffected [Re(1)–Os(3) 2.9249(3), Re(1)–Os(2) 2.9307(3) Å for **1**; Re(1)–Os(1) 2.9095(4), Re(1)–Os(2) 2.9591(4) Å for **1**]. The interplanar angle of the butterfly also increases slightly upon phosphine substitution [161.2° in **3**; 159.5° in **1**]. The Os–P bond distance of 2.3821(17) Å is quite similar to that observed in its pyridine-2-thiolate analogue $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-pyS})$ [2.3487(7) Å] [13], but is significantly shorter than that found in $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-mbt})$ [2.496(2) Å] [12] in which the phosphine occupies an axial coordination site on the wingtip osmium. The Re–N [2.201(6) Å] and Os–S [2.3986(16) and 2.4053(17) Å] bond distances are also very similar to those found in the parent cluster **1**.
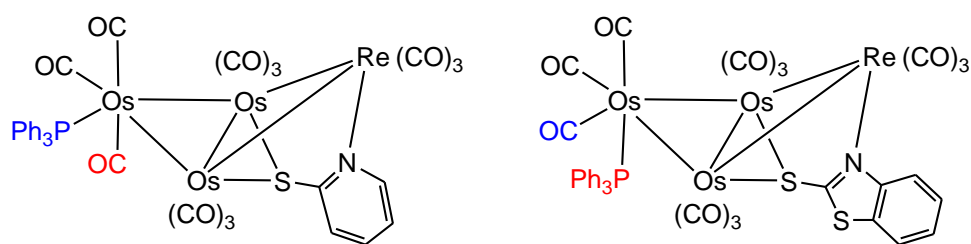
Chart 1. Coordination site occupied by PPh_3 in $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-pyS})$ [13] and $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-mbt})$ [12].

The solid-state structure of **3** persists in solution. The pattern of the IR spectra of **3** is very similar to that reported for analogous $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-pyS})$ [13]. It shows separate sets of resonances in its ^{1}H NMR spectrum for thpymS and PPh_3 ligands. It displays three resonances at δ 4.13, 3.21 and 1.87, each integrates to 2H, in the aliphatic region for the methylene protons of the thpymS ligand and a broad singlet at δ 6.40 integrating to 1H for the

N-H proton of the same ligand. The phenyl protons of the PPh$_3$ ligand appeared as a multiplet centered at δ 7.47 in the aromatic region. Cluster **3** show only a singlet at δ 7.0 in its ^{31}P{^{1}H} NMR spectrum due to the phosphorus of PPh$_3$ ligand which is consistent with the solid-state structure.

Cluster **4** has been characterized by elemental analysis and spectroscopic data since repeated attempts to grow single crystals of this cluster were unsuccessful. The IR spectrum of **4** are very similar to those reported for crystallographically characterized analogous clusters ReOs$_3$(CO)$_{11}$(PPh$_3$)$_2$(µ$_3$-pyS) [13] and ReOs$_3$(CO)$_{11}$(PPh$_3$)$_2$(µ$_3$-mbt) [12] which contains two PPh$_3$ ligands, one bonded to the wingtip osmium and the other coordinated to one of the hinge osmium atoms occupying an equatorial position on each osmium. The ^{1}H NMR spectra display three multiplets in the aliphatic region [δ 4.19, 3.30 and 19.5], each integrating to 2H, and a broad singlet at δ 6.34 integrating to 1H for the methylene and N-H protons of the thpymS ligand respectively. Separate sets of resonances have also been observed in the aromatic region of its ^{1}H NMR spectrum for the phenyl protons of the two PPh$_3$ ligands. Cluster **4** also exhibits two equally intense doublets at δ 10.0 and 6.5 (J 4 Hz) in its ^{31}P{^{1}H} NMR spectrum indicating the presence of two PPh$_3$ ligands. The small J$_{P-H}$ (4 Hz) coupling constant indicates that the PPh$_3$ ligands are bonded to different metal centers which is consistent with the proposed structure.

In contrast, we were able to isolate only the mono-phosphine substituted cluster ReRu$_3$(CO)$_{12}$(PPh$_3$)(µ$_3$-thpymS) (**5**) in 56% yield from a similar reaction between **2** and PPh$_3$. No bis-phosphine substituted tetranuclear butterfly cluster was isolated from this reaction. Cluster **5** has also been characterized by IR and NMR spectroscopic data together with single crystal X-ray diffraction analysis. The solid-state molecular structure of **5** is shown in Fig. 3, selected bond lengths and angles being listed in the caption. Akin to **3**, the cluster contains a butterfly core of four metals, three ruthenium atoms and a rhenium, with rhenium occupying a wingtip position. The location as well as the coordination mode of the thpymS ligand are also similar i.e., it bridges the hinge ruthenium atoms using the sulfur while coordinates to rhenium using one of the ring nitrogen. The PPh$_3$ ligand occupies one of the equatorial positions of the wingtip ruthenium as observed in **4**. The triruthenium wing of the butterfly in **5** [Ru(1)–Ru(2) 2.8971(9), Ru(1)–Ru(3) 2.7551(9), Ru(2)–Ru(3) 2.8647(10) Å] are slightly bigger than that in the parent cluster **2** [Ru(1)–Ru(2) 2.841(1), Ru(1)–Ru(3) 2.760(1), Ru(2)–Ru(3) 2.847(1) Å] [16] which can be explained as a consequences of carbonyl substitution by

phosphine. The interplanar angle of the butterfly in **5** is 161.1° which is slightly greater than that observed in the parent cluster **2** (159.5°) [16] and the Ru–P bond distance of 2.3827(15) Å found in **5** is within the range reported in literature [9,26-28]. The Re–N [2.190(5) Å] and Ru–S [2.3796(16) and 2.3776(16) Å] bond distances are very close to those observed in the parent cluster **2** [Re–N 2.189(7) Å and Ru–S 2.380(3) Å].
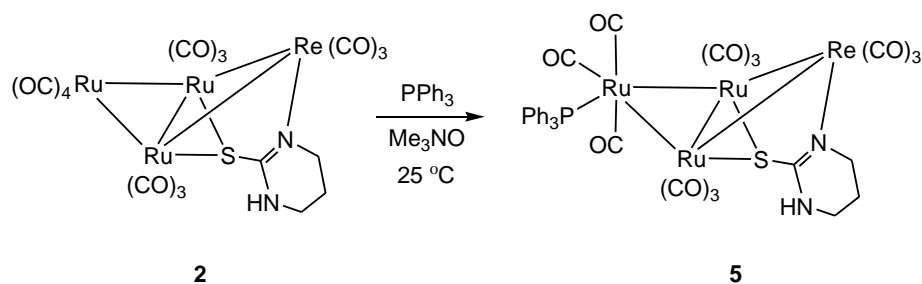
Scheme 3. Reaction of ReRu$_3$(CO)$_{13}$(μ$_3$-thpymS) (**2**) with PPh$_3$

The solution spectrocopic data of **5** indicates that the solid-state structure persists in solution. The ^{1}H NMR spectrum showed three resonances, each integrating to 2H, centered at δ 4.03, 3.36 and 1.94 and a broad singlet at δ 6.51, integrating to 1H, for the methylene and N-H protons of the thpymS ligand, respectively. The spectrum also displays resonances in the aromatic region for the phenyl protons of the PPh$_3$ ligand. In addition, the ^{31}P{^{1}H} NMR spectrum exhibits only a singlet at δ 32.6 due to the phosphorus of PPh$_3$ which is in accord with the solid-state structure.

We also treated **5** with PPh$_3$ under similar conditions in order to obtain the ruthenium analog of **4**, but this resulted in the breakdown of the tetranuclear core. Two products were isolated from that reaction and their IR and NMR spectra were not very informative. Repeated attempts to grow singe crystals of these products were also unsuccessful. However, the ^{1}H and ^{31}P{^{1}H} NMR spectral data shows that none of these products contains two PPh$_3$ ligands as observed in **4**. The interplanar angle of the butterfly observed in **3** (161.2°) and **5** (161.1°) are almost identical, so we may rule out the steric factor for this discrepancy in their reactions with PPh$_3$. The real reason remains obscure from the present study and further works on their reactivity towards phosphines having different steric and electronic properties are currently ongoing in our laboratory to figure out the reason behind this discrepancy.

4. Conclusions

In summary, we have investigated the reactions of two tetranuclear mixed-metal butterfly clusters $ReM_3(CO)_{13}(\mu_3\text{-thpymS})$ (**1**, M = Os; **2**, M = Ru) with PPh_3 in the presence of Me_3NO. Reaction between **1** and PPh_3 afforded two phosphine-substituted clusters $ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-thpymS})$ (**3**) and $ReOs_3(CO)_{11}(PPh_3)_2(\mu_3\text{-thpymS})$ (**4**). In mono-substituted **3**, the incoming PPh_3 ligand occupies one of the equatorial coordination sites of the wingtip osmium, while the second PPh_3 ligand is bound to one of the hinge osmium atoms in bis-substituted **4**. Cluster **3** also reacted with PPh_3 under similar conditions to give **4** which indicates the sequential formation of mono-and bis-phosphine substituted clusters during the reaction. In contrast, a similar reaction between **2** and PPh_3 afforded only the mon-phosphine substituted cluster $ReRu_3(CO)_{12}(PPh_3)(\mu_3\text{-thpymS})$ (**5**). Attempts to synthesize the ruthenium analogue of **4** were unsuccessful which we suggest is due to the breakdown of the tetranuclear core when **5** was treated with PPh_3 under similar conditions.

5. Acknowledgments

6. Supplementary data

CCDC 1818351, CCDC 1818354 and CCDC 1818355 contain supplementary crystallographic data for **1**, **3**, and **5**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 1. Crystal data and structure refinement details for compounds **1**, **3** and **5**

| Compound	1	3	5
Empirical formula	$C_{17}H_7N_2O_{13}Os_3ReS$	$C_{34}H_{22}N_2O_{12}Os_3PReS$	$C_{34}H_{22}N_2O_{12}PReRu_3S$
Formula weight	1236.11	1470.36	1202.97
Temperature (K)	150(1)	150(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71075
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	19.2749(3)	14.4710(5)	14.440(5)
b (Å)	9.29333(15)	16.3007(6)	16.257(5)
c (Å)	13.5639(3)	16.5460(6)	16.557(5)
α (°)	90	90	90
β (°)	90.4718(16)	101.883(4)	101.898(3)
γ (°)	90	90	90
Volume (Å^3)	2429.59(7)	3819.4(2)	3803(2)
Z	4	4	4
Density (calculated) (Mg/m^3)	3.379	2.557	2.101
Absorption coefficient (mm^{-1})	20.760	13.267	4.501
$F(000)$	2184.0	2680.0	2296
Crystal size (mm^3)	$0.24 \times 0.18 \times 0.11$	$0.33 \times 0.26 \times 0.21$	$0.29 \times 0.22 \times 0.18$
Θ range for data collection (°)	3.004 to 25.998	3.025 to 25.996	1.78 to 27.45
Index ranges	$-23 \leq h \leq 22,$	$-16 \leq h \leq 17,$	$-18 \leq h \leq 16,$
	$-11 \leq k \leq 11,$	$-18 \leq k \leq 20,$	$-20 \leq k \leq 11,$
	$-16 \leq l \leq 16$	$-20 \leq l \leq 20$	$-21 \leq l \leq 16$
Reflections collected	25567	36438	12387
Independent reflections [R_{int}]	4776 [$R_{int} = 0.0633$]	7482 [$R_{int} = 0.0575$]	8304 [$R_{int} = 0.0239$]
Data / restraints / parameters	4776 / 0 / 334	12546 / 0 / 487	8304 / 0 / 487
Goodness of fit on F^2	1.113	1.014	1.140
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0273$, $wR_2 = 0.0647$	$R_1 = 0.0320$, $wR_2 = 0.0742$	$R_1 = 0.0380$, $wR_2 = 0.0925$
R indices (all data)	$R_1 = 0.0297$, $wR_2 = 0.0660$	$R_1 = 0.0378$, $wR_2 = 0.0788$	$R_1 = 0.0483$, $wR_2 = 0.1010$
Largest diff. peak and hole (e. Å^{-3})	1.66 and -1.86	1.95 and -2.31	0.67 and -2.21
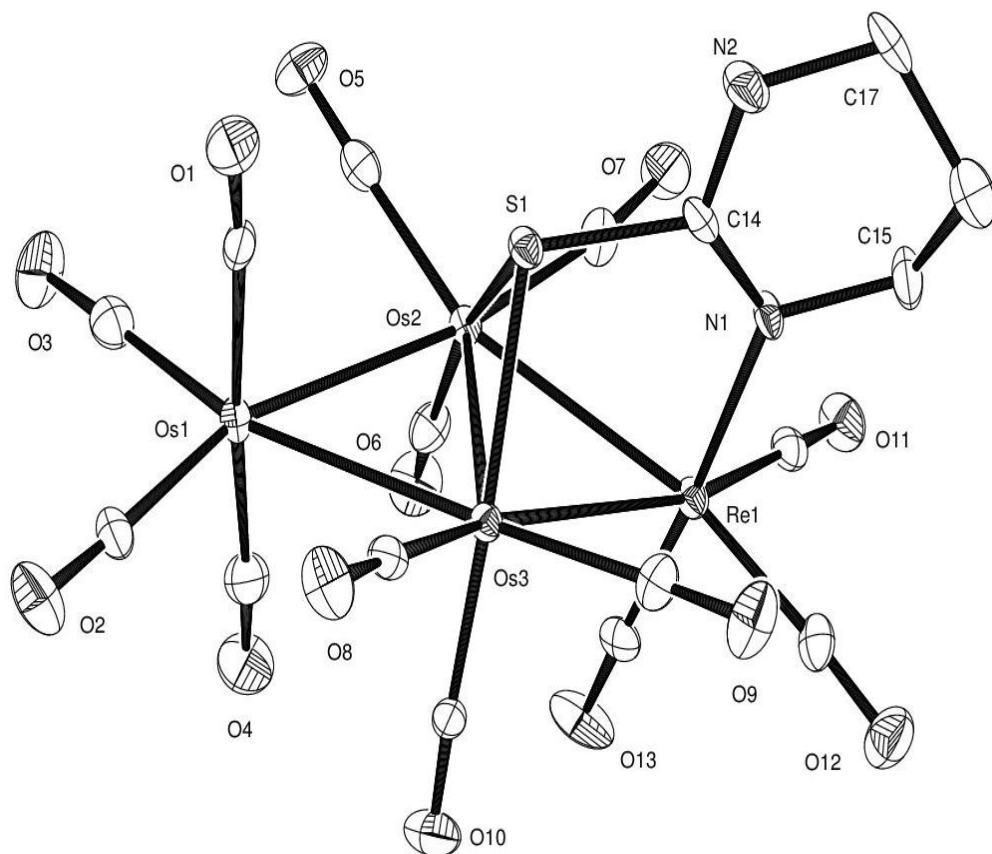
Fig. 1. The solid-state molecular structure of ReOs$_3$(CO)$_{13}$(μ_3-thpymS) (**1**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Os(1)–Os(3) 2.8596(3), Os(1)–Os(2) 2.8650(3), Os(2)–Os(3) 2.7626(4), Re(1)–Os(3) 2.9249(3), Re(1)–Os(2) 2.9307(3), Re(1)–N(1) 2.181(5), Os(2)–S(1) 2.4081(15), Os(3)–S(1) 2.3979(16); N(1)–Re(1)–Os(3) 85.13(13), N(1)–Re(1)–Os(2) 84.72(12), S(1)–Os(2)–Re(1) 81.07(4), S(1)–Os(2)–Os(3) 54.74(4), S(1)–Os(2)–Os(1) 81.78(4), Os(2)–S(1)–Os(3) 70.17(4), Os(3)–Os(1)–Os(2) 57.708(8), Os(3)–Os(2)–Os(1) 61.048(9), Os(2)–Os(3)–Os(1) 61.244(9), Os(3)–Re(1)–Os(2) 56.299(8), Re(1)–Os(2)–Os(1) 119.536(11), Re(1)–Os(2)–Os(3) 61.745(9), Re(1)–Os(3)–Os(1) 119.917(11), Re(1)–Os(3)–Os(2) 61.956(9).
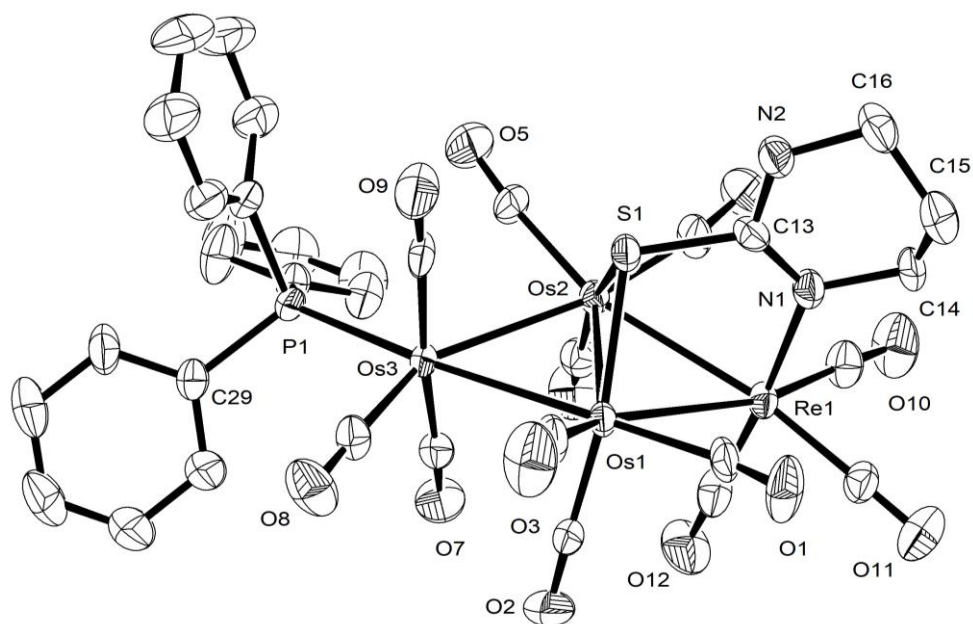
Fig. 2. The solid-state molecular structure of ReOs$_3$(CO)$_{12}$(PPh$_3$)(μ_3-thpymS) (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)–Os(3) 2.8807(4), Os(1)–Os(2) 2.7618(3), Os(2)–Os(3) 2.9165(4), Re(1)–Os(1) 2.9095(4), Re(1)–Os(2) 2.9591(4), Os(3)–P(1) 2.3821(17), Re(1)–N(1) 2.201(6), Os(2)–S(1) 2.4053(17), Os(1)–S(1) 2.3986(16); N(1)–Re(1)–Os(1) 85.12(15), N(1)–Re(1)–Os(2) 85.90(15), Os(1)–Re(1)–Os(2) 56.140(9), Os(3)–Os(1)–Os(2) 62.204(9), S(1)–Os(1)–Re(1) 81.24(4), S(1)–Os(1)–Os(3) 82.02(4), Os(1)–Os(2)–Os(3) 60.897(9), Re(1)–Os(2)–Os(1) 61.021(9), Re(1)–Os(2)–Os(3) 119.193(11), Os(2)–Os(3)–Os(1) 56.898(9), Os(2)–Os(1)–Re(1) 62.839(10), Os(3)–Os(1)–Re(1) 122.141(11), P(1)–Os(3)–Os(2) 117.63(4), P(1)–Os(3)–Os(2) 174.50(4), P(1)–Os(3)–C(8) 91.6(2), P(1)–Os(3)–C(8) 89.4(2).
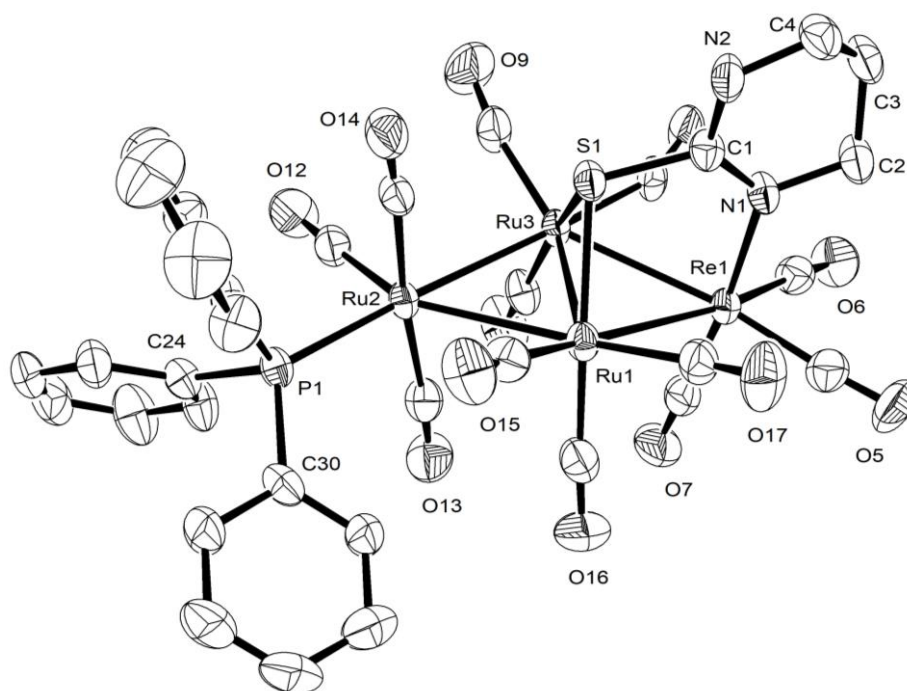
Fig. 3. The solid-state molecular structure of ReRu$_3$(CO)$_{12}$(PPh$_3$)(μ_3-thpymS) (**5**). Hydrogen atoms are omitted for clarity. Selected bond lengths(Å) and angles (°): Ru(1)–Ru(2) 2.8971(9), Ru(1)–Ru(3) 2.7551(9), Ru(2)–Ru(3) 2.8647(10), Re(1)–Ru(1) 2.9437(9), Re(1)–Ru(3) 2.9015(8), Re(1)–N(1) 2.190(5), Ru(1)–S(1) 2.3796(16), Ru(3)–S(1) 2.3776(16), Ru(2)–P(1) 2.3827(15); N(1)–Re(1)–Ru(1) 86.13(11), Ru(3)–Ru(1)–Ru(2) 60.84(2), Ru(3)–Ru(2)–Ru(1) 57.13(2), Ru(1)–Ru(3)–Ru(2) 62.028(16), P(1)–Ru(2)–Ru(3) 176.03(4), Ru(2)–Ru(3)–Re(1) 121.79(2), S(1)–Ru(1)–Ru(3) 54.58(4), S(1)–Ru(1)–Re(1) 80.11(4), Ru(3)–Ru(1)–Re(1) 61.108(16).

References

[1] Selected reviews: (a) R.D. Adams, In *Comprehensive Organometallic Chemistry II*, E.W. Abel, F.G.A. Stone, G. Wilkinson, Eds. Elsevier, Oxford, 1995, Vol. 10, pp 1-22. (b) Y. Chi, D.K. Hwang, In *Comprehensive Organometallic Chemistry II*, E.W. Abel, F.G.A. Stone, G. Wilkinson, Eds. Elsevier, Oxford, 1995, Vol. 10, pp 85-185. (c) P. Braunstein, J. Rosé, In *Comprehensive Organometallic Chemistry II*, E.W. Abel, F.G.A. Stone, G. Wilkinson, Eds. Elsevier, Oxford, 1995, Vol. 10, pp 351-385.

[2] (a) L.H. Gade, *Angew. Chem., Int. Ed. Engl.*, 2000, 39, 2658-2678. (b) M. Herberhold, G.-X. Jin, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, 964-966. (*c*) B. Bosnich, *Inorg. Chem.*, 1999, 38, 2554-2562. (d) S. Liu, G.-X. Jin, *Dalton Trans.*, 2007, 949-954. (*e*) Y.-Q. Chen, J. Zhang, S. Cai, X.-F. Hou, H. Schumann, G.-X. Jin, *J. Chem. Soc., Dalton Trans.*, 2007, 749-758. (f) J. N.L. Dennett, J. Jacke, G. Nilsson, A. Rosborough, M.J. Ferguson, M. Wang, R. McDonald, J. Takats, *Organometallics*, 2004, 23, 4478-4485.

[3] (*a*) R.D. Adams, B. Captain, M.D. Smith, *Angew. Chem. Int. Ed.*, 2006, 45, 1109-1112. (*b*) R.D. Adams, B. Captain, L. Zhu, *Inorg. Chem.*, 2006, 45, 430-436. (c) T. Tanase, R.A. Begum, *Organometallics*, 2001, 20, 106-114. (d) M.M. Dell'Anna, S. J. Trepanier, R. McDonald, M. Cowie, *Organometallics*, 2001, 20, 88-99. (e) P. Mathur, A.K. Das, M. Hossain, C.V.V. Satyanarayana, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, *J. Organomet. Chem.*, 1997, 532, 189-199.

[4] (a) N. T. Lucas, J. P. Blitz, S. Petrie, R. Stranger, M. G. Humphrey, G. A. Health and V. Otieno-Alego, *J. Am. Chem. Soc.*, 2002, 124, 5139-5153; (b) P. Mathur, A.K. Bhunia, S.M. Mobin, V.K. Singh, C. Srinivasu, *Organometallics*, 2004, 23, 3694-3700; (c) J.N. L. Dennett, S.A.R. Knox, K.M. Anderson, J.P.H. Charmant, A.G. Orpen, *J. Chem. Soc., Dalton Trans.*, 2005, 63-73; (d) L. Quebatte, R. Scopelliti, K. Severin, *Angew. Chem., Int. Ed.*, 2004, 43, 1520- 1524.

[5] (a) R.D. Adams, T.S. Barnard, Z. Li, W. Wu, J.H. Yamamato, *J. Am. Chem. Soc.*, 1994, 116, 9103-9113; (b) R.D. Adams, T.S. Barnard, *Organometallics*, 1998, *17*, 2567-2573; (c) R.D. Adams, T.S. Barnard, *Organometallics*, 1998, 17, 2885-2890; (d) A.J. Bridgeman, M.J. Mays, A.D. Woods, *Organometallics*, 2001, 20, 2932-2935.

(6) (a) Y. Ishii, M. Hidai, *Catal. Today*, 2001, *66*, 53-61; (b) S. Gauthier, R. Scopelliti, K. Severin, *Organometallics*, 2004, 23, 3769-3771; (c) P. Braunstein, J. Rosé, In *Catalysis by Di- and Polynuclear Metal Clusters*, R.D. Adams, F. A. Cotton, Eds. Wiley: New York,

1998; pp 443-508; (d) A.M. Trzeciak, J.J. Ziolkowski, *Coord. Chem. Rev.*, 1999, 190-192, 883-900.

[7] (a) P. Kalck, *Polyhedron*, 1988, 7, 2441-2450; (b) E.K. Van den Beuken, B.L. Feringa, *Tetrahedron*, 1998, 54, 12985-13011; (c) P. Braunstein, J. Rosé, In *Metal Clusters in Catalysis*, P. Braunstein, L.A. Oro and P.R. Raithby, Eds.; Wiley-VCH, Weinheim, Germany, 1999, Vol. 2, pp 616-677.

[8] S. Ghosh, S.E. Kabir, S. Pervin, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, H.W. Roesky, *Z. Anorg. Allg. Chem.* 2009, 635, 76-87.

[9] A.K. Raha, S. Ghosh, I. Hossain, S.E. Kabir, B.K. Nicholson, G. Hogarth, L. Salassa, *J. Organomet. Chem.* 2011, 696, 2153-2160.

[10] S. Ghosh, S.E. Kabir, S. Pervin, A.K. Raha, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, L. Salassa, H.W. Roesky, *Dalton Trans.* 2009, 3510-3518.

[11] S.E. Kabir, J. Alam, S. Ghosh, K. Kundu, G. Hogarth, D.A. Tocher, G.M.G. Hossain, H.W. Roesky, *Dalton Trans.* 2009, 4458-4467.

[12] S. Ghosh, K.N. Khanam, M.K. Hossain, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, G. Hogarth, S.E. Kabir, *J. Organomet. Chem.* 2010, 695, 1146-1154.

[13] S. Ghosh, K.N. Khanam, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, G. Hogarth, S.E. Kabir, *New J. Chem.* 2010, 34, 1875-1884.

[14] S. Ghosh, F.K. Camellia, K. Fatema, M.I. Hossain, M.R. Al-Mamun, G.M.G. Hossain, G. Hogarth, S.E. Kabir, *J. Organomet. Chem.* 2011, 696, 2935-2942.

[15] S. Ghosh, M.S.A. Mia, E. Begum, G.M.G. Hossain, S.E. Kabir, *Inorg. Chim. Acta* 2012, 384, 76-82.

[16] M.F. Ahmad, J.C. Sarker, K.A. Azam, S.E. Kabir, S. Ghosh, G. Hogarth, T.A. Siddiquee, M.G. Richmond, *J. Organomet. Chem.* 2013, 728, 30-37.

[17] P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, 29, 169-247.

[18] E. Sappa, A. Tiripicchio, A. J. Carty and G. E. Toogood, *Prog. Inorg. Chem.*, 1987, 35, 437-625, and references therein.

[19] (*a*) A. Sivaramakrishna, H. S. Clayton, B. C. E. Makhubela and J. R. Moss, *Coord. Chem.*, 2008, 252, 1460-1485. (*b*) I. Ojima, Z. Li, R. J. Donovan and P. Ingallina, *Inorg. Chim. Acta*, 1988, 270, 279-284. (c) V. Ferrand, G. Süss-Fink, A. Neels and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1998, 3825-3831.

[20] E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer, *Chem. Rev.*, 1979, 79, 91-137.

[21] CrysAlisPro; Oxford Diffraction: Yarnton, England, 2015.

[22] G.M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr. 64 (2008) 112-122.

[23] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

[24] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.aK. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339-341.

[25] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.

[26] (a) S. Ghosh, S. Rana, D.A. Tocher, G. Hogarth, E. Nordlander, S.E. Kabir, *J. Organomet. Chem.*, 2009, 694, 3312-3319; (b) M. D. H. Sikder, S. Ghosh, S. E. Kabir, G. Hogarth, D. A. Tocher, *Inorg. Chim. Acta*, 2011, 376, 170-174; (c) S. Ghosh, G. Hogarth, S. E. Kabir, E. Nordlander, L. Salassa, D. A. Tocher, *J. Organomet. Chem.*, 2011, 696, 1982-1989; (d) M. M. M. Khan, M. F. Ahmad, S. Rajbangshi, T. A. Siddiquee, S. Ghosh, S. E. Kabir, *Polyhedron* 2015, 101, 103-108.

[27] (a) M. I. Hossain, M. D. H. Sikder, S. Ghosh, S. E. Kabir, G. Hogarth, L. Salassa, *Organometallics* 2012, 31, 2546-2558; (b) M. K. Hossain, S. Rajbangshi, A. Rahaman, M. A. H. Chowdhury, T. A. Siddiquee, S. Ghosh, M. G. Richmond, E. Nordlander, G. Hogarth, S. E. Kabir, *J. Organomet. Chem.* 2014, 760, 231-239; (c) M. J. Hossain, S. Rajbangshi, M. M. M. Khan, S. Ghosh, G. Hogarth, E. Rosenberg, K. I. Hardcastle, M. G. Richmond, S. E. Kabir, *J. Organomet. Chem.* 2014, 767, 185-195.

[28] (a) M. M. Uddin, N. Begum, S. Ghosh, J. C. Sarker, D. A. Tocher, G. Hogarth, M. G. Richmond, E. Nordlander, S. E. Kabir, *J. Organomet. Chem.* 2016, 812, 197-206; (b) M. M. M. Khan, S. Ghosh, A. Rahaman, D. A. Tocher, M. G. Richmond, S. E. Kabir, *J. Organomet. Chem.* 2017, 843, 75-86; (c) S. Rajbangshi, S. Ghosh, G. Hogarth, S. E. Kabir, *J. Clust. Sci.* 2015, 26, 169-185.

Graphical Abstract

Investigation on the reactivity of tetranuclear Group 7/8 mixed-metal clusters toward triphenylphosphine

Md. Rassel Moni, Md. Jadu Mia, Shishir Ghosh, Derek A. Tocher, Shaikh M. Mobin, Tasneem A. Siddiquee, Shariff E. Kabir

The reactions of two tetranuclear mixed-metal clusters, $ReM_3(CO)_{13}(\mu_3\text{-thpymS})$ (M = Os, Ru), with PPh_3 have been investigated.