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Syntheses and Study of Microwave-Induced Production of
Novel Triosmium Carbonyl Complexes with Multiple
Bis(diphenylphosphino)methane Ligands

An Honors College Project Thesis

Presented to

The Department of Chemistry and Biochemistry

Abilene Christian University

In Partial Fulfillment

Of the Requirements for

Honors Scholar

by

Soo Hun Yoon

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This Project Thesis, directed and approved by the candidate's committee,
has been accepted by the Honors College of Abilene Christian University
in partial fulfillment of the requirements for the distinction

HONORS SCHOLAR

Dr. Jason Morris, Dean of the Honors College

Date

Advisory Committee

Dr. Gregory Powell, Committee Chair

Dr. Cynthia Powell, Committee Member

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Dr. Kim Pamplin, Department Head

Abstract

New triosmium carbonyl complexes containing multiple bis(diphenylphosphino)methane (dppm) ligands were synthesized via reactions of $\text{Os}_3(\text{CO})_{12}$ with excess dppm under microwave irradiation. The new complexes have been characterized by IR, NMR, mass spectrometry, and X-ray crystallography. Three of the four complexes produced, $\text{Os}_3(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})[\mu_3\text{-Ph}_2\text{PCHP}(\text{C}_6\text{H}_4)\text{Ph}]$ (**2**), $\text{Os}_3(\text{CO})_6[\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}]_2$ (**3**), and $\text{Os}_3(\mu\text{-H})(\text{CO})_6[\mu_3\text{-PhPCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}][\mu_3\text{-PhPCH}(\text{C}_6\text{H}_4)\text{PPh}]$ (**4**), contain two dppm ligands in a triosmium cluster, while the fourth, $\text{Os}_3(\mu\text{-H})(\text{CO})_5(\text{dppm})[\mu_3\text{-PhPCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}][\mu_3\text{-PhPCH}(\text{C}_6\text{H}_4)\text{PPh}]$ (**5**), contain three dppm ligands, the first of its kind. All of the new complexes contain at least one dppm ligand which underwent C–H and/or C–P bond activation. Complex **2** is a 48e cluster containing two dppm ligands, one intact and one that spans all three osmium sites through a phosphorous atom and the cyclometalated and ortho-metalated carbon atoms. Complex **3** in contrast, is a 46e cluster with two ortho-metalated dppm ligands. Complexes **4** and **5** are 50e clusters with similar metallic framework containing one cyclometalated dppm ligand and one ortho-metalated dppm ligand.

1. Introduction

Triosmium carbonyl is a metal cluster, a compound containing metal to metal bonds. Due to its stability in air and moisture, it is a good candidate to produce metal complexes, which are compounds that contain ligands attached to metal atoms. Ligands are ions or molecules that form coordinate covalent bonds to metals by providing both of the electrons required for each bond. If one molecule or ion forms multiple bonds to the same metal atom, then it is referred to as a chelating ligand. If it bonds to multiple metal atoms, then it is called a bridging ligand.

The bidentate diphosphine ligand, bis(diphenylphosphino)methane (dppm), has frequently been used in metal cluster chemistry because it is able to either chelate or bridge the metal atoms. Past studies have successfully reacted $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ with dppm ligands to yield clusters chelated by varying numbers of dppm ligands [1,2]. These reactions have been a subject of interest due to the possibility of studying various reactions such as ortho-metalation, cyclometalation, and reductive elimination, along with C-H and C-P bond activation, as a result of the close proximity and reaction of dppm ligands to multiple metal binding sites within the cluster [1]. Additionally, the dppm ligand is able to maintain the trimetal cluster intact through intramolecular phospho-bridges, with potential use in stoichiometric and catalytic reactions [1].

The reaction of $\text{Os}_3(\text{CO})_{12}$ with dppm yielded triosmium metal complexes containing one or two chelating dppm ligands such as $\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})$, $\text{Os}_3(\text{CO})_9(\mu\text{-dppm})(\mu^1\text{-dppm})$, and $\text{Os}_3(\text{CO})_8(\mu\text{-dppm})_2$ (**1**) [3,4]. Although the $\text{Ru}_3(\text{CO})_{10}(\mu\text{-dppm})$, $\text{Ru}_3(\text{CO})_8(\mu\text{-dppm})_2$, and $\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})$ complexes have been extensively investigated and characterized [2], the reactivity of **1**, the bis-dppm osmium complex, has

only been explored once involving protonation by trifluoroacetic acid [1]. Ruthenium clusters containing three dppm ligands have also been synthesized, but no clusters of osmium, which is in the same chemical family as ruthenium, containing three or more dppm ligands have been reported [5].

Many recent studies have shown microwave heating to be an efficient system for producing various osmium carbonyl complexes [6-11]. Thus, in pursuit of a tris-dppm osmium cluster, $\text{Os}_3(\text{CO})_{12}$ was reacted with excess dppm in various solvents under microwave heating. The majority of the products contained two dppm ligands, as well as hydride ligands (H^-) formed from the cleavage of C-H bonds. In addition to efforts to synthesize triosmium clusters containing three dppm ligands, attempts were made to optimize the production of **1** using microwave heating and to study the thermolysis of **1**.

2. Experimental

2.1. Materials and Methods

All syntheses were carried out in a Discover-SP monomode microwave reactor (2455MHz, CEM Corp., Matthew, NC). Reagents, along with a magnetic stir bar, were placed in a 35-mL glass vessel and sealed with a PTFE-lined cap before being placed in the reactor. All chemical manipulations were carried out under a highly efficient fume hood due to the toxicity of CO and metal carbonyl compounds. A maximum pressure setting of 300 psi and maximum power setting of 300 watts were used for all reactions. The fume hood sash was lowered during, and a few minutes after reactions, as a precaution for reactions under pressure. Os₃(CO)₁₂ was prepared by the carbonylation of OsO₄ following a published procedure [11]. Bis(diphenylphosphino)methane (dppm) was purchased from Strem. 1,2-dichlorobenzene was purchased from Sigma-Aldrich, while other solvents were obtained from Pharmco-Asper. All reagents purchased were used as received. Preparative thin-layer chromatography (TLC) was performed on Analtech silica gel 60 (0.50 mm) plates. Infrared spectroscopy was carried out in a Nicolet Avatar 320 FT-IR spectrometer with a CaF₂ solution cell. The ESI mass spectra were collected in the positive ion mode at the University of North Texas (UNT) mass spectrometry facility, with all samples run in acetonitrile (MeCN) with added KI as the carrier matrix. X-ray crystallography data was obtained at UNT. Elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, GA.

2.2. Synthesis of $Os_3(CO)_8(dppm)_2$ (**1**)

$Os_3(CO)_{12}$ (74.8 mg, 0.0825 mmol) and excess dppm (66.6 mg, 0.1732 mmol) were collected in a microwave reaction vessel along with 7.0 mL of 1,2-dichlorobenzene. The mixture was heated and stirred in the microwave reactor at 170°C for 5 minutes, resulting in an orange solution. The solvent was removed via evaporation. The resulting residue was redissolved in CH_2Cl_2 before TLC separation in an eluent of 1.8:1 hexanes/ CH_2Cl_2 , which produced three bands. The top band ($R_f = 0.83$) consisted of 1.1 mg of unreacted $Os_3(CO)_{12}$. IR (ν_{CO} , $CHCl_3$): 2068(s), 2034(vs), 2015(m), and 2000(w) cm^{-1} . Band 2 ($R_f = 0.37$) consisted of 1.4 mg (1.4% yield) of $Os_3(CO)_{10}(dppm)$. IR (ν_{CO} , $CHCl_3$): 2091(w), 2065(vw), 2028(m), 2011(vs), and 1958(m) cm^{-1} . Band 3 ($R_f = 0.15$) consisted of 109 mg (84.5% yield) of yellow cluster **1**. IR (ν_{CO} , $CHCl_3$): 2048(m), 1994(m), 1964(vs), 1942(m), and 1895(w) cm^{-1} . This compound was confirmed by growing single crystals and determining that the unit cell matched the previously reported values.

2.3. Synthesis of $Os_3(\mu-H)_2(CO)_6(\mu-dppm)[\mu_3-Ph_2PCHP(C_6H_4)Ph]$ (**2**) and $Os_3(CO)_6[\mu_2-Ph_2PCH_2P(C_6H_4)Ph]_2$ (**3**)

$Os_3(CO)_{12}$ (60.1 mg, 0.0663 mmol) and dppm (58.3 mg, 0.152 mmol) were added to 6.0 mL of ethanol (EtOH) in a microwave reaction vessel. This mixture was stirred and irradiated for 6 minutes at 160°C in the microwave reactor. The resulting solution was a cloudy yellow mixture. The solvent was removed by rotary evaporation. The remaining residue was dissolved in CH_2Cl_2 and differentiated by TLC using an eluent of 1.8:1 hexanes/ CH_2Cl_2 . Three major bands were collected. Band 1 ($R_f = 0.38$) consisted of 54.6 mg (54.6% yield) of bright yellow **2**. IR (ν_{CO} , $CHCl_3$): 2054(w), 2011(sh), 1998(vs),

1977(s), 1935(m), 1919(sh) cm^{-1} . Anal. Calc. for crystals with two molecules of CH_2Cl_2 per Os_3 molecule: $\text{C}_{58}\text{H}_{48}\text{O}_6\text{P}_4\text{Cl}_4\text{Os}_3$: C, 41.53; H, 2.88%. Found: C, 41.17; H, 3.02%. MS for $[\mathbf{2}+\text{K}^+]$: m/z calculated 1546.63, found 1546.93. Band 2 ($R_f = 0.28$) afforded 22.1 mg (22.1% yield) of yellow **3**. IR (ν_{CO} , CHCl_3): 2048(w), 2009(w, sh), 1975(vs), 1943(w), 1932(w) cm^{-1} . Anal. Calc. for $\text{C}_{56}\text{H}_{42}\text{O}_6\text{P}_4\text{Os}_3$: C, 44.67; H, 2.81%. Found: C, 43.93; H, 2.84%. MS for $[\mathbf{3}+\text{K}^+]$: m/z calculated for 1547.04, found 1548.80. Band 3 ($R_f = 0.20$) consisted of 11.4 mg (11.0% yield) of $\text{Os}_3(\text{CO})_8(\text{dppm})_2$ (**1**).

2.4. Synthesis of $\text{Os}_3(\mu\text{-H})(\text{CO})_6[\mu_3\text{-PhPCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}][\mu_3\text{-PhPCH}(\text{C}_6\text{H}_4)\text{PPh}]$ (**4**)

$\text{Os}_3(\text{CO})_{12}$ (158.6 mg, 0.1749 mmol) and an excess of dppm (141.4 mg, 0.3678 mmol) were placed along with 8.0 mL of 1,2-dichlorobenzene in a microwave reaction vessel. This mixture was irradiated with stirring for 2 minutes at 120 °C in the microwave reactor, and then without stirring for 10 minutes at 175 °C. The resulting solution was brown. The solvent was removed and the residue was dissolved in CH_2Cl_2 before TLC separation. A 1.3:1 hexanes/ CH_2Cl_2 eluent was used which resulted in four visible bands. Band 1, red, ($R_f = 0.49$) consisted of 5.9 mg of an unknown compound. IR (ν_{CO} , CHCl_3): 2074(w), 2050(m), 2029(m), 2015(m), 1992(s), 1965(m), 1939(m) cm^{-1} . Band 2, dark yellow ($R_f = 0.44$) consisted of 92.6 mg (38.4%) of cluster **4**. IR (ν_{CO} , CHCl_3): 2050(s), 2030(vs), 1991(vs), 1968(s), 1937(m) cm^{-1} . Anal. Calc. for $\text{C}_{45}\text{H}_{32}\text{O}_7\text{P}_4\text{Os}_3$: C, 39.18; H, 2.34%. Found: C, 38.77; H, 2.36%. $[\mathbf{4}+\text{H}^+]$: m/z calculated for 1272.98, found 1273.16. The other bands were too small for complete characterization.

2.5. *Synthesis of $Os_3(\mu-H)(CO)_5(dppm)[\mu_2-PhPCH_2P(C_6H_4)Ph][\mu_2-PhPCH(C_6H_4)PPh]$ (5)*

$Os_3(CO)_{12}$ (89.0 mg, 0.0981 mmol) and dppm (301.8 mg, 0.785 mmol) were added along with 8.0 mL of 1,2-dichlorobenzene into a reaction vessel. This mixture was irradiated and stirred in the microwave reactor for 15 minutes at 205 °C. A dark orange solution formed. The solvent was removed, and the residue was redissolved in CH_2Cl_2 and separated by TLC using an eluent of 1:1 hexanes/ CH_2Cl_2 . Three bands were collected. The top band ($R_f = 0.53$) consisted of 74.7 mg (44.6%) of cluster **5**. IR (ν_{CO} , $CHCl_3$): 1997(sh), 1980(vs), 1948(s), 1920(m), and 1893(sh) cm^{-1} . Anal. Calc. for $C_{68}H_{54}O_5Os_3P_6 \cdot C_6H_{14}$: C, 49.55; H, 3.82%. Found: C, 49.56; H, 3.63%. The contents of the other bands were too small for complete characterization.

2.6. *Conversion of $Os_3(CO)_8(dppm)_2$ (1) to $Os_3(\mu-H)_2(CO)_6(\mu-dppm)[\mu_3-Ph_2PCHP(C_6H_4)Ph]$ (2)*

$Os_3(CO)_8(dppm)_2$ (**1**) (10 mg, 0.0064 mmol), along with 2.0 mL of EtOH, were placed in a 10 mL reaction vessel. The combination was stirred and heated in the microwave reactor for 8 minutes at 150 °C. This produced a cloudy yellow solution. The solvent was allowed to evaporate, and the residue was dissolved in CH_2Cl_2 and separated by TLC with an eluent of 1:1 hexanes/ CH_2Cl_2 . The only visible band besides the baseline consisted of 7.2 mg (75% yield) of cluster **2**. In a similar experiment, a 30.1 mg sample of **1** was placed in a 35-mL reaction vessel with 8.0 mL of diglyme. Microwave irradiation at 185°C for 5 minutes resulted in 22.1 mg (76.2% yield) of **2**. Refluxing **1** in toluene for 90 minutes resulted in no change in yields.

2.7. Reactions in acetonitrile/water

In order to determine whether the presence of water had any effect on the overall reaction, Os₃(CO)₁₂ (62.3 mg, 0.0687 mmol) and excess dppm (60.7 mg, 0.158 mmol) were added to a mixture of 5.0 mL of MeCN and 1.0 mL of distilled water in a reaction vessel. The mixture was irradiated and stirred for 5 minutes at 165 °C. Separation by TLC of the resulting solution, after the removal of solvent and dissolution in CH₂Cl₂, resulted in 47.6 mg (46.0% yield) of **2**, 22.7 mg (21.9% yield) of **3**, and 1.4 mg (1.5% yield) of **4**.

2.8. Reactions in butanols

In an attempt to determine the effect of a different solvent on the reaction, mixtures of Os₃(CO)₁₂ and dppm were heated in various butanols. Os₃(CO)₁₂ (61.0 mg, 0.0673 mmol) and dppm (60.9 mg, 0.158 mmol) were added to a reaction vessel with 6.0 mL of *n*-butanol. The mixture was irradiated and stirred in the microwave reactor for 7 minutes at 195 °C. TLC was carried out using an eluent of 1:1.2 hexanes/CH₂Cl₂ to yield 52.1 mg (51.4%) of **2**, 5.2 mg (5.6%) of cluster **4**, and 3.6 mg (3.1%) of cluster **5**.

Another reaction involved the irradiation of Os₃(CO)₁₂ (72.1 mg, 0.0795 mmol) and dppm (72.2 mg, 0.188 mmol) in 6.0 mL of *tert*-butanol at 175°C for 7 minutes. TLC was performed to isolate bands which yielded 59.6 mg (49.7%) of **2**, 25.3 mg (21.2%) of **3**, and 5.9 mg (4.3%) of **5**.

2.9. X-ray crystallography

Single crystals of **2**, **3**, and **5** suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into CH₂Cl₂ solutions of the complexes. Single crystals of **4** were obtained by partial evaporation of a CH₂Cl₂/hexane solution. The reported crystal structure determinations were carried out by Dr. Vladimir Nesterov at the University of North Texas.

3. Results and Discussion

3.1. Microwave Syntheses

Microwave irradiation proved to be a more efficient method than conventional heating for the synthesis of $\text{Os}_3(\text{CO})_8(\text{dppm})_2$ (**1**). Previous investigations reported a 14% yield of cluster **1** prepared by direct reaction of $\text{Os}_3(\text{CO})_{12}$ with dppm ligands in refluxing toluene for 8 hours [2], and a 68% yield (50% yield based on $\text{Os}_3(\text{CO})_{12}$) produced by heating $\text{Os}_3(\text{CO})_{10}(\text{dppm})$ with additional dppm in refluxing toluene for 2 hours [3]. In comparison, our method using microwave irradiation produced cluster **1** in 85% yield by heating $\text{Os}_3(\text{CO})_{12}$ with excess dppm for only 5 minutes at 170°C in 1,2-dichlorobenzene.

3.2. Syntheses of complexes 2-5

$\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3$ has been prepared previously in 77% yield by refluxing a 3.1:1 mixture of dppm and $\text{Ru}_3(\text{CO})_{12}$ in toluene [2]. Even though ruthenium and osmium are in the same chemical group, it is well known that $\text{Ru}_3(\text{CO})_{12}$ is much more reactive than $\text{Os}_3(\text{CO})_{12}$. Attempts were made to produce the osmium analog, $\text{Os}_3(\text{CO})_6(\mu\text{-dppm})_3$, which has not yet been synthesized, by reactions of $\text{Os}_3(\text{CO})_{12}$ with three or more mole equivalents of dppm. The reactions were carried out in a variety of solvents at temperatures above their normal boiling points, however this resulted in the preparation of complexes **2-5**. Complexes **2-4** contain two dppm ligands while cluster **5** is the only triosmium carbonyl cluster that contains three dppm ligands. The reactions that led to the highest yields of clusters **2-5** are reported in the experimental section. These are summarized in Table 1.

Many additional reactions were carried out in different solvents with dppm/Os₃(CO)₁₂ ratios of 3:1, 4:1 and 6:1 and with temperatures in the range 160–205 °C, but these resulted in somewhat lower yields of 2–5. The solvent appears to make only a slight difference in the product distribution. Moreover, the decomposition to intractable solids increased with higher temperatures. It is worth noting that cluster **4** is produced in double-digit yield only when the reaction mixture is not stirred, and that cluster **5** is formed in reasonable yield only when a large excess of dppm is used with stirring.

Table 1. Summary of reaction conditions and yields for the syntheses of **1-5**.

| Os ₃ /dppm Ratio | Solvent | Temp. (°C) | Time (min.) | Percent yield of cluster complexes | | | | |
|-----------------------------|-----------------------|------------|-------------|------------------------------------|----------|----------|----------|----------|
| | | | | 1 | 2 | 3 | 4 | 5 |
| 1:2.1 | DCB* | 170 | 5 | 85% | - | - | - | - |
| 1:2.1 | DCB (no stir) | 175 | 10 | - | - | - | 38% | - |
| 1:2.3 | DCB (no stir) | 190 | 5 | - | 43% | 19% | 21% | - |
| 1:8 | DCB | 205 | 15 | - | - | - | - | 45% |
| 1:2.3 | EtOH | 160 | 6 | 11% | 55% | 22% | - | - |
| 1:2.3 | MeCN/H ₂ O | 165 | 5 | - | 46% | 22% | 2% | - |
| 1:2.4 | <i>t</i> -BuOH | 175 | 7 | - | 50% | 21% | - | 4% |
| 1:2.4 | <i>n</i> -BuOH | 195 | 7 | - | 51% | - | 6% | 3% |

* DCB = 1,2-dichlorobenzene

3.3. X-ray diffraction structures

Figure 1 illustrates the structure of Os₃(μ-H)₂(CO)₆(μ-dppm)[μ₃-Ph₂PCHP(C₆H₄)Ph] (**2**). During the conversion of Os₃(μ-dppm)₂(CO)₈ (**1**) into **2**, one dppm ligand remains unchanged while the other ligand undergoes ortho-metalation and cyclometalation. It loses two H atoms in the process which end up as hydride ligands. All of the phosphorus atoms have moved from equatorial positions in cluster **1** to axial

positions in cluster **2** resulting in each P atom being *trans* to another P atom. The hydride-bridged Os–Os bonds in **1** are on average 0.05 Å longer than the non-hydride-bridged Os–Os metal bond. The activated dppm ligand in **1** functions as a 6e donor ligand and also caps one of the two triangular metal faces.

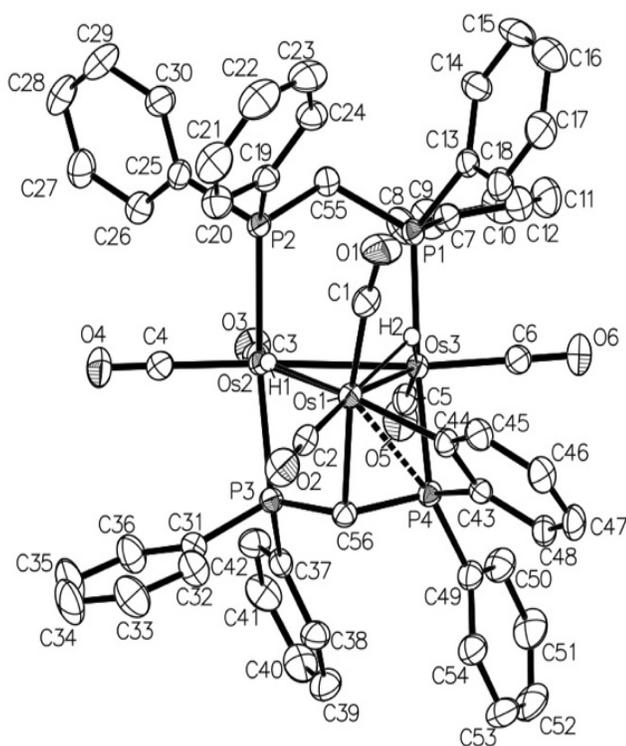


Figure 1. Thermal ellipsoid plot of the molecular structure of **2** at the 50% probability level.

In cluster **2** there is a close contact (shown as a dashed line in Fig. 1) between one osmium atom, Os(1), and the phosphorus atom bound to both the cyclometalated methine group and the ortho-metalated phenyl group, P(4). The distance between Os(1) and P(4) is 2.861(1) Å, while the average lengths of the other four Os–P bonds are 2.357(5) Å. These

observations along with comparison to similar structures previously reported, indicate that this is simply a consequence of the structurally imposed geometries of the ortho-metalated/cyclometalated dppm ligands in these complexes. Select bond distances from x-ray diffraction structures are reported in Table 2.

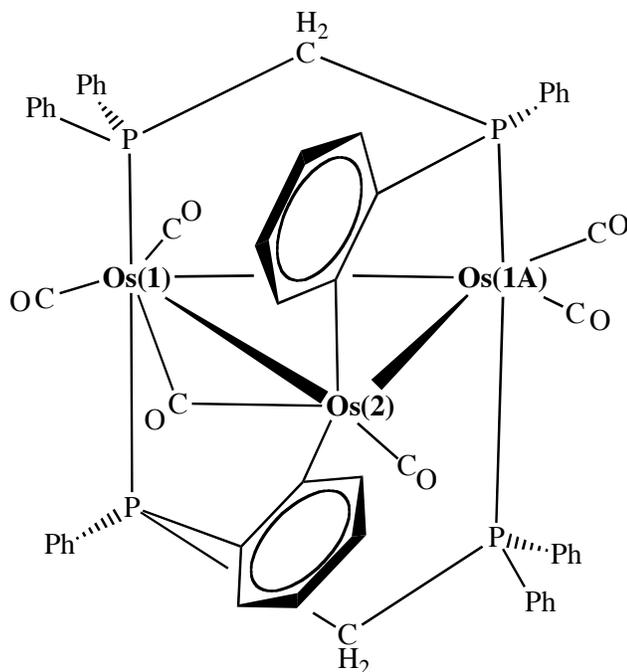


Figure 2. Illustration of the molecular structure of **3**.

Multiple attempts were made to characterize $\text{Os}_3(\text{CO})_6[\mu_3\text{-Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}]_2$ (**3**) by X-ray crystallography. However, the crystals grown displayed poor quality, and the R-values were in excess of 12%. While the attempts to grow high-quality crystals of **3** were not successful, all the crystals displayed a common disorder of the Os_3 triangle involving a skewed position adjacent to a 2-fold axis that bisects the $\text{Os}(1)\text{--Os}(1\text{A})$ bond. Despite the disorder, it is clear that both dppm ligands have undergone C–H bond cleavage to give phenyl groups that are ortho-metalated to the same Os atom. Moreover, all P atoms take

on axial positions. An illustration of the molecular structure is depicted in Figure 2. The diffraction data give the appearance of two Os(2) atoms in proximity to one another, sharing two bridging CO ligands. However, there is only one Os(2) atom that is bound to two CO ligands. One of the CO groups functions as a bridging ligand and asymmetrically spans one of the two Os–Os vectors that contains the doubly metalated Os center. The structure appears to contain 46e and is formally unsaturated, possibly due to the steric congestion associated with the face-capping $\text{Ph}_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}$ ligands.

The molecular structures of $\text{Os}_3(\mu\text{-H})(\text{CO})_7[\mu_3\text{-PhPCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}][\mu_3\text{-PhPCH}(\text{C}_6\text{H}_4)\text{PPh}]$ (**4**) and $\text{Os}_3(\mu\text{-H})(\text{CO})_5(\text{dppm})[\mu_2\text{-PhPCH}_2\text{P}(\text{C}_6\text{H}_4)\text{Ph}][\mu_3\text{-PhPCH}(\text{C}_6\text{H}_4)\text{PPh}]$ (**5**) are illustrated in Figures 3 and 4, respectively. These structures were determined to be 50e clusters containing only two Os–Os bonds each. In both clusters **4** and **5**, the hydride-bridged Os–Os bond length is very long at 3.1957(4) and 3.2494(4) Å, respectively, while the non-hydride-bridged Os–Os bond length is shorter at 2.9066(4) and 2.9886(4) Å, respectively. In both clusters **4** and **5**, one dppm ligand, which has lost a phenyl group and two hydrogen atoms, is cyclometalated through the methylene group and contains an *o*-phenylene group bridging the two P atoms. Another dppm ligand which lost a phenyl group and one hydrogen atom, is ortho-metalated through one phenyl group and contains a phenylphosphido group bridging two Os atoms. Cluster **5**, however, contains a third intact dppm ligand that is chelated instead of bridged. This molecule is the first example of an Os_3 carbonyl cluster with three dppm ligands. Both clusters contain a phosphido ligand that serves to tether the non-bonding Os(1) and Os(2) centers in **4** and the Os(2) and Os(3) centers in **5**.

Due to distortions of the Os_3 resulting from bridging phosphido group, it is difficult to assign axial and equatorial positions to the phosphorus atoms in **4** and **5**. In cluster **4**, the two P atoms bonded to Os(1) are *cis* to each other, while the two P atoms bonded to Os(3) are *trans* to each other. In cluster **5**, there are two *cis* P atoms on Os(2) and two *trans* P atoms on Os(1), while the three P atoms on Os(3) are in both *cis* and *trans* orientations. Clusters **4** and **5** have remarkably similar core geometries as illustrated in Figure 5. The only significant differences are the position of the hydride ligand, the associated shifting of CO ligands to accommodate the hydride ligand, and the substitution of two *cis* CO ligands in **4** for one chelating dppm ligand in **5**.

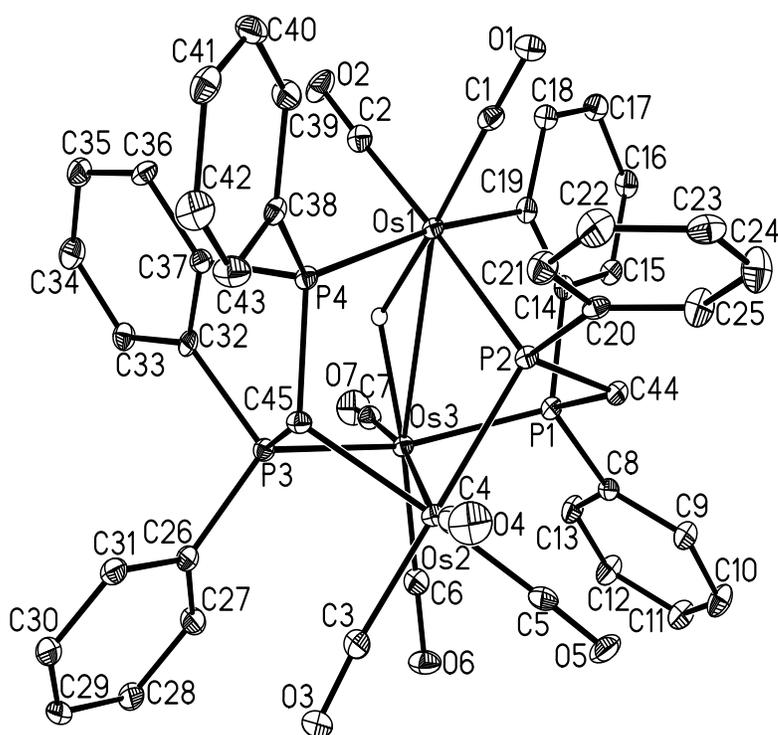


Figure 3. Thermal ellipsoid plot of the molecular structure of **4** at the 50% probability level.

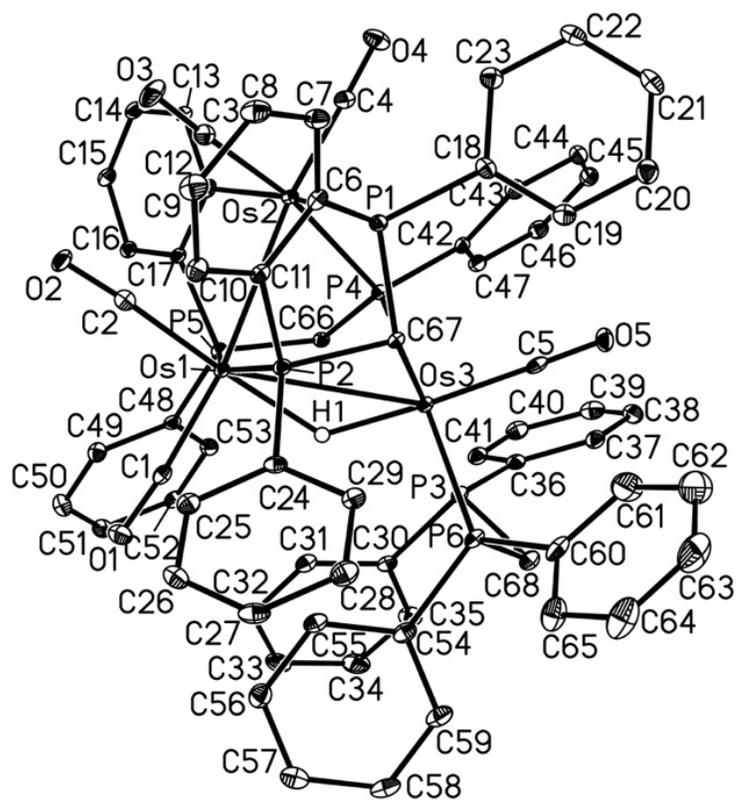
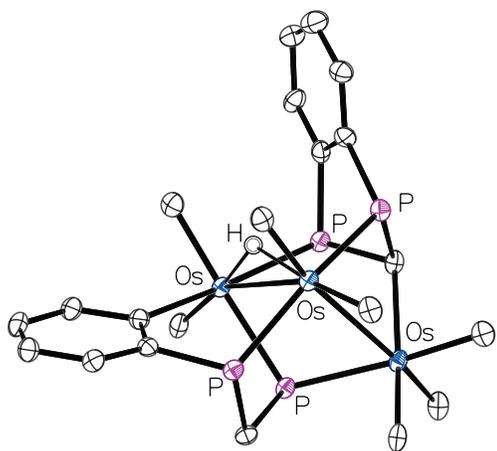
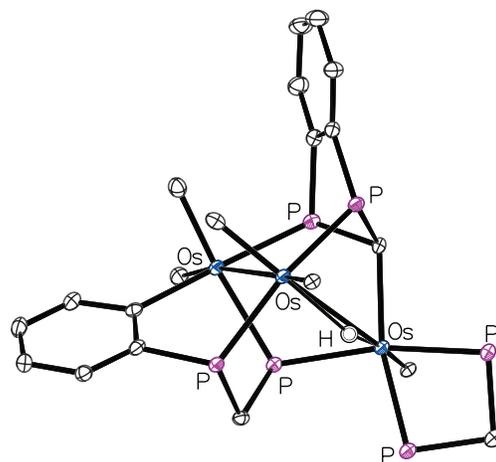


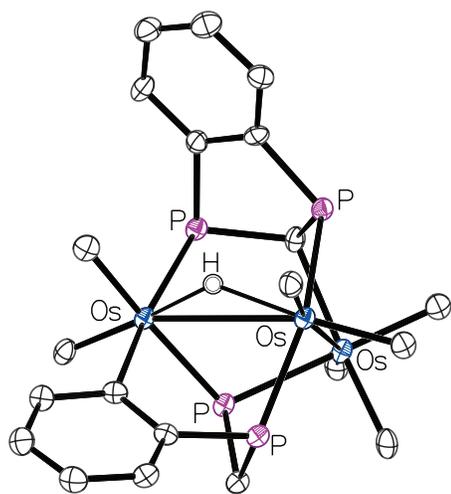
Figure 4. Thermal ellipsoid plot of the molecular structure of **5** at the 50% probability level.



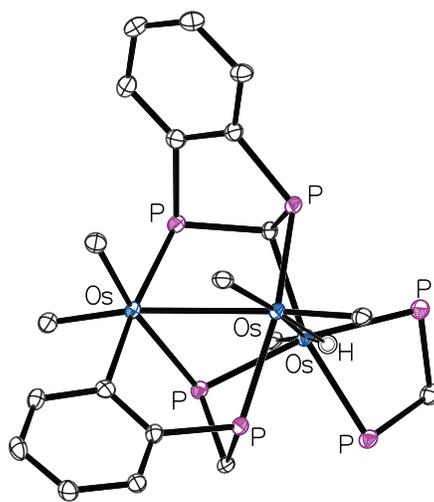
4a



5a



4b



5b

Figure 5. Similarities of the coordination geometries of **4** and **5**. Two views (**a** and **b**) of the central portion of each cluster are shown.

Table 2. Select Bond Distances (Angstroms [\AA]) from X-ray Diffraction Structures.

| Bonds/Clusters | 2 | 4 | 5 |
|-----------------------|-----------|-----------|-----------|
| Os(1)-Os(2) | 3.0147(4) | - | 2.9886(4) |
| Os(1)-Os(3) | 3.0409(3) | 3.1957(4) | 3.2496(4) |
| Os(2)-Os(3) | 2.9788(4) | 2.9066(4) | - |
| Os(1)-P(2) | - | 2.407(2) | 2.3430(9) |
| Os(1)···P(4) | 2.8608(9) | - | - |
| Os(1)-P(4) | - | 2.375(2) | - |
| Os(1)-P(5) | - | - | 2.3420(9) |
| Os(2)-P(1) | - | - | 2.3648(9) |
| Os(2)-P(2) | 2.3540(9) | 2.409(2) | - |
| Os(2)-P(3) | 2.347(1) | - | - |
| Os(2)-P(4) | - | - | 2.3971(8) |
| Os(3)-P(1) | 2.364(1) | 2.349(2) | - |
| Os(3)-P(3) | - | 2.335(2) | 2.3506(9) |
| Os(3)-P(4) | 2.364(1) | - | 2.3940(8) |
| Os(3)-P(6) | - | - | 2.3972(9) |

3.4. *Effect of water*

Attempts to determine the effects of water on our reactions were made, as all procedures were carried out in the presence of air, not excluding moisture. The synthesis of **1** described in section 2.2 was repeated with the addition of 0.5 mL of distilled water to the reaction mixture. The resulting yield was 82%, which was slightly lower than the 85% yield obtained without water. Slightly larger amounts of unreacted $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{10}(\text{dppm})$ were also seen with the addition of water. In a separate study described in section 2.7, a mixture of acetonitrile and water was used as the reaction medium. This produced clusters **2** and **3** in good yields, and a small amount of **4**. When this experiment was repeated under N_2 with freshly distilled anhydrous acetonitrile as the solvent, excluding water, it resulted in an almost identical distribution of products. Thus moisture has no significant effects on the outcome of these reactions.

3.5. *Comparison of analogous ruthenium and osmium metal clusters containing multiple dppm ligands.*

The thermolysis of **1**, as described in section 2.6, resulted in a good yield of **2** with no additional reactions or conversions to **3** or **4** detected at temperatures up to 200°C. The transformation of **1** to **2** results in one dppm ligand that is unchanged and two C-H bond cleavages, but no P-C bond activation.

In comparison, the thermolysis of $\text{Ru}_3(\text{CO})_8(\mu\text{-dppm})_2$ (**6**) involves the transformation to $\text{Ru}_3(\mu\text{-H})(\text{CO})_7[\mu_3\text{-}\eta^4\text{-PhPCHP}(\text{C}_6\text{H}_4)\text{Ph}](\mu\text{-dppm})$ (**7**) at 95 °C due to a loss of a benzene, followed by the formation of $\text{Ru}_3(\text{CO})_7(\mu_3\text{-PPh})(\mu_3\text{-}\eta^2\text{-CHPPh}_2)(\mu\text{-}$

dppm) (**8**) at 110°C due to a loss of H₂ [13]. One P-C bond and two C-H bonds are broken on one dppm ligand, while the other dppm ligand remains unchanged.

The triruthenium cluster loses a phenyl group more easily than the triosmium cluster. Ortho-metalation of one phenyl group and cyclometalation of one methylene group occurs on at least one activated dppm ligand in the preparation of both cluster **2** and **7**. However, Cluster **2** is a 48e cluster with three Os–Os metal bonds, while both products of the thermolysis of Ru₃(CO)₈(μ-dppm)₂ are 50e metal clusters with only two Ru-Ru metal bonds.

4. Conclusion

Microwave irradiation is an efficient mode of preparing new triosmium metal complexes containing multiple dppm ligands. The reaction of $\text{Os}_3(\text{CO})_{12}$ with excess dppm ligands in a microwave reactor has led to the preparation of new clusters **2–5**, and also the synthesis $\text{Os}_3(\text{CO})_8(\mu\text{-dppm})_2$ (**1**) in higher yields. These new clusters (**2–5**) have at least one dppm ligand that has undergone C–H and/or C–P bond activation. Attempts to synthesize $\text{Os}_3(\text{CO})_6(\mu\text{-dppm})_3$ via microwave heating proved unsuccessful, despite the fact that $\text{Ru}_3(\text{CO})_6(\mu\text{-dppm})_3$ is easily prepared from reactions of $\text{Ru}_3(\text{CO})_{12}$ with dppm using conventional heating techniques. However, no ruthenium counterparts of clusters **2–5** have been reported. The presence of water, and use of other solvents at temperatures above their normal boiling points seem to have no effect on the overall reactions or yields excepts for cluster **4**, which is only produced in significant yield in the absence of any stirring. Both clusters **4** and **5** contain a very long hydrogen-bridged Os–Os bond, with cluster **5** possessing the longest Os–Os bond observed as of yet.

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