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Reversible C-H bond activation at a triosmium centre: A comparative study of the reactivity of unsaturated triosmium clusters Os₃(CO)₈(μ-dppm)(μ-H)₂ and Os₃(CO)₈(μ-dppf)(μ-H)₂ with activated alkynes


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Graphical Abstract

Reversible C-H bond activation at a triosmium centre: A comparative study of the reactivity of unsaturated triosmium clusters $\text{Os}_3\text{(CO)}_8(\mu\text{-dppm})(\mu\text{-H})_2$ and $\text{Os}_3\text{(CO)}_8(\mu\text{-dppf})(\mu\text{-H})_2$ with activated alkynes


The reactivity of two unsaturated triosmium clusters $\text{Os}_3\text{(CO)}_8(\mu\text{-dppm})(\mu\text{-H})_2$ and $\text{Os}_3\text{(CO)}_8(\mu\text{-dppf})(\mu\text{-H})_2$ toward activated alkynes has been investigated.
Reversible C-H bond activation at a triosmium centre: A comparative study of the reactivity of unsaturated triosmium clusters Os$_3$(CO)$_8$(µ-dppm)(µ-H)$_2$ and Os$_3$(CO)$_8$(µ-dppf)(µ-H)$_2$ with activated alkynes

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ABSTRACT

Heating a benzene solution of the unsaturated cluster Os$_3$(CO)$_8$(µ-dppm)(µ-H)$_2$ (1) [dppm = bis(diphenylphosphino)methane] with MeO$_2$CC≡CCO$_2$Me (DMAD) or EtO$_2$CC≡CCO$_2$Et (DEAD) at 80 °C furnished the dinuclear compounds Os$_2$(CO)$_4$(µ-dppm)(µ-η$_2$:η$_1$;κ$_1$-RO$_2$CCCHCO$_2$R)(µ-H) (3a, R = Me, 3b, R = Et) and the saturated trinuclear complexes Os$_3$(CO)$_7$(µ-dppm)(µ-η$_2$;η$_1$;η$_1$-RO$_2$CCCCO$_2$R)(µ-H)$_2$ (4a, R = Me, 4b, R = Et). In contrast, similar reactions using unsaturated Os$_3$(CO)$_8$(µ-dppf)(µ-H)$_2$ (2) [dppf =
bis(diphenylphosphino)ferrocene] afforded only the trinuclear complexes Os$_3$(CO)$_8$(µ-dppf)(µ-η$_2$;η$_1$-RO$_2$CCHCCO$_2$R)(µ-H) (5a, R = Me; 5b, R = Et) and Os$_3$(CO)$_7$(µ-dppf)(µ-η$_2$;η$_1$;η$_1$-RO$_2$CCHCCO$_2$R)(µ-H)$_2$ (6a, R = Me; 6b, R = Et). Control experiments confirm that 5a and 5b decarbonylate at 80 °C to give 6a and 6b, respectively. Both 5a and 5b exist as a pair of isomers in solution, as demonstrated by $^1$H NMR and $^{31}$P{$^1$H} NMR spectroscopy. DFT calculations on cluster 5a (as the dppf-Me$_4$ derivative) indicate that the isomeric mixture derives from a torsional motion that promotes the conformational flipping of the cyclopentadienyl groups of the dppf-Me$_4$ ligand relative to the metallic plane. VT NMR measurements on clusters 6a and 6b indicate that while the hydride ligand associated with the dppf-bridged Os-Os bond is nonfluxional at room temperature, the second hydride rapidly oscillates between the two non-dppf-bridged Os-Os edges. DFT examination of this hydride fluxionality confirms a “windshield wiper” motion for the labile hydride that gives rise to a time-average coupling of this hydride to both phosphorus centers of the dppf ligand. Thermolysis of 6a and 6b in refluxing toluene yielded Os$_3$(CO)$_7$(µ-dppf)(µ-η$_2$;η$_1$;η$'_1$-CCHCO$_2$R) (7a, R= Mc; 7b, R= Et). The vinylidene moieties in 7a and 7b derive from the carbon-carbon bond cleavage of coordinated alkyne ligands, and these two products exhibit high thermal stability in refluxing toluene.

**Keywords:** Unsaturated osmium clusters; Diphosphines; Reversible C-H bond activation; Aactivated alkynes; C-C bond scission; DFT.

1. Introduction

Over the past three decades, the chemistry of triosmium complexes bearing a bridging bis(diphenylphosphino)methane (dppm) ligand has received considerable attention because of their interesting chemistry, giving rise to many novel and potentially useful compounds [1-12]. In contrast, fewer examples of triosmium carbonyl cluster complexes containing the more flexible backbone functionalized derivative, 1,1’-bis(diphenylphosphino)ferrocene (dppf), have been reported [12-14]. The high reactivity associated with electronic and coordinative unsaturation in mononuclear transition metal complexes has been extensively studied due to their potential catalytic applications and interesting chemistry [15]. In comparison and notwithstanding the widespread interest in cluster chemistry, the number of unsaturated clusters is limited [1, 15-17]. Among these, the most studied example of electronically unsaturated
cluster is Os₃(CO)₁₀(µ-H)₂ [17, 18] which is unsaturated based on its 46e count, and it exhibits rich and diverse chemistry that includes fundamental bond activation processes at a wide range of substrates. The reactivity of this unsaturated cluster towards alkynes was studied with particular interest since coordinatively unsaturated hydride complexes play an important role in various homogeneous catalytic processes [19].

The coordination of an alkyne to trinuclear metal complexes depends on both the metal and the substituents on the alkyne [20]. Such reactions lead to a number of different products, with hydrometalation to yield alkenyl complexes being the most prevalent. As early as 1984, Mays and Dawoodi [18i] demonstrated that Os₃(CO)₁₀(µ-H)₂ reacts with the activated alkyne CF₃C≡CCF₃ to give the zwitterionic alkenyl complex Os₃(CO)₁₀[µ₃-CF₃CCC(H)CF₃](µ-H) in which the hydrocarbyl fragment caps the osmium triangle. Smith and coworkers reported that the reaction of the orthometalated dppm derivative Os₃(CO)₈[µ-Ph₂PCH₂P(Ph)C₆H₄](µ-H)₂ with diphenylacetylene led to the formation of the 46e cluster Os₃(CO)₇(PhC≡CPh)(µ-dppm), in which the alkyne was bonded in a µ₃-η²(μ) mode. They also reported that the addition of CO to the latter resulted in Os₃(CO)₇(µ-CO)(PhC≡CPh)(µ-dppm) in which the alkyne is bonded in a µ₁-η²(l) mode [3a,b]. Recently, we also reported the reactions of Os₃(CO)₉(µ₃-benzoheterocycle)(µ-H), another type of electronically unsaturated triosmium cluster, with alkynes which yielded various products via insertion of alkynes into the metal-hydride bond [21].

Although the reactivity of the unsaturated cluster Os₃(CO)₁₀(µ-H)₂ has extensively been investigated [17, 18], few studies have hitherto been published involving the dppm and dppf derivatives Os₃(CO)₉(µ-dppm)(µ-H)₂ (1) and Os₃(CO)₉(µ-dppf)(µ-H)₂ (2). In a recent contribution, we reported the reactivity of the unsaturated compounds 1 and 2 towards Ph₃SnH, which is highly dependent on the nature of diphosphines [12]. With the rigid dppm ligand in 1, the stannylene complex Os₃(CO)₇(µ-SnPh₂)$_{2}$(µ-dppm)(H)₂ was the major product, resulting from both Sn-H and Sn-C bond activation in addition to the minor products Os₃(CO)₉(SnPh₃)$_{2}$(µ-dppm)(µ-H)₂ and Os₃(CO)₉(SnPh₃){µ-Ph₂PCH₂P(Ph)C₆H₄}(µ-H)₂. Cluster 2 containing the highly flexible dppf ligand gives a mixture of mono-, di- and triosmium complexes that include
Os(CO)$_4$(SnPh$_3$)$_2$H, Os$_2$(CO)$_4$(SnPh$_3$)$_2$(µ-HSnPh)$_2$(µ-dppf)(µ-H) and Os$_3$(CO)$_8$(SnPh$_3$)(µ-dppf)H(µ-H)$_2$ [12].

Exposing the previously reported reactivity of electron-deficient triosmium clusters toward alkynes and the reactivity of the resulting alkyne derivatives, we thought it would be useful to perform a similar study of the reactions of activated alkynes with unsaturated triosmium hydride clusters Os$_3$(CO)$_8$(µ-dppm)(µ-H)$_2$ (1) and Os$_3$(CO)$_8$(µ-dppf)(µ-H)$_2$ (2). These show significant difference in reactivity depending on the flexibility of diphosphine. Herein we report our results on the reactions of the activated alkynes DMAD and DEAD with 1 and 2 which are quite different as expected. New modes of cluster reactivity are demonstrated, and the resulting products characterized by a combination of spectroscopic methods and X-ray diffraction analyses.

2. Experimental Section

2.1. General procedures

Unless otherwise stated, all reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Reagent-grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer, and NMR spectra were recorded on a Varian Unity Plus 500 spectrometer. All chemical shifts are reported in δ units and are referenced to the residual protons of the deuterated solvents (¹H) and to external H$_3$PO$_4$ (³¹P). Elemental analyses were performed by the Microanalytical Laboratories of the Wazed Miah Science Research Center at Jahangirnagar University. DMAD and DEAD were purchased from Aldrich Chemical Co. and used without further purification. Clusters Os$_3$(CO)$_8$(µ-dppm)(µ-H)$_2$ [22] and Os$_3$(CO)$_8$(µ-dppf)(µ-H)$_2$ [13] were prepared according to the literature procedures. Product separations were performed by TLC in air on 0.5 mm silica gel (GF$_{254}$-type 60, E. Merck, Germany) glass plates.
2.2. Reaction of Os$_3$(CO)$_8$(µ-dppm)(µ-H)$_2$ (I) with DMAD at 80 °C

A benzene solution (20 mL) of I (50 mg, 0.042 mmol) and DMAD (30 mg, 0.21 mmol) was heated to reflux for 4 h. The solvent was removed under reduced pressure and the residue separated by TLC on silica gel. Elution with cyclohexane/CH$_2$Cl$_2$ (3:2, v/v) developed four bands. The first band was unreacted I (trace) and the second band afforded Os$_2$(CO)$_4$(µ-dppm)(µ-η$^2$;η$^1$-κ$^1$-MeO$_2$CCCHCO$_2$Me)(µ-H) (3a) (18 mg, 24%) as pale yellow crystals, while the third band gave Os$_3$(CO)$_7$(µ-dppm)(µ$_3$-η$^2$;η$^1$;η$^1$-DMAD)(µ-H)$_2$ (4a) (15 mg, 27%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. The fourth band was too small for complete characterization. Spectral data for 3a: Anal. Calcd. for C$_{35}$H$_{30}$O$_8$Os$_2$P$_2$: C, 37.32; H, 2.88. Found: C, 37.63; H, 2.95. IR (νCO, CH$_2$Cl$_2$): 2031 s, 1997 vs, 1963 vs, 1925 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.68 (m, 2H), 7.54 (m, 2H), 7.48 (m, 1H), 7.39 (m, 2H), 7.26 (m, 3H), 7.18 (m, 3H), 7.07 (m, 2H), 7.01 (m, 3H), 6.86 (m, 2H), 5.32 (s, CH$_2$Cl$_2$), 4.75 (d, J 24, 15 Hz, 1H), 4.43 (d, J 5 Hz, 1H), 4.01 (d, J 24, 15 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), -12.92 (dd, J 9, 7 Hz, 1H). $^{31}$P{$^1$H} NMR(CDCl$_3$): δ -2.3 (d, J 52 Hz, 1P), -11.9 (d, J 52 Hz, 1P). Spectral data for 4a: Anal. Calcd. for C$_{38}$H$_{30}$O$_{11}$Os$_3$P$_2$: C, 35.24; H, 2.34. Found: C, 35.41; H, 2.53. IR (νCO, CH$_2$Cl$_2$): 2070 vs, 2035 s, 2013 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.58 (m, 2H), 7.49 (m, 2H), 7.43 (m, 1H), 7.35 (m, 2H), 7.21 (m, 3H), 7.13 (m, 3H), 7.02 (m, 2H), 6.96 (m, 3H), 6.81 (m, 2H), 4.71 (m, 1H), 3.97 (m, 1H), 3.73 (s, 3H), 3.63 (s, 3H), -15.90 (t, J 11.5 Hz, 1H), -19.85 (d, J 33 Hz, 1H). $^{31}$P{$^1$H} NMR(CDCl$_3$): δ -21.5 (d, J 45 Hz, 1P), -23.4 (d, J 45 Hz, 1P).

2.3. Reaction of I with DEAD at 80 °C

The reaction of I (50 mg, 0.042 mmol) and DEAD (36 mg, 0.21 mmol) followed a protocol similar to that described in the above procedure. Here the workup afforded Os$_2$(CO)$_4$(µ-dppm)(µ-η$^2$;η$^1$-κ$^1$-EtO$_2$CCCHCO$_2$Et)(µ-H) (3b) (13 mg, 29%) as pale yellow crystals and Os$_3$(CO)$_7$(µ-dppm)(µ$_3$-η$^2$;η$^1$;η$^1$-DEAD)(µ-H)$_2$ (4b) (9 mg, 16%) as red crystals from hexane/CH$_2$Cl$_2$ at 4 °C. Spectral data for 3b: Anal. Calcd. for C$_{37}$H$_{30}$O$_8$Os$_2$P$_2$: C, 42.36; H, 3.27. Found: C, 42.50; H, 3.41%. IR (νCO, CH$_2$Cl$_2$): 2031 s, 1996 vs, 1924 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.68 (m, 2H), 7.54 (m, 2H), 7.47(m, 1H), 7.40 (m, 2H), 7.26 (m, 3H), 7.17(m, 3H), 7.07 (m, 3H).
7.03 (m, 5H), 6.86 (m, 2H), 4.82 (m, 1H), 4.47 (d, J 8 Hz, 1H), 4.35 (m, 1H), 4.08 (m, 4H), 1.29 (t, J 6 Hz, 3H), 1.23 (t, J 8 Hz, 3H), -12.93 (dd, J 12, 8 Hz). $^{31}$P{$^1$H} NMR(CDCl$_3$): δ -2.1 (d, J 52 Hz, 1P), -11.8 (d, J 52 Hz, 1P). Spectral data for 4b: Anal. Calcd. for C$_{40}$H$_{34}$O$_{11}$Os$_3$P$_2$: C, 36.31; H, 2.59. Found: C, 36.82; H, 2.65. IR (νCO, CH$_2$Cl$_2$): 2069 vs, 2035 s, 2012 s, 1989 s cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 7.56 (m, 5H), 7.38 (m, 6H), 7.22 (m, 9H), 4.41 (m, 2H), 4.25 (m, 1H), 4.13 (m, 1H), 3.94 (m, 2H), 1.31 (t, J 7.5 Hz, 3H), 1.0 (t, J 7.5 Hz, 3H), -15.77 (dd, J 16, 12 Hz, 1H), -19.81 (d, J 32 Hz, 1H). $^{31}$P{$^1$H} NMR (CDCl$_3$): δ -22.1 (d, J 44 Hz, 1P), -23.7 (d, J 44 Hz, 1P).

2.4. Reaction of 1 with DMAD at 110 °C

A toluene solution (20 mL) of 1 (50 mg, 0.042 mmol) and DMAD (30 mg, 0.21 mmol) was heated to reflux for 3 h. A similar chromatographic separation and work up described above afforded only 3a (26 mg, 35%).

2.5. Reaction of 1 with DEAD at 110 °C

A mixture of 1 (50 mg, 0.042 mmol) and DEAD (36 mg, 0.21 mmol) was heated in boiling toluene (20 mL) for 3h. A similar chromatographic separation and work up described above furnished only 3b (19 mg, 42%).

2.6. Thermolysis of 4a and 4b

A toluene solution (15 mL) of 4a (15 mg, 0.012 mmol) was heated for 2 h maintaining the bath temperature 80 °C. The reaction mixture did not show any significant change during this period. The bath temperature was then raised to 110 °C and heating was continued for further 2 h which led to unspecific decomposition. A similar chromatographic separation described above led to the recovery of unreacted 4a (7 mg) only. Thermal treatment of 4b following the abovementioned protocol showed similar results i.e., only led to the recovery of unreacted 4b (5 mg).
2.7. Reaction of Os₃(CO)₈(µ-dppf)(µ-H)₂ (2) with DMAD

A benzene solution (30 mL) of 2 (0.10 g, 0.075 mmol) and DMAD (45 µL, 0.37 mmol) was heated to reflux for 2.5 h, during which time the color of the solution changed from green to yellow. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (1:1, v/v) developed two bands which afforded, in order of elution, Os₃(CO)₈(µ-dppf)(µ-η²;η¹-MeO₂CCHCCO₂Me)(µ-H) (5a) (17 mg, 30%) and Os₃(CO)₇(µ-dppf)(µ-η²;η¹;η¹-DMAD)(µ-H)₂ (6a) (25 mg, 46%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at -4 °C. Spectral data for 5a: Anal. Calcd. for C₄₈H₃₆FeO₁₂Os₃P₂·CH₂Cl₂: C, 37.29; H, 2.43. Found: C, 37.65; H, 2.54. IR (νCO, CH₂Cl₂): 2077 s, 2037 vs, 2013 vs, 1990 vs, 1966 w cm⁻¹. ¹H NMR (CDCl₃): both isomer, δ 7.74 (m, 6H), 7.61-7.56 (m, 12H), 7.46 (m, 3H), 7.37 (m, 8H), 7.29 (m, 3H), 7.14 (m, 2H), 7.07 (m, 6H), 5.30 (s, CH₂Cl₂), 5.01 (s, 1H), 4.83 (s, 1H), 4.38 (s, 1H), 4.35 (s, 1H), 4.30 (s, 1H), 4.26 (s, 2H), 4.13 (s, 1H), 3.97 (s, 1H), 3.85 (s, 1H), 3.77 (s, 2H), 3.70 (s, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.60 (s, 1H), 3.56 (s, 2H), 3.41 (s, 3H), 2.98 (s, 3H), -17.67 (t, J 10 Hz, 1H), -17.81 (dd, J 15, 10 Hz). ³¹P{¹H} NMR (CDCl₃): both isomer, δ 3.1 (s, 1P), -6.0 (s, 1P), -8.3 (s, 1P), -9.0 (s, 1P). Spectral data for 6a: Anal. Calcd. for C₄₇H₃₆FeO₁₁Os₃P₂·CH₂Cl₂: C, 38.53; H, 2.48. Found: C, 38.75; H, 2.66. IR (νCO, CH₂Cl₂): 2076 vs, 2035 s, 2011 s, 1970 w, 1941 w cm⁻¹. ¹H NMR (25 °C, CDCl₃): δ 7.53 (m, 4H), 7.42 (m, 16H), 4.34 (s, 2H), 4.18 (s, 2H), 4.07 (s, 2H), 3.98 (m, 2H), 3.41 (s, 6H), -16.65 (t, J 10 Hz, 1H), -19.80 (t, J 10 Hz, 1H). ³¹P{¹H} NMR (CDCl₃, -40 °C): δ 3.2 (s, 1P), -9.7 (s, 1P).

2.8. Reaction of 2 with DEAD

A solution of 2 (0.10 g, 0.075 mmol) and DEAD (59 µL, 0.37 mmol) in benzene (30 mL) was heated to reflux for 3 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (1:1, v/v) afforded two bands, which gave the following compounds in order of elution, Os₃(CO)₈(µ-dppf)(µ-η²;η¹-EtO₂CCHCCO₂Et)(µ-H) (5b) (15 mg, 26%) and Os₃(CO)₇(µ-dppf)(µ-η²;η¹;η¹-DEAD)(µ-H)₂ (6b) (24 mg, 63%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at -4 °C.
Spectral data for 5b: Anal. Calcd for C_{50}H_{40}FeO_{12}Os_{3}P_{2}: C 39.46; H 2.65. Found: C 39.62; H, 2.78%. IR (νCO, CHCl₃): 2077 vs, 2036 vs, 2012 vs, 1990s, 1967w cm⁻¹. ¹H NMR (CDCl₃): both isomer (aromatic protons), δ 7.76 (m, 5H), 7.60 (m, 5H), 7.55 (m, 6H), 7.46-7.37 (m, 16H), 7.29 (m, 2H), 7.14 (m, 1H), 7.07 (m, 5H); major isomer (Cp and Et protons), 4.30 (s, 1H), 4.25 (s, 1H), 4.14 (m, 3H), 3.96 (s, 1H), 3.91 (m, 4H), 3.90 (s, 1H), 3.78 (s, 1H), 3.70 (s, 1H), 1.24 (t, 10 Hz, 3H), 0.85 (t, 10Hz, 3H), minor isomer (Cp and Et protons), 4.83 (s, 1H), 4.34 (s, 1H), 4.27 (s, 1H), 3.94 (s, 1H), 3.87 (s, 1H), 3.82 (m, 2H), 3.75 (s, 1H), 3.61 (s, 1H), 3.51 (s, 1H), 3.46 (m, 2H), 1.00 (t, 10 Hz, 3H), 0.72 (t, 10 Hz, 3H); major isomer (hydride), -17.69 (t, J 10 Hz, 1H), minor isomer (hydride), -17.76 (t, J 10 Hz, 1H). ³¹P{¹H} NMR (CDCl₃): major isomer, δ 3.0 (s, 1P), -8.4 (s, 1P); minor isomer, δ -6.0 (s, 1P), -8.9 (s, 1P). Spectral data for 6b: Anal. Calcd. for C_{49}H_{40}FeO_{11}Os_{3}P_{2}: C, 39.41; H, 2.70. Found: C, 39.61; H, 2.85%. IR (νCO, CHCl₃): 2076 vs, 2035 vs, 1970 m, 1941m cm⁻¹. ¹H NMR (CDCl₃): δ 7.56 (br, m, 4H), 7.42 (m, 16H), 4.08 (br, 2H), 3.94 (overlapping singlets, 6H), 3.83 (m, 4H), 1.00 (t, J 10 Hz, 6H), -16.70 (t, J 10 Hz, 1H), -19.12 (t, J 10 Hz, 1H). ³¹P{¹H} NMR (CDCl₃, 25 °C): δ -6.5(br, s).

2.9. Conversion of 5a to 6a

A benzene solution (20 mL) of 5a (20 mg, 0.075 mmol) was heated to reflux for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CHCl₃ (1:1, v/v) developed two bands. The major band afforded 6a (18 mg, 89%), while the minor band gave unreacted 5a (trace).

2.10. Conversion of 5b to 6b

A similar thermolysis of 5b (20 mg, 0.075 mmol), following the above mentioned protocol, at 80 °C for 3.5 h afforded 6b (18 mg, 90%) after chromatographic separation and workup.

2.11. Thermolysis of 6a
A toluene solution (20 mL) of 6a (25 mg, 0.017 mmol) was heated to reflux for 3.5 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH$_2$Cl$_2$ (1:1, v/v) developed two bands. The major band gave Os$_3$(CO)$_7$(μ-dppf)(μ-η$_2$;η$_1$;κ$_1$-CCHCO$_2$CH$_3$) (7a) (24 mg, 50%) as yellow crystals after recrystallization from hexane/CH$_2$Cl$_2$ at -4 °C, and the minor band (trace) was not characterized. Spectral data for 7a: Anal. Calcd for C$_{45}$H$_{32}$FeO$_9$Os$_3$P$_2$: C, 38.46; H, 2.30. Found: C, 38.65; H, 2.48. IR (νCO, CH$_2$Cl$_2$): 2038 vs, 1989 s, 1959 w, 1942 sh cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 8.07 (m, 2H), 7.76 (m, 3H), 7.58 (m, 4H), 7.51 (m, 3H), 7.32 (m, 3H), 7.20 (m, 4H), 7.01 (m, 1H), 5.33 (s, 1H), 4.32 (s, 1H), 4.25 (s, 1H), 4.09 (s, 1H), 3.81 (s, 1H), 3.73 (s, 1H), 3.70 (s, 1H), 3.33 (s, 1H), 2.83 (s, 3H). $^{31}$P{$_1$H} NMR (CDCl$_3$): δ 14.5 (s, 1P), 7.1 (s, 1P).

2.12. Thermolysis of 6b

A similar thermolysis of 6b (25 mg, 0.016 mmol) at 110 °C for 3.5 h gave Os$_3$(CO)$_7$(μ-dppf)(μ-η$_2$;η$_1$;κ$_1$-CCHCO$_2$Et) (7b) (12 mg, 48%) as yellow crystals after recrystallization from hexane/CH$_2$Cl$_2$ at -4 °C. Spectral data for 7b: Anal. Calcd for C$_{46}$H$_{34}$FeO$_9$Os$_3$P$_2$·CH$_2$Cl$_2$: C, 37.53; H, 2.41. Found: C, 37.76; H, 2.65. IR (νCO, CH$_2$Cl$_2$): 2038 vs, 1989 s, 1959 m, 1943 sh cm$^{-1}$. $^1$H NMR (CDCl$_3$): δ 8.07 (m, 2H), 7.74 (m, 3H), 7.58 (m, 4H), 7.48 (m, 5H), 7.32 (m, 1H), 7.19 (m, 3H), 7.01 (m, 2H), 5.33 (s, 1H), 5.30 (s, CH$_2$Cl$_2$), 5.28 (s, 1H), 5.04 (s, 1H), 4.32 (s, 1H), 4.24 (s, 1H), 4.10 (s, 1H), 3.81 (s, 1H), 3.70 (s, 1H), 3.34 (s, 1H), 3.19 (m, 1H), 2.93 (m, 1H), 0.96 (t, J 10 Hz, 3H). $^{31}$P{$_1$H} NMR (CDCl$_3$): δ 14.2 (s, 1P), 6.8 (s, 1P).

2.13. X-ray crystallography

Single crystals of 3a, 4b, 5a, 6a, 6b, and 7b suitable for single-crystal X-ray diffraction analyses were mounted on Nylon loops with inert oil or Apiezon grease. For compound 3a, data were collected on a Bruker D8 SMART APEX CCD diffractometer. For compound 4b, data were collected on a Rigaku XtaLab mini bench-top diffractometer. Data for compounds 5a, 6a, 6b and 7b were measured on an Agilent Technologies Super Nova diffractometer. Data collection temperatures and X-ray sources are reported in Table 1 together with other crystallographic
details. Data reduction and absorption corrections were carried out using SAINT+ and SADABS [23] for 3a and with Crystal Clear [24] for 4b. For compounds 5a, 6a, 6b and 7b, data reduction and absorption corrections were carried out with Crysalis Pro [25]. Structures were solved by direct methods and refined by difference fourier synthesis using the SHELX [26] suite of programs within either the WinGX [27] or Olex 2 [28] graphical user interfaces. Non-hydrogen atoms were refined anisotropically and hydrogens included using a riding model. Hydride ligands were located as weak features in the final electron density maps. The quality of the single crystals of 5a available for XRD analysis was relatively poor which led to the collection of low quality data hence the resolution of the data set for this complex is poor.

2.14. Computational Methodology

The DFT calculations were carried out with the Gaussian 09 package of programs [29] using the B3LYP hybrid functional. This functional is comprised of Becke's three-parameter hybrid exchange functional (B3) [30] and the correlation functional of Lee, Yang, and Parr (LYP) [31]. The iron and osmium atoms were described with the Stuttgart-Dresden effective core potential and SDD basis set [32], and the 6-31G(d’) basis set [33] was employed for the P, O, C, and H atoms. To facilitate the calculations, the phenyl groups on the dppf ligand were replaced with methyl groups (dppf-Me4).

The reported geometries for clusters A-D_alt were fully optimized, and the analytical Hessian was evaluated at each stationary point to confirm that the geometry was an energy minimum (no negative eigenvalues). Intrinsic reaction coordinate (IRC) calculations were performed on TSDD_alt in order to establish the reactant and product species associated with this transition-state structure. Unscaled vibrational frequencies were used to make zero-point and thermal corrections to the electronic energies and the resulting free energies are reported in kcal/mol relative to the specified standard. Standard state corrections were applied to all species to convert concentrations from 1 atm to 1 M according to the treatise of Cramer [34]. The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program [35].
3. Results and discussion

3.1. Reactions of Os$_3$(CO)$_8$(µ-dppm)(µ-H)$_2$ (1) with DMAD and DEAD

Refluxing cluster 1 with DMAD or DEAD in benzene afforded the dinuclear compounds Os$_2$(CO)$_4$(µ-η$_2$;η$_1$;κ$^1$-RO$_2$CCCHCO$_2$R)(µ-H) (3a, R = Me, 24%; 3b, R = Et, 29%) and the saturated trinuclear complexes Os$_3$(CO)$_7$(µ-dppm)(µ$_3$-η$_2$;η$_1$-RO$_2$CCCO$_2$R)(µ-H)$_2$ (4a, R = Me, 27%; 4b, R = Et, 16%) after chromatographic separation. Scheme 1 highlights the results of the reaction of cluster 1 with the two alkynes. The formation of dinuclear products in this reaction is consistent with that observed from the photochemical reaction of Os$_3$(CO)$_{12}$ with DMAD [36]. Compounds 3a and 3b were the only products isolated when the same reactions were carried out in toluene at 110 °C. Heating compounds 4a and 4b at 80-110 °C did not produce any of 3a and 3b indicating that these trinuclear clusters do not serve as precursor for the dinuclear products i.e., they are formed via different reaction pathways. Both the dinuclear compounds were characterized by a combination of elemental analyses, infrared and $^1$H and $^{31}$P($^1$H) NMR spectroscopy, together with a single crystal X-ray diffraction analysis for 3a.

![Scheme 1](image)

An ORTEP diagram of the molecular structure of 3a is depicted in Fig. 1 and selected bond distances and angles are quoted in the caption. The molecule has 34 valence electrons and consists of a dinuclear framework of two osmium atoms where the Os-Os bond is spanned by

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11
edge-bridging hydride and dppm ligands. Each osmium center contains two terminal CO groups and bonded to “flyover” $\mu$-$\eta^2$-$\eta^1$-$\kappa^1$-MeO$_2$CCCHCO$_2$Me ligand which functions as a 5e donor. It is coordinated to the dimetallic centre through the alkenyl functionality in a $\sigma$, $\pi$-vinyl fashion in such a way that the C(5) carbon is coordinated to Os(1) through an Os-C $\sigma$-bond [Os(1)-C(5) 2.143(8) Å] and a $\pi$ interaction between C(5)-C(6) and Os(2) [Os(2)-C(5) 2.141(8) Å and Os(2)-C(6) 2.177(9) Å]. The alkenyl carbon, C(6), is also bonded to a hydrogen atom. A similar bonding mode of the alkenyl ligand was reported in the diiron compound Fe$_2$(CO)$_4$(µ-PPh$_2$)(µ-dppm)(µ-$\eta^2$-$\eta^1$-MeO$_2$CCCHCO$_2$Me), obtained from the reaction of Fe$_2$(CO)$_4$(µ-H)(µ-CO)(µ-PPh$_2$)(µ-dppm) with DMAD [37]. There is also an additional bonding interaction between a carbonyl oxygen, O(5), of one of the carboxylate groups and the Os(1) atom. The C(5)-C(6) bond distance in 3a [1.460(11)] is significantly shorter than the expected sp$^3$-sp$^3$ carbon-carbon single bond distance and is very similar to the carbon-carbon bond distance in Os$_3$(CO)$_9$($\mu$-$\eta^2$-$\eta^1$-$\kappa^1$-MeO$_2$CCCHCO$_2$Me)(µ-C$_7$H$_4$NS) [21a]. The conversion of the alkyne to an alkenyl moiety is facilitated by the transfer of one of the original hydride ligands in 1 to the DMAD substrate. The Os-Os distance of 2.9254(6) Å in 3a is slightly longer than found in Os$_2$(CO)$_8$($\mu$-$\eta^1$-$\eta^1$-DMAD) [36] [2.8975(1)Å] and Os$_2$(CO)$_8$($\mu$-$\eta^1$-$\eta^1$-CH$_2$CHCO$_2$Me) [38] (2.8850(1) Å). The Os-P bond lengths in 3a, while are asymmetrical in nature, [Os(1)-P(1) 2.303(2), Os(2)-P(2) 2.346(2) Å] agree with those Os-P bond distances reported for the parent compound 1 [1b] [2.336(5) and 2.337(5) Å] whose Os-P bond distances that are highly symmetrical.

**Place Figure One Here**

The spectroscopic data for 3a are consistent with the solid-state structure. Moreover, the spectral data for 3b closely parallel the data recorded for 3a, confirming that both products possess a similar structure. The IR spectra recorded for 3a and 3b in the carbonyl region show four strong bands, whose frequencies and intensities are virtually identical as expected for this genre of tetracarbonyl complexes. In addition to the well-separated resonances associated with the dppm ligand and ester groups, the $^1$H NMR spectra display a doublet at $\delta$ 4.43 (J 5 Hz) for 3a and 4.47 (J 8 Hz) for 3b due to the C-H proton of the alkyne ligand which couples to one of the phosphorus atoms of the dppm ligand. The hydride region in the $^1$H NMR spectra shows a
doublet of doublets at $\delta$ -12.92 (J 9, 7 Hz) for 3a and -12.93 (J 8, 12 Hz) for 3b, each integrating for 1H, confirming the presence of an edge-bridging hydride ligand coupled to both phosphorus atoms. The $^{31}$P{\textsuperscript{1}H} NMR spectra recorded for 3a and 3b reveal two doublets [$\delta$ -2.3 and -11.9 (J 52 Hz) for 3a; $\delta$ -2.1 and -11.8 (J 52 Hz) for 3b], reaffirming the presence of inequivalent phosphorus atoms in the formulated structures of 3a and 3b.

Compounds 4a and 4b were characterized by analytical and spectroscopic methods, together with a single crystal X-ray diffraction analysis for 4b. An ORTEP diagram of the molecular structure of 4b is shown in Fig. 2 with selected bond distances and angles contained in the caption. Compound 4b is electronically saturated and contains 48 valence electrons. The three osmium atoms display a scalene triangular array based on three distinctly different metal-metal bond lengths [Os(1)-Os(3) 2.7881(17), Os(1)-Os(2) 2.8729(19), Os(2)-Os(3) 3.0128(13) Å] and the dpmp ligand bridges the Os(1)-Os(2) bond. The presence of seven terminal carbonyl ligands, two edge-bridging hydride ligands, and a face-capping DEAD ligand complete the ligand coordination sphere. The $\mu_3$-DEAD ligand, which acts as a 4e donor, interacts with all three metal atoms through an $\eta^2(\pi)$-interaction between C(8)-C(9) and Os(1) [Os(1)-C(8) 2.251(8) and Os(1)-C(9) 2.060(7) Å] and through two formal Os-C $\sigma$-bonds to Os(2) and Os(3) [Os(2)-C(8) 2.153(8) and Os(3)-C(9) 2.063(8) Å]. The C(8)-C(9) bond distance in 4b [1.408(10)] compares well to the C-C bond distance of 1.40(2) Å in the related alkyne-substituted cluster Os$_3$(CO)$_{10}$($\mu_3$-$\eta^2$; $\eta^1$; $\eta^1$-DMAD) [39]. The two Os-P bond distances are nearly equal in length [Os(1)-P(1) 2.355(3), Os(2)-P(2) 2.340(2) Å] and comparable to the Os-P distances in the parent cluster 1 [2.336(5) and 2.337(5) Å] [1a]. The hydrides in 4b could not be located from the structural studies, but are assumed to span Os(1)-Os(2) and Os(2)-Os(3) edges based on the disposition of the ancillary ligands about the three osmium centers.

Place Figure 2 Here

The spectroscopic recorded for 4b are consistent with the solid-state structure. Given the similarity of the IR and NMR data of 4a and 4b, we conclude that these products are isostructural. The spectroscopic data for 4a and 4b are summarized in the experimental section.
Important features displayed by both products include two distinct hydride resonances that appear as a triplet and doublet. The former represents the hydride that shares the Os-Os edge with the bridging dppm ligand while the doublet is assigned to an adjacent Os-Os bond whose splitting is attributed to the vicinal phosphorus atom of the dppm ligand. The observed $^2J_{\text{PH}}$ coupling in the latter hydride confirms that the hydrides are non-fluxional under these conditions. Finally, the two doublets recorded in the $^{31}\text{P}$ NMR spectrum for the dppm ligand in each product are consistent with the formulated structure.

3.2. Reactions of $\text{Os}_3(\text{CO})_8(\mu\text{-dppf})(\mu\text{-H})_2$ (2) with DMAD and DEAD

Two sets of new triosmium complexes, $\text{Os}_3(\text{CO})_8(\mu\text{-dppf})(\mu-\eta^2;\eta^1\text{-RO}_2\text{CCHCCO}_2\text{R})(\mu\text{-H})$ (5a, $R = \text{Me}$, 30%; 5b, $R = \text{Et}$, 46%) and $\text{Os}_3(\text{CO})_7(\mu\text{-dppf})(\mu_3-\eta^2;\eta^1;\eta^1\text{-RO}_2\text{CCCCO}_2\text{R})(\mu\text{-H})_2$ (6a, $R = \text{Me}$, 26% 6b, $R = \text{Et}$, 63%), were obtained when 2 was reacted with DMAD and DEAD, respectively, in refluxing benzene. Scheme 2 shows these reactions leading to the new triosmium clusters 5a,b and 6a,b.
Scheme 2

Clusters 5a and 5b have been characterized by a combination of IR, and $^1$H and $^{31}$P{$^1$H} NMR spectroscopy, and the solid-state structure of 5a has been established by single-crystal X-ray diffraction analysis. The molecular structure of 5a, which is depicted in Fig. 3 and whose caption includes pertinent bond distances and bond angles, confirms the formal insertion of the alkyne into one of the hydride bonds in cluster 1 to yield an edge-bound alkenyl moiety. The closed triangular array of osmium atoms exhibits three distinctly different metal-metal bond lengths that range from 2.8156(5) Å [Os(1)-Os(3)] to 3.1191(5) Å [Os(1)-Os(2)] with a mean distance of 2.9514 Å. There are eight terminal carbonyl groups in 5a and one of the CO groups at the Os(CO)$_4$ center in 1 has migrated to the adjacent Os(2) atom in 5a. The dppf ligand bridges the Os(1)-Os(2) edge, and while the position of the hydride ligand in 5a could not be located crystallographically, its association with the Os(1)-Os(2) edge is confirmed 1) by the disposition of the ancillary ligands about this Os-Os bond and 2) the fact that it is split into a triplet due to equal coupling with both phosphorus atoms of the dppf ligand [40]. The μ-MeO$_2$CCHCCO$_2$Me ligand asymmetrically spans the Os(1)-Os(3) edge and displays a formal $\sigma$ bond to Os(1) [Os(1)-C(9) 2.097(9) Å] and a $\pi$-bond interaction to Os(3) [Os(3)-C(9) 2.212(8) Å, Os(3)-C(10) 2.274(9) Å]. The $\sigma$-$\eta^2$vinyl-type interaction observed here is in keeping with the bond lengths found in other trimetallic systems with similar alkyne-derived ligands [41, 42]. The bridging alkenyl ligand acts as a 3e electron donor, and the $\pi$-coordinated C(9)-C(10) double bond [1.453(13) Å] is elongated ca. 0.1 Å with respect to a free C=C double bond of an alkene.

Place Figure 3 Here

The recorded IR spectra in the ν(CO) region for 5a and 5b are similar, and the two clusters are assumed to be isostructural with respect to the distribution of their ligands about the Os$_3$ framework. Aside from the phenyl, cyclopentadienyl and RO$_2$CCHCCO$_2$R (R = Me, Et) proton resonances in the $^1$H NMR spectra, the hydride region of each product exhibits a triplet and a doublet of doublets at δ −17.67 (major) and −17.81 (minor) for 5a and δ −17.69 (major) and −17.76 (minor) for 5b, respectively, suggesting that each cluster exists as two isomers in solution. The existence of isomers is mirrored in the $^{31}$P{$^1$H} NMR spectra of 5a and 5b based
on two sets of singlets for the inequivalent phosphorus atoms, as summarized in the experimental section.

The possible composition of the 5a isomers was investigated by DFT, and here we employed the X-ray diffraction structure of 5a as our starting point. Geometry optimization of 5a using an ancillary dppf-Me₄ ligand furnished species C whose structure is shown in Fig. 4. The calculated structure for C shows good agreement with the solid-state structure of 5a and reinforces the proposed location of the edge-bridging hydride across the dppf-Me₄-bridged Os-Os edge. We also optimized the structures of the starting cluster 2 (species A) and DMAD (species B) in order to evaluate the thermodynamics for the formation of C. The reaction of A with B to give C is exergonic, and the product lies 19.7 kcal/mol below the reactants. The potential energy (ΔG) surface for the reaction is shown in Fig. 5. Species C_alt was confirmed as the minor component of the isomers that constitute 5a, and the main difference between C and C_alt concerns the disposition of the cyclopentadienyl rings of the dppf-Me₄ ligand relative to the metallic plane. We have described a similar torsional motion of the cyclopentadienyl ligands in the parent cluster 2 in our earlier report [13]. The free energy difference between the two species is small (ΔG = 0.7 kcal/mol) and favors C. The computed K_eq value of 0.30 for the C ⇌ C_alt is somewhat greater than the experimentally found value of 0.53 for the isomer pair. This difference between the measured value of K_eq (0.53) and the computed value (0.30) can be attributed to the fact that DFT calculations were performed in the gas phase and no solvent correction has been applied.

**Place Figures 4 and 5 Here**

Independent control experiments established that compounds 5a,b are precursors to 6a,b. Thermolysis of 5a and 5b cluster in refluxing toluene leads to CO loss and the formation of the corresponding product 6a and 6b, respectively. This conversion of alkenyl complexes (5a,b) to alkyne and hydride complexes (6a,b) is quite unusual as normally an alkyne inserts into the metal-hydride bond to give an alkenyl complex [20, 21]. However, an alkyne-hydride intermediate has been proposed to form during α-β isomerisation of alkenyl ligands at binuclear
centers via this kind of conversion (Scheme 3) [43, 44]. The only difference between the two systems is that the alkenyl to alkyne conversion is reversible during α-β isomerisation of alkenyls at the binuclear centers, whereas the alkyne is ‘trapped’ here due to loss of CO which requires a change in coordination mode of the alkyne to preserve the EAN count of 48 at the trinuclear centers.

![Scheme 3](image)

Both 6a and 6b were isolated by chromatography and structurally characterized by X-ray crystallography. The molecular structures of 6a and 6b are depicted in Figs. 6 and 7, respectively. Compounds 6a and 6b consist of a closed triangular array of osmium atoms where one of the polyhedral faces is capped by the alkyne ligand. The transformation from 5a,b to 6a,b confirms that the original edge-bridging alkenyl moiety undergoes a C-H bond activation during the reaction. The Os-Os bond common to the bridging dppf and hydride ligands [Os(1)-Os(2) 3.0719(6) Å for 6a; Os(1)-Os(3) 3.0685(6) Å for 6b] is longer than the other hydride-bridged Os-Os edge [Os(2)-Os(3) 2.8726(17) Å for 6a; and Os(2)-Os(3) 2.8649(5) for 6b]. The mean Os-Os bond distance in 6a and 6b is similar to that in 4b. The coordinated alkyne in each product displays the expected σ,π model of ligand bonding where the Os-C distances for the σ bonds [Os(1)-C(11) 2.080(3) Å, Os(2)-C(8) 2.129(3) Å for 6a; Os(1)-C(9) 2.084(3) Å, Os(3)-C(8) 2.146(3) Å for 6b] are shorter than the associated Os-C π distances [Os(3)-C(8) 2.215(3) Å, Os(3)-C(11) 2.300(3) Å for 6a; Os(2)-C(8) 2.235(3) Å, Os(2)-C(9) 2.308(3) Å for 6b]. The Os-P bond distances [Os(1)-P(2) 2.3437(8) Å, Os(2)-P(1) 2.3588(8) Å for 6a; Os(1)-P(1)2.3498(10)Å, Os(3)-P(2) 2.3653(8) Å for 6b] are similar to those distances found in the starting cluster 2 [13]. Both products are electron precise based on an electron count of 48 valence electrons.
The IR spectra recorded for clusters 6a and 6b are identical in the terminal ν(CO) region and consistent with a common distribution of the ancillary ligands about each Os$_3$ polyhedron. Both clusters exist as a mixture of two isomers in CDCl$_3$ solution that are in rapid equilibrium. Since the NMR spectral data for the two clusters are similar in nature, we will only discuss the properties of 6a in detail. The $^{31}$P NMR spectrum of 6a at room temperature reveals a broad resonance at δ -3.8 that is barely distinguishable from the baseline, and the visible absence of inequivalent phosphorus nuclei confirms the existence of a fluxional process. The exchange process creates a time-average environment for the dppf ligand and the nature of the broadened $^{31}$P resonance allows us to approximate the temperature of coalescence (T$_c$) as 298 K. The $^1$H NMR spectrum exhibits two triplets at δ -16.65 and -19.80 at 298 K whose splitting pattern indicates that the two hydrides are coupled to both phosphorus atoms of the dppf ligand. Identical splitting patterns for the hydrides signal a rapid exchange of the hydride associated with the Os-Os bond that is adjacent to the dppf-bridged Os-Os bond. While a triplet resonance is expected for the hydride that shares the Os-Os edge common to the dppf ligand, the second hydride is situated asymmetrically to the dppf ligand (see the solid-state structure) and should display either a doublet or a doublet of doublets instead of a triplet resonance. Figs. 8 and 9 show the VT $^{31}$P and $^1$H NMR spectra, respectively recorded for cluster 6a over the temperature range 318-233 K.

Lowering the temperature to 233 K leads to two sharp singlets at δ -9.7 and 3.2 in the $^{31}$P NMR spectrum, and while the high-field triplet at δ -19.80 does not exhibit any appreciable change in the $^1$H NMR spectra as the temperature is lowered, the triplet at δ -16.65 transforms to a doublet with $J_{PH} = 20$ Hz as the slow-exchange limit is approached. These data support a fluxional process that serves to equilibrate the latter hydride between the two Os-Os edges that are not bridged by the dppf ligand. Hydride mobility about polynuclear metal clusters is a well-
established phenomenon [45]. At 233 K, two distinct $^{31}\text{P}$ and $^1\text{H}$ resonances are expected, with one hydride effectively coupled to only one of the $^{31}\text{P}$ centers. The $\Delta G^\ddagger$ value for the equilibration of the hydride between adjacent Os-Os vectors is estimated as 11.9 kcal/mol based on a separation frequency of the $^{31}\text{P}$ resonances ($\Delta \nu = 2363$ Hz) and a $T_c$ of 298 K [46]. Scheme 4 illustrates the hydride exchange process that is consistent with the VT NMR data.

![Scheme 4](image)

To better understand the observed ligand fluxionality in 6a, we have investigated different possible hydride exchange schemes employing species D as a starting point. Equilibration of the hydride between the two non-dppf supported Os-Os bonds proceeds via the transition state $\text{TSDD}_\text{alt}$ that contains a triply bridged hydride ligand (Chart). The computed $\Delta G^\ddagger$ value for the forward motion of the hydride is 7.2 kcal/mol in agreement with the experimentally estimated value for hydride fluxionality. The motion exhibited by the migratory hydride is analogous to the windshield-wiper effect displayed by related ligands across the polyhedral face of other metal clusters [45b,e, 47]. The product of hydride transit is $D_\text{alt}$, and it lies 1.1 kcal/mol lower in energy than D due to slight differences in the disposition of the dppf-Me$_4$ and carbonyl ligands about the cluster. Under conditions of rapid exchange, the hydride would exhibit a time-average environment between the Os-Os bonds and display mutual coupling to both phosphines, giving rise to the observed triplet resonance at $\delta$ -16.65.
3.3. Carbon-carbon bond cleavage of the coordinated alkyne ligand in 6a and 6b

The cleavage of carbon-carbon bonds is a potentially useful way of generating reactive organic fragments at a metal center [48]. To this end, we have been exploring the reactions of coordinated alkynes at different metal clusters and can report that the coordinated alkyne ligands in 6a,b yield new clusters containing a vinylidene moiety when heated at elevated temperatures. Thermolysis of 6a and 6b in toluene at 110 °C, followed by the usual chromatographic separation, afforded Os₃(CO)₇(µ-dppf)(µ-3,η¹;η¹;κ¹-CCHCO₂R) (7a, R = Me, 50%; 7b, R = Et, 48%) (Scheme 2). While we have not been able to identify the missing alkyne-derived atoms in these reactions, we can confirm that corresponding formates HCO₂Me and HCO₂Et are not observed in those reactions that are monitored by NMR. The cluster products are relatively stable under the reaction conditions and show no evidence of decomposition when heated in refluxing toluene over the course of several hours. Compounds 7a and 7b have been characterized spectroscopically in solution and by X-ray diffraction analysis in the case of 7b, whose structure is shown in Fig. 10.

Place Figure 10 Here
The Os-Os bond distances in 7b range from 2.7740(11) Å [Os(1)–Os(3)] to 3.0481(11) Å [Os(1)–Os(2)], leading to a triangular array of osmium similar in nature to that found in clusters 6a and 6b. The most noteworthy feature in 7b is the face-capping CCHCO₂Et ligand that derives from the coordinated DEAD ligand in 6b. The CCHCO₂Et ligand, which functions as a 6e donor, is coordinated to the cluster in a µ₃-η²;η¹;κ¹ fashion, where the C(8) and C(9) atoms exhibit Os-C distances consistent with a σ,π model of bonding common to other vinylidene ligands [49]. Here the two σ bonds are represented by the Os(1)-C(8) [2.131(11) Å] and Os(2)-C(8) [1.963(15) Å] vectors and the π interaction is defined by Os(3)-C(8) [2.187(12) Å] and Os(3)-C(9) [2.331(14) Å] vectors. There is also an additional donation of 2e to the Os(1) center from the O(8) carbonyl oxygen of the ester moiety. Cluster 7b contains 48 valence electrons and be viewed as an electron-precise cluster containing three metal-metal bonds. The dpff ligand bridges the Os(1) and Os(2) centers, and of the seven terminal carbonyl groups, three are located at the Os(3) center with the remaining four CO groups distributed pair wise at the other two metal centers.

The spectroscopic data recorded for 7a is consistent with the formulated structure containing an ancillary CCHCO₂Me vinylidene ligand, and this premise is underscored by the near identical IR spectra displayed by 7a and 7b. In addition to the phenyl proton resonances in the aromatic region, the ¹H NMR spectrum of each product also contains nine equal intensity singlets [δ 5.33, 5.04, 4.32, 4.25, 4.09, 3.81, 3.73, 3.70, 3.33 for 7a and δ 5.33, 5.28, 5.04, 4.32, 4.24, 4.10, 3.81, 3.70, 3.34 for 7b] ascribed to the eight distinct cyclopentadienyl protons and one unique vinylic proton. The methyl group in the CCHCO₂Me moiety appears as a singlet at δ 2.83 in 7a, while the ethyl group associated with the CCHCO₂Et ligand exhibits a triplet at δ 0.96 for the methyl group and two multiplets at δ 3.19 and 2.93, the latter two assigned to the diastereotopic methylene hydrogens. Each cluster exhibits a pair of ³¹P singlets [δ 14.5 and 7.1 for 7a; δ 14.2 and 6.8 for 7b] due to the nonequivalent ³¹P nuclei.

4. Conclusions

The reactions of the unsaturated triosmium clusters Os₃(CO)₈(µ-dppm)(µ-H)₂ (1) and Os₃(CO)₈(µ-dpf)(µ-H)₂ (2) with activated alkynes DMAD and DEAD are examined. Cluster 1

21
reacts with these alkynes to furnish the dinuclear Os$_2$(CO)$_4$(µ-dppm)(µ-η$^2$;η$^1$;κ$^1$-RO$_2$CCCHCO$_2$R)(µ-H) (3a, R = Me; 3b, R = Et) and the trinuclear Os$_3$(CO)$_7$(µ-dppm)(µ$_3$-η$^2$;η$^1$;η$^1$-RO$_2$CCCCO$_2$R)(µ-H)$_2$ (4a, R = Me; 4b). In contrast, no cluster fragmentation has been observed when 2 is allowed to react with these alkynes under comparable conditions, instead yielding the trinuclear Os$_3$(CO)$_6$(µ-dppf)(µ-η$^2$;η$^1$-RO$_2$CCHCCO$_2$R)(µ-H) (5a, R = Me; 5b, R = Et) and Os$_3$(CO)$_7$(µ-dppf)(µ$_3$-η$^2$;η$^1$;η$^1$-RO$_2$CCCHCO$_2$R)(µ-H)$_2$ (6a, R = Me; 6b, R = Et). Independent control experiments reveal that 5a and 5b serve as precursors to 6a and 6b, respectively. These data are interesting inasmuch that the latter products are not formed as the initial products of ligand substitution and that alkyne insertion into an Os-H bond precedes the formal π coordination of the alkyne by the cluster in the present examples. The computed thermodynamics for the reaction reinforce this claim. However, this observation strengthened the reversible alkenyl to alkyne and hydride conversion proposed for the α-β isomerisation of alkenyl ligands at binuclear centers [43, 44]. Both 5a and 5b exist as a pair of isomers in solution due to a torsional rotation within the cyclopentadienyl rings of the dppf ligand with respect to the osmium triangle. This fluxionality has been computationally evaluated for 5a and the energy difference between the two isomers is small (∆G = 0.7 kcal/mol). CO loss in 5a and 5b is facile, and the accompanying unsaturated clusters facilitate the C-H bond activation of the alkenyl moiety to yield the π-coordinated clusters 6a and 6b. Thermolysis of the latter two clusters leads to alkyne activation and formation of the vinylidene-substituted clusters 7a and 7b. The alkyne activation observed here is related to the carbon-carbon cleavage reported for triruthenium compound [η$^5$-C$_5$Me$_5$Ru]$_3$(µ-H)$_3$(µ$_3$-H)$_2$ in its reaction with methylmethacrylate to furnish [η$^5$-C$_5$Me$_5$Ru]$_3$(µ$_3$-CH=CCO$_2$Me)(µ$_3$-CH)(µ-H)$_2$ together with 2 equivalents of 2-methylbutanoic acid [48e]. In contrast, formation of such vinylidene-substituted clusters via alkyne activation was not observed upon heating of 4a and 4b. Overall, the present work shows that the flexibility of substituted-diphosphine plays key role in the reactivity of unsaturated Os$_3$(CO)$_6$(µ-diphosphine)(µ-H)$_2$ towards alkynes. Experiments designed to elucidate the mechanism of carbon-carbon double bond cleavage and further investigation using a wider range of alkynes are underway, and the results will be reported in due course.

5. Acknowledgments
Part of this work was carried out by SEK at the University of Göttingen, who acknowledges the von Humboldt Foundation for providing research support during his stay at the University of Göttingen. MGR thanks the Robert A. Welch Foundation (grant B-1093) for financial support and acknowledges computational resources through UNT's High-Performance Computing Services and CASCaM. We also thank Prof. Michael B. Hall (TAMU) for providing us a copy of his JIMP2 program.

6. Supplementary data

Figs. S1-S3, showing CH$_2$Cl$_2$ proton resonance in the $^1$H NMR spectrum of compounds 3a, 5a and 7b, can be found in Electronic Supplementary Information (ESI). Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1517049 (for 3a), CCDC 1517050 (for 4b), CCDC 1517051 (for 5a), CCDC 1517052 (for 6a), CCDC 1517053 (for 6b) and CCDC 1517054 (for 7b) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk). Atomic coordinates for all optimized structures reported here are available from MGR upon request.

References


[35] (a) JIMP2, version 0.091, a free program for the visualization and manipulation of molecules: M.B. Hall, R.F. Fenske, Inorg. Chem. 11 (1972) 768; (b) J. Manson, C.E. Webster, M.B. Hall, Texas A&M University, College Station, TX, 2006: http://www.chem.tamu.edu/jimp2/index.html.


[46] (a) Here the free energy of activation has been computed using the Eyring equation: \( \Delta G^\ddagger = RT_c \ln(k_B T_c / \hbar k_c) \), where the physical constants \( k_B \) and \( \hbar \) have their normal meanings and \( T_c \) and \( k_c \) represent the coalescence temperature and the rate constant at coalescence. The value for \( k_c \) has been estimated as a function of \( \Delta \nu \) according to the equation: \( k_c = (0.5)^{1/2} \pi \Delta \nu \); (b) J.W. Akitt, B.E. Mann, NMR and Chemistry, Stanley Thornes, UK, 2000.
Table 1. Crystallographic data and structure refinement for 3a, 4b, 5a, 6a, 6b, and 7b.

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31
Fig. 1. ORTEP drawing of the molecular structure of Os$_2$(CO)$_4$(µ-dppm)(µ-η$_2$-η$_1$;κ$^1$-MeO$_2$CCCHCO$_2$Me)(µ-H) (3a) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Os(1)-Os(2) 2.9254(6), Os(1)-P(1) 2.303(2), Os(2)-P(2) 2.346(2), Os(1)-C(5) 2.143(8), Os(1)-O(5) 2.170(6), Os(2)-C(5) 2.141(8), Os(2)-C(6) 2.177(9), C(5)-C(6) 1.460(11), C(6)-C(7) 1.437(12), C(5)-C(9) 1.455(12), O(5)-C(7) 1.237(10), Os(2)-C(5)-Os(1) 86.1(3), C(5)-Os(2)-C(6) 39.5(3), O(5)-Os(1)-P(1) 175.98(17), O(5)-Os(1)-Os(2) 85.42(16), P(1)-Os(1)-Os(2) 90.58(6), P(2)-Os(2)-Os(1) 92.55(6), P(1)-C(11)-P(2) 113.4(5), C(5)-C(6)-Os(2) 68.9(5), C(7)-O(5)-Os(1) 109.6(6).
Fig. 2. ORTEP drawing of molecular structure of $\text{Os}_3(\text{CO})_7(\mu$-dppm)(µ$_3$-$\eta^2$;$_1$-$\eta^1$)
$\text{EtO}_2\text{CCCO}_2\text{Et})(\mu$-H)$_2$ (4b) showing 50% probability thermal ellipsoids. Selected bond lengths
(Å) and angles (°): Os(1)-Os(3) 2.7881(17), Os(1)-Os(2) 2.8729(19), Os(2)-Os(3) 3.0128(13),
Os(1)-P(1) 2.355(3), Os(2)-P(2) 2.340(2), Os(1)-C(8) 2.251(8) Os(1)-C(9) 2.260(7), Os(2)-C(8)
2.153(8), Os(3)-C(9) 2.063(8), C(8)-C(9) 1.408(10), C(8)-C(10) 1.478(11), C(9)-C(13)
1.493(11); Os(1)-Os(2)-Os(3) 56.49(4), Os(1)-Os(3)-Os(2) 59.22(4), Os(3)-Os(1)-Os(2)
64.28(14), C(8)-Os(1)-C(9) 36.4(3), C(8)-Os(1)-Os(3) 70.70(19), C(8)-Os(1)-Os(2) 47.82(19),
C(9)-Os(1)-Os(2) 68.8(2), C(9)-Os(1)-Os(3) 46.8(2), Os(3)-C(9)-Os(1) 80.2(3).
Fig. 3. ORTEP drawing of molecular structure of Os$_3$(CO)$_8$(µ-dppf)(µ-η$^2$;η$^1$;η$^1$-CH$_3$O$_2$CCHCCO$_2$CH$_3$)(µ-H) (5a) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Os(1)-Os(3) 2.8156(5), Os(1)-Os(2) 3.1191(5), Os(2)-Os(3) 2.9195(5), Os(1)-C(9) 2.097(9), Os(3)-C(9) 2.212(8), Os(3)-C(10) 2.274(9), Os(1)-P(1) 2.338(2), Os(2)-P(2) 2.377(2), C(9)-C(10) 1.435(13), C(9)-C(11) 1.495(13), C(10)-C(13) 1.509(14); Os(3)-Os(1)-Os(2) 58.670(13), Os(1)-Os(3)-Os(2) 65.865(14), Os(3)-Os(2)-Os(1) 55.464(12), C(9)-Os(3)-C(10) 37.3(3), P(1)-Os(1)-Os(2) 114.06(6), P(2)-Os(2)-Os(1) 117.57(6), C(9)-Os(1)-Os(2) 90.4(2), C(9)-Os(1)-Os(3) 51.0(2), C(9)-Os(3)-Os(1) 75.8(2), C(10)-Os(3)-Os(1) 86.0(2), Os(1)-C(9)-Os(3) 81.6(3).
Fig. 4. B3LYP-optimized structures for cluster compounds A-D_alt and the transition state TSDD_alt. The structures for the alkyne DMAD (B) and liberated CO are not shown.
Fig. 5. Potential energy surface for the conversion of A and B to give D_alt and CO. Energy values are $\Delta G$ in kcal/mol with respect to A and B.
Fig. 6. ORTEP drawing of molecular structure of Os₃(CO)₇(µ-dppf)(µ₂-η²:η¹:η¹-CH₃O₂CCC-CO₂CH₃)(µ-H)₂ (6a) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Os(1)-Os(2) 3.07188(17), Os(1)-Os(3) 2.79180(17), Os(2)-Os(3) 2.87256(17), Os(1)-P(2) 2.3437(8), Os(2)-P(1) 2.3588(8), Os(1)-C(11) 2.080(3), Os(3)-C(11) 2.300(3), Os(3)-C(8) 2.215(3), C(8)-C(11) 1.421(4), Os(2)-C(8) 2.129(3); Os(1)-Os(3)-Os(2) 65.665(4), Os(3)-Os(1)-Os(2) 58.433(4), Os(3)-Os(2)-Os(1) 55.902(4), Os(2)-C(8)-Os(3) 82.77(10), P(2)-Os(1)-Os(2) 115.944(19), P(1)-Os(2)-Os(1) 114.702(19), C(8)-Os(3)-C(11) 36.62(11), Os(1)-C(11)-Os(3) 79.03(10), C(8)-C(11)-Os(1) 114.9(2), C(8)-C(11)-Os(3) 68.44(16).
Fig. 7. ORTEP drawing of the molecular structure of Os$_3$(CO)$_7$(µ-dppf)(µ$_3$-η$_1$:η$_1$:η$_1$-EtOOCCCOOE)(µ-H)$_2$ (6b) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Os(1)-Os(2) 2.7849(6), Os(1)-Os(3) 3.0685(6), Os(2)-Os(3) 2.8649(5), Os(1)-P(1) 2.3498(10), Os(3)-P(2) 2.3653(8), Os(1)-C(9) 2.084(3), Os(2)-C(8) 2.235(3), Os(2)-C(9) 2.308(3), Os(3)-C(8) 2.146(3), C(8)-C(9) 1.417(4), Os(1)-Os(2)-Os(3) 65.774(16), Os(2)-Os(1)-Os(3) 58.368(8), Os(2)-Os(3)-Os(1) 55.858(13), P(1)-Os(1)-Os(3) 117.71(2), C(8)-Os(2)-C(9) 36.29(11), C(9)-Os(2)-Os(1) 47.16(7), C(8)-Os(2)-Os(3) 47.82(8), P(2)-Os(3)-Os(1) 115.63(3), Os(3)-C(8)-Os(2) 81.66(10), Os(1)-C(9)-Os(2) 78.53(9).
Fig. 8. VT $^{31}$P{¹H} NMR spectra of 6a recorded over the temperature range 298-233 K.

Fig. 9. VT ¹H NMR spectra of 6a recorded over the temperature range 298-233 K.
Fig. 10. ORTEP drawing of the molecular structure of Os$_3$(CO)$_7$(μ-dppf)(μ$_3$-η$^2$-η$^1$;η$^1$;κ$^1$-CCHCOOEt)] (7b) showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Os(1)-Os(3) 2.7740(11), Os(1)-Os(2) 3.0481(11), Os(2)-Os(3) 2.8082(11), Os(1)-P(1) 2.390(5), Os(2)-P(2) 2.339(4), Os(1)-C(8) 2.138(15), Os(2)-C(8) 1.98(2), Os(3)-C(8) 2.185(17), Os(3)-C(9) 2.341(19), C(8)-C(9) 1.42(2), Os(1)-O(8) 2.134(12), Os(3)-Os(1)-Os(2) 57.45(3), Os(3)-Os(2)-Os(1) 56.37(3), Os(1)-Os(3)-Os(2) 66.19(3), Os(1)-C(8)-Os(3) 79.8(6), Os(2)-C(8)-Os(1) 95.4(8), Os(2)-C(8)-Os(3) 84.6(7), C(8)-Os(3)-C(9) 36.4(7), O(8)-Os(1)-Os(3) 82.2(2), O(8)-Os(1)-Os(2) 117.6(2), P(1)-Os(1)-Os(2) 116.00(11), P(2)-Os(2)-Os(1) 116.12(11).
Highlights

• New triosmium clusters containing bridging dppm/dpf and alkyne ligands
• Alkyne activation at diphosphine-bridged triosmium clusters
• Computational analysis of ligand fluxionality in triosmium clusters bearing flexible diphosphine and alkyne
• Reversible C-H bond activation at a triosmium centre
• Alkenyl to alkyne and hydride