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Microwave-induced dppm ligand substitution in triosmium clusters: Structural and DFT evaluation of Os_3 clusters containing multiply activated dppm ligands through cyclometalation, ortho metalation, and P–C bond cleavage

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ABSTRACT

Four new triosmium carbonyl complexes containing multiple dppm ligands were produced by microwave heating of solutions containing $Os_3(CO)_{12}$ and excess dppm. Three of these complexes, $Os_3(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})[\mu_3\text{-}Ph_2PCHP(C_6H_4)Ph]$ (**2**), $Os_3(CO)_6[\mu_3\text{-}Ph_2PCH_2P(C_6H_4)Ph]_2$ (**3**), and $Os_3(\mu\text{-}H)(CO)_6[\mu_3\text{-}PhPCH_2P(C_6H_4)Ph][\mu_3\text{-}PhPCH(C_6H_4)PPh]$ (**4**), contain two dppm ligands per Os_3 unit, while the fourth, $Os_3(\mu\text{-}H)(CO)_5(dppm)[\mu_3\text{-}PhPCH_2P(C_6H_4)Ph][\mu_3\text{-}PhPCH(C_6H_4)PPh]$ (**5**), is the first example of an Os_3 cluster containing three dppm ligands. Microwave heating was also used to prepare the known complex $Os_3(\mu\text{-dppm})_2(CO)_8$ (**1**) more efficiently than previously reported. The new complexes **2**–**5** have been characterized by IR, NMR, mass spectrometry, and X-ray crystallography. In addition, the bonding in these complexes has been examined by electronic structure calculations. All of the new complexes contain at least one dppm ligand that has undergone C–H and/or C–P bond activation. Complex **2** is a 48e cluster that contains one intact dppm ligand and one face-capping dppm ligand that coordinates all three osmium sites through the phosphine moieties and cyclometalated and ortho-metalated carbon atoms. Complex **3** is a 48e cluster with two ortho-metalated dppm ligands while complexes **4** and **5** are 50e clusters that possess a common metallic framework with one cyclometalated dppm ligand and one ortho-metalated dppm ligand.

1. Introduction

The bidentate diphosphine ligand bis(diphenylphosphino)methane (dppm) has been widely used in metal cluster chemistry. Reactions of $Os_3(CO)_{12}$ with dppm have yielded triosmium cluster complexes with one or two bridging dppm groups including $Os_3(CO)_{10}(\mu\text{-dppm})$, $Os_3(CO)_9(\mu\text{-dppm})(\eta^1\text{-dppm})$, and $Os_3(CO)_8(\mu\text{-dppm})_2$ (**1**) [1,2]. Although the tris-dppm cluster $Ru_3(CO)_6(\mu\text{-dppm})_3$ has been prepared, the analogous Os_3 cluster with three dppm ligands has not been reported [3,4]. We thought it might be possible to produce $Os_3(CO)_6(dppm)_3$ in a microwave reactor since microwave heating has been shown to be effective for the synthesis of a number of osmium carbonyl complexes [5–10]. To that end, we began to carry out reactions of $Os_3(CO)_{12}$ with excess dppm in a variety of solvents. It soon became obvious that the majority of the products contained only two dppm ligands, and that C–H bond cleavage was occurring to give hydride ligands.

Reactions of triruthenium and triosmium clusters containing dppm ligands often involve C–H and C–P bond activation [11]. The possibilities of reactions such as ortho metalation, cyclometalation, and reductive elimination are enhanced by the proximity of the dppm ligands to multiple metal binding sites. While the chemistries of $Ru_3(CO)_{10}(\mu\text{-dppm})$, $Ru_3(CO)_8(\mu\text{-dppm})_2$, and $Os_3(CO)_{10}(\mu\text{-dppm})$ have been extensively explored [11], the reactivity of the bis-dppm osmium complex $Os_3(CO)_8(\mu\text{-dppm})_2$ (**1**) has been the subject of only one investigation involving its protonation by

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trifluoroacetic acid [3]. In addition to continuing our attempts to synthesize an Os_3 cluster with three dppm ligands, we turned our attention to optimizing the preparation of cluster **1** and studying the thermolysis of **1**. Herein we report on our progress toward these goals.

2. Experimental

2.1. Materials and methods

All syntheses were performed in a Discover-SP monomode microwave reactor (2455 MHz, CEM Corp., Matthew, NC). Reagents and a magnetic stir bar were placed in a 35-mL glass vessel that was sealed with a PTFE-lined cap before insertion into the reactor. A maximum pressure setting of 300 psi was used for all reactions. Due to the toxicity of CO and metal carbonyl compounds, all manipulations were carried out in a highly efficient fume hood. For reactions under pressure, special precautions were taken to lower the fume hood sash for a few minutes following the release of pressure from the reactor. Bis(diphenylphosphino)methane (dppm) was purchased from Strem and 1,2-dichlorobenzene was purchased from Sigma-Aldrich. Other solvents were obtained from Pharmco-Aaper. All purchased reagents were used as received. $Os_3(CO)_{12}$ was prepared by the carbonylation of OsO_4 according to a published procedure [12]. Preparative thin-layer chromatography (TLC) was carried out on Analtech silica gel 60 (0.50 mm) plates. Infrared spectra were obtained using a Nicolet Avatar 320 FT-IR spectrometer with a CaF_2 solution cell. The ^1H and ^{31}P NMR spectra were recorded at 499 MHz and 201 MHz, respectively, on a Varian VNMRS-500 spectrometer. The reported ^1H and ^{31}P assignments were ascertained through a combination of 2D NMR techniques that included COSY, HMQC, HMBC, and NOESY. The reported ^{31}P chemical shifts are referenced to external H_3PO_4 (85%), taken to have δ 0.0. Here positive chemical shifts are to low field of the external standard. All ^{31}P NMR spectra were run in the proton-decoupled mode, and the simulated $^{31}P\{1H\}$ NMR spectra were established by using the available program gNMR. The ESI mass spectra were collected in the positive ion mode at the UNT mass spectrometry facility, with all samples run in MeCN with added KI as the carrier matrix.

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

$Os_3(CO)_{12}$ (74.8 mg, 0.0825 mmol) and dppm (66.6 mg, 0.173 mmol) were added to a reaction vessel along with 7.0 mL of 1,2-dichlorobenzene. This mixture was irradiated and stirred in the microwave reactor at 170 °C for 5 min to produce an orange solution. After removal of the solvent, the residue was redissolved in CH_2Cl_2 before TLC separation. An eluent of 1.8:1 hexanes/CH_2Cl_2 was used to produce 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}. The identity of this compound was confirmed by growing single crystals and determining that the unit cell matched the previously reported values.

2.3. Synthesis of $Os_3(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})[\mu_3\text{-}Ph_2PCHP(C_6H_4)Ph]$ (**2**) and $Os_3(CO)_6[\mu_2\text{-}Ph_2PCH_2P(C_6H_4)Ph]_2$ (**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 in a reaction vessel. This mixture was irradiated and stirred in the microwave reactor for 6 min at 160 °C. The solvent was removed from the resulting cloudy yellow mixture by rotary evaporation. The residue was dissolved in CH_2Cl_2 and separated by TLC with an eluent of 1.8:1 hexanes/CH_2Cl_2. 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: $C_{58}H_{48}O_6P_4Cl_4Os_3$: C, 41.53; H, 2.88%. Found: C, 41.17; H, 3.02%. MS for [$\mathbf{2}+K^+$]: *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}, $CHCl_3$): 2047(w), 2008(w, sh), 1975(vs), 1945(w), 1931(w), 1907(w, sh), 1796(w, br) cm^{-1}. Anal. Calc. for $C_{56}H_{42}O_6P_4Os_3$: C, 44.67; H, 2.81%. Found: C, 43.93; H, 2.84%. MS for [$\mathbf{3}+K^+$]: *m/z* calculated for 1547.04, found 1548.80. Band 3 ($R_f = 0.20$) consisted of 11.4 mg (11.0% yield) of $Os_3(CO)_8(dppm)_2$ (**1**).

2.4. Synthesis of $Os_3(\mu\text{-}H)(CO)_6[\mu_3\text{-}PhPCH_2P(C_6H_4)Ph][\mu_3\text{-}PhPCH(C_6H_4)PPh]$ (**4**)

$Os_3(CO)_{12}$ (0.159 g, 0.175 mmol) and dppm (0.141 g, 0.368 mmol) were placed in a reaction vessel along with 8.0 mL of 1,2-dichlorobenzene. This mixture was irradiated and stirred in the microwave reactor for 2 min at 120 °C and then irradiated without stirring at 175 °C for 10 min. The solvent was removed from the resulting brown solution and the residue dissolved in CH_2Cl_2 before TLC separation. A 1.3:1 hexanes/CH_2Cl_2 eluent was used to produce four bands. The top red band ($R_f = 0.49$) 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}. Dark yellow band 2 ($R_f = 0.44$) consisted of 92.6 mg (38.4%) of cluster **4**. IR (ν_{CO}, $CHCl_3$): 2050(s), 2030(vs), 1991(vs), 1968(s), 1938(m), 1885(w) cm^{-1}. Anal. Calc. for $C_{45}H_{32}O_7P_4Os_3$: C, 39.18; H, 2.34%. Found: C, 38.77; H, 2.36%. [$\mathbf{4}+H^+$]: *m/z* calculated for 1272.98, found 1273.16. The contents of the other bands were too small for complete characterization.

A similar reaction involving 73.8 mg (0.0814 mmol) of $Os_3(CO)_{12}$ and 72.0 mg (0.187 mmol) of dppm in 7.0 mL of 1,2-dichlorobenzene was carried out at 190 °C for 5 min with no stirring. Yields were 52.1 mg (42.5%) of **2**, 23.3 mg (19.0%) of **3**, and 23.2 mg (20.7%) of **4**.

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

$Os_3(CO)_{12}$ (89.0 mg, 0.0981 mmol) and dppm (0.302 g, 0.785 mmol) were added to a reaction vessel along with 8.0 mL of 1,2-dichlorobenzene. This mixture was irradiated and stirred in the microwave reactor at 205 °C for 15 min. A dark orange solution formed. After removal of the solvent, 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(m, sh), 1980(vs), 1949(s), 1920(s), and 1893(m, 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 **1** to **2**

A 10 mg (0.0064 mmol) sample of $Os_3(CO)_8(dppm)_2$ (**1**) was placed in a 10-mL reaction vessel along with 2.0 mL of ethanol. Stirring and heating in the microwave reactor for 8 min at 150 °C produced a cloudy yellow solution. The solvent was allowed to evaporate, and the residue was dissolved in CH_2Cl_2 and separated