



Fluorous triosmium clusters. Preparation, properties, and reactivity of $\text{Os}_3(\text{CO})_{11}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$ and $\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}_2$. Crystal structure of $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_2\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$. Ring opening metathesis polymerization of norbornene by $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\{\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3\}$

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ABSTRACT

Several fluorous phosphine ligand triosmium carbonyl cluster derivatives, e.g., $\text{Os}_3(\text{CO})_{11}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$ (**1**) and $\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}_2$ (**2**) have been synthesized in order to assess their properties in fluorocarbon, or fluorous, phases. Cluster **1** reacts with PPh_3 above 100 °C to substitute one or two carbonyl ligands and provide the mixed ligand derivatives $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$, (**3**) and $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_2\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$, (**4**). The crystal structure of **4** has been determined by single crystal X-ray diffraction. At circa 102 °C and 1 atm H_2 , **1** will form the unsaturated compound $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$ (**5**) in modest yield. Compound **5** and the related compound $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\{\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3\}$ (**6**) are obtained more cleanly by treating $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with the corresponding fluorous phosphine ligand at room temperature followed by decarbonylation in refluxing hexane. Compounds **1–6** have been characterized by employment of IR and ^1H NMR and ^{31}P NMR spectroscopy. Partition coefficients between fluorous and non-fluorous solvents have been determined. The use of **6** as a ROMP catalyst with norbornene in a variety of organic and universal solvents is described.

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1. Introduction

The generally robust character of triosmium clusters has led to widespread examination of their catalytic activity in liquid phases [1]. Triosmium dodecacarbonyl is known to participate in the catalytic activation of C–N bonds through alkyl exchange between tertiary amines [2]. Tertiary amines undergo a similar catalytic transformation in the presence of the cluster anion $[\text{Os}_3(\text{CO})_9(\mu_3\text{-S})(\mu\text{-H})]^-$ [3]. The 46-electron, unsaturated cluster $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ has been identified as an alkene and quinoline hydrogenation catalyst [4], and as an alkene isomerization catalyst also capable of catalytically transforming allylic alcohols to aldehydes and ketones [5]. Catalytic alkene hydrogenation has been observed in the presence of both the cluster anion $[\text{HOs}_3(\text{CO})_{11}]^-$ [6], and the supported silica cluster $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{OSi}\equiv)$ [7]. Triosmium cluster complexes have also been employed as models of acknowledged

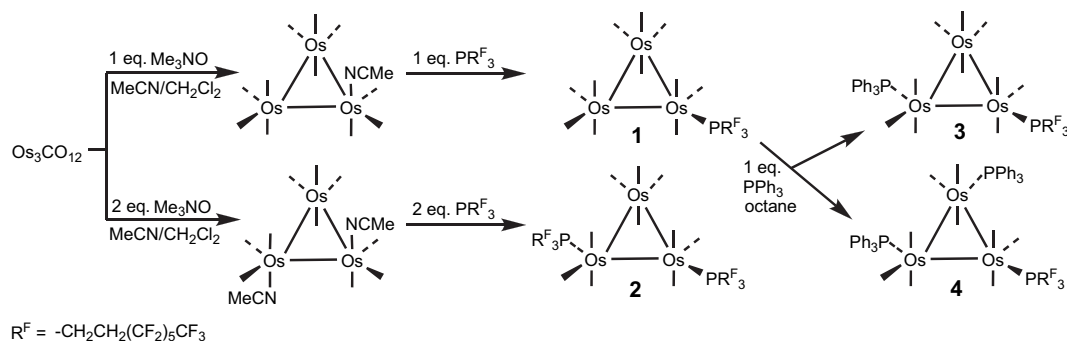
triruthenium cluster based catalysts, including the synthesis of analogues of proposed intermediates [8].

In their seminal work describing the details of fluorous biphasic catalytic systems (FBS) Horváth and Rábai employed the “pony-tailed” tertiary phosphine compound $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ to achieve catalyst solubility in liquid fluorocarbon phases [9]. In a recent review of catalysis by transition metal (carbonyl) clusters, Dyson states that transition metal cluster catalysis under the auspices of FBS is a heretofore unexplored area [10]. Including FBS, a second green chemistry application of fluorous phosphine transition metal complexes is demonstrated by their solubility and catalytic activity in supercritical carbon dioxide [11]. We have prepared (Scheme 1) the clusters $\text{Os}_3(\text{CO})_{11}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$, (**1**), and $\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}_2$, (**2**), in order to begin our exploration of triosmium cluster behavior, reactivity, and catalytic activity in liquid, fluorocarbon-dominated, “fluorous”, phases.

An important industrial application of olefin metathesis is the synthesis of polyalkenamers by ring-opening metathesis polymerization of cyclic alkenes. Polynorbornene by ROMP was first achieved by a catalytic system of TiCl_4 with co-catalyst $\text{Li}[\text{Al}(n\text{-C}_7\text{H}_{15})_4]$

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Scheme 1.

plus the monomer in benzene [12]. ROMP of norbornene was subsequently accomplished by employing ethanolic solutions of the monomer plus the late transition metal salts $RuCl_3 \cdot 3H_2O$, $OsCl_3 \cdot 3H_2O$, or $IrCl_3 \cdot 3H_2O$ [13]. Late transition metal catalysts are more robust than their early transition metal counterparts, as the early transition metal systems are sensitive to oxygen and water [14]. The first industrial facility (1976) to manufacture polynorbornene employed the catalytic system of $RuCl_3 \cdot 3H_2O$ in *n*-butanol [15].

Osmium complexes have been utilized in a small number of catalytic systems that provide polynorbornene by ROMP. The first such system, mentioned above, used $OsCl_3 \cdot 3H_2O$ as catalyst/precursor [13]. Chronologically, OsO_4 , $OsH_4(PPh_3)_3$, $Os(p\text{-cymene})Cl_2(PCy_3)$, $Cp^*Os_2Br_4$ (and related compounds), and $OsHCl(CO)(P^iPr_3)_2$ have been reported to possess norbornene ROMP activity [14,16]. Finally, the unsaturated $46e^-$ triosmium cluster $(\mu-H)_2Os_3(CO)_{10}$ has demonstrated norbornene ROMP activity [17]. Our interest in the cluster $(\mu-H)_2Os_3(CO)_9L$, where L is a “fluoroponytailed” tertiary phosphine compound, stems from recent work in our group concerning the polymerization of diazomethane by a variety of $(\mu-H)_2Os_3(CO)_9L$ clusters, L = phosphine, as models for chain growth in the Fischer–Tropsch reaction [18]. Herein, we describe our preparation (Scheme 2) and characterization of $(\mu-H)_2Os_3(CO)_9\{P(C_6H_4-4-CH_2CH_2(CF_2)_7CF_3)_3\}$, (**6**) and our discovery that ring-opening metathesis polymerization of norbornene occurs in the presence of **6**. The perfluoroalkyl-substituted triarylphosphine ligand imparts fluoruous solubility to **6**; in the context of Fluorous Biphasic Catalytic Systems, this fluorocarbon solubility

should result in the preferential solubilization of **6** in fluoruous media [9].

2. Experimental

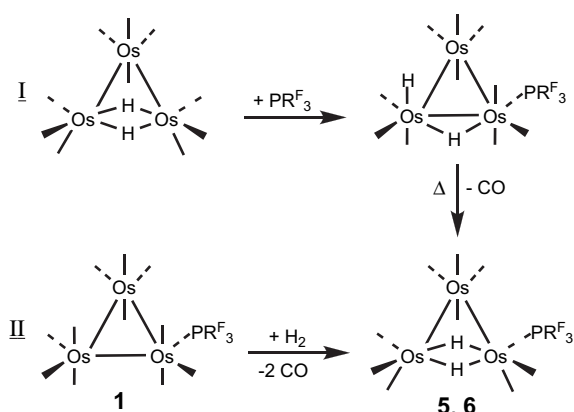
2.1. General information

Unless otherwise specified, all preparations and syntheses were performed under a nitrogen atmosphere while employing standard Schlenk techniques. Solvents were treated as follows: perfluoromethyldecalin, perfluoromethylcyclohexane, and benzotrifluoride were distilled from phosphorus pentoxide; dichloromethane and acetonitrile were distilled from calcium hydride; isooctane and octane were dried over anhydrous magnesium sulfate; hexane and toluene were distilled from sodium; ethyl ether (Fisher) was used as received; CFC-113 (Aldrich), $CDCl_3$, CD_2Cl_2 , and C_6D_6 (CIL) were used as received. Hydrogen (Matheson) was used as received. Trimethylamine-*N*-oxide dihydrate (Aldrich) was twice sublimed *in vacuo*. Triphenylphosphine (Aldrich) was recrystallized from benzene. Norbornene (Alfa Aesar, 99%) was used as received. $Os_3(CO)_{12}$ (Strem, 99%) was used as received. Pre-coated F_{254} silica gel TLC plates, 20 cm \times 20 cm \times 250 μ m (EMD Chemicals) were used as received. The compounds $Os_3(CO)_{11}(CH_3CN)$, $Os_3(CO)_{10}(CH_3CN)_2$, and $(\mu-H)_2Os_3(CO)_{10}$ were prepared by literature methods [19]. The fluoroponytail phosphine compounds $P(CH_2CH_2(CF_2)_5CF_3)_3$ and $P(C_6H_4-4-CH_2CH_2(CF_2)_7CF_3)_3$ were prepared by literature methods [20].

Infrared spectra were obtained on a Perkin–Elmer Model 1600 FT-IR spectrometer using a liquid cell with KBr plates. A Varian Unity-500 MHz spectrometer was used to obtain 1H , ^{19}F , and ^{31}P NMR spectra. The ^{19}F NMR and ^{31}P NMR chemical shifts are reported versus $CFCl_3$ and 85% H_3PO_4 respectively. The ^{19}F NMR assignments for **1–6** are consistent with the assigned ^{19}F NMR signals of the free ligands [20]. A Mettler H51 analytical balance, readability: 0.01 mg, typical: $U = 1\%$, was employed in the gravimetric determination of fluoruous/non-fluorous partitioning [21]. Field desorption mass spectra were performed on a Micromass 70-VSE mass spectrometer by the staff of the Mass Spectrometry Center of the School of Chemical Sciences. Elemental analyses were conducted by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

2.2. Preparation of $Os_3(CO)_{11}P(CH_2CH_2(CF_2)_5CF_3)_3$ (**1**)

A 25 mL Schlenk tube containing a magnetic stir bar was charged with 50.0 mg, 0.0544 mmol, of $Os_3(CO)_{11}(CH_3CN)$, both 5.0 mL of CH_2Cl_2 and 10.0 mL of a 0.0065 M, 0.065 mmol, solution of $P(CH_2CH_2(CF_2)_5CF_3)_3$ in $C_6H_5CF_3$ were added by syringe. The



5: $R^F = -CH_2CH_2(CF_2)_5CF_3$; Paths I and II
6: $R^F = -C_6H_4-4-CH_2CH_2(CF_2)_7CF_3$; Path I

Scheme 2.

Schlenk tube was placed in an oil bath at 75 °C for 45 min, and samples were periodically removed to monitor reaction progress by infrared spectroscopy. The solvents were removed under vacuum, and the residue was dissolved in ethyl ether and subjected to TLC separation. A mixture of *n*-pentane/dichloromethane/benzotrifluoride, 9:1:1, was employed as the eluent. Compound **1** moved as a yellow band, $R_f = 0.70$, and was isolated as a viscous, yellow liquid (0.0598 g, 56%) after extraction from the silica gel with dichloromethane. Anal. Calcd. for $C_{35}H_{12}F_{39}O_{11}Os_3P$: C, 21.55; H, 0.62. Found: C, 21.71; H, 0.91. IR (cyclohexane): $\nu(\text{CO})$, 2112 (m), 2060 (s), 2035 (s), 2024(vs), 2009 (w), 1994 (m), 1977 (m), 1959 (w) cm^{-1} . Mass Spec. (FD): m/z 1952 $[M^+]$. ^1H NMR (CDCl_3): δ 2.32 (2H, m, PC^1H_2), 2.24 (2H, m, $\text{C}^2\text{H}_2\text{CF}_2$). ^{19}F NMR (CDCl_3): δ_F -81.12 (3F, t, J_{FF} 12 Hz, C^8F_3), -115.01 (2F, m, C^3F_2), -122.19 (2F, m, C^4F_2), -123.20 (2F, m, C^6F_2), -123.53 (2F, m, C^7F_2), -126.51 (2F, m, C^5F_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ_P -19.66 (1P, s).

2.3. Preparation of $Os_3(\text{CO})_{10}(\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_2)$ (**2a–b**)

The procedure was analogous to that for **1**. In a typical synthesis 40.0 mg, 0.0429 mmol, of $Os_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ in CH_2Cl_2 was treated with 10.0 mL of a 0.0050 M, 0.050 mmol, solution of $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ in $\text{C}_6\text{H}_5\text{CF}_3$. Compound **2** was developed as a yellow band, $R_f = 0.15$, and was isolated as a viscous, yellow liquid (0.0509 g, 40%) following extraction from the silica gel with benzotrifluoride. Anal. Calcd. for $C_{58}H_{24}F_{78}O_{10}Os_3P_2$: C, 23.26; H, 0.81. Found: C, 22.97; H, 0.75. IR (CH_2Cl_2): $\nu(\text{CO})$, 2093 (m), 2034 (s), 2016 (sh), 2008(vs), 1972 (m), 1962 (m), 1952 (w) cm^{-1} . Mass Spec. (FD): m/z 2996 $[M^+]$. ^1H NMR ($\text{C}_6\text{H}_5\text{CF}_3/\text{C}_6\text{D}_6$): both isomers, δ 2.28 (2H, m, PC^1H_2), 2.10 (2H, m, $\text{C}^2\text{H}_2\text{CF}_2$). ^{19}F NMR ($\text{C}_6\text{H}_5\text{CF}_3/\text{C}_6\text{D}_6$): both isomers, δ_F -82.32 (3F, t, J_{FF} 10 Hz, C^8F_3), -115.56 (2F, m, C^3F_2), -122.89 (2F, m, C^4F_2), -124.00 (2F, m, C^6F_2), -124.27 (2F, m, C^7F_2), -127.42 (2F, m, C^5F_2). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{H}_5\text{CF}_3/\text{C}_6\text{D}_6$): **2a**, δ_P -21.38 (1P, s), and -25.54 (1P, s); ($\text{C}_6\text{H}_5\text{CF}_3/\text{C}_6\text{D}_6$): **2b**, δ_P -27.42 (2P, s).

2.4. Reactions of **1** with PPh_3 . Formation of $Os_3(\text{CO})_{10}(\text{PPh}_3)\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$ (**3a–c**) and $Os_3(\text{CO})_9(\text{PPh}_3)_2\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}$ (**4**)

A 50 mL round bottom Schlenk flask was charged with 50.0 mg, 0.0256 mmol, of **1**, 8.1 mg, 0.031 mmol, of PPh_3 , and 10.0 mL of octane. The Schlenk tube was heated in an oil bath for *circa* 1 h with solvent reflux. The octane was removed under vacuum, and the residue was dissolved in ethyl ether and subjected to TLC separation. A mixture of *n*-pentane/dichloromethane/benzotrifluoride, 9:1:1, was employed as the eluent. Three strongly colored bands, two yellow and one yellow-orange, were recovered by extraction from the silica gel with dichloromethane, and identified as compounds **1** ($R_f = 0.70$, 10.0 mg), **3** ($R_f = 0.55$), and **4** ($R_f = 0.20$). Compound **3** was isolated as a viscous, yellow liquid (231 mg) and compound **4** was isolated as a viscous, orange liquid (143 mg). The respective yields were 52% and 29%, based on the amount of **1** converted.

An analogous reaction with 50.0 mg, 0.0256 mmol, of **1** and 36.8 mg, 0.140 mmol, of PPh_3 in 10.0 mL of octane, with solvent reflux for 90 min, provided compounds **1**, **3**, and **4** as follows: **1**, 65 mg; **3**, 74 mg, 15% conversion; **4**, 212 mg, 39% conversion.

Compound 3. Anal. Calcd. for $C_{52}H_{27}F_{39}O_{10}Os_3P_2$: C, 28.58; H, 1.25. Found: C, 28.82; H, 1.17. IR (cyclohexane): $\nu(\text{CO})$, 2090 (m), 2034 (s), 2013 (sh), 2004(vs), 1978 (m), 1962 (m), 1949 (w), 1940(w) cm^{-1} . Mass Spec. (FD): m/z 2186 $[M^+]$. ^1H NMR (CD_2Cl_2 , -40 °C): all isomers, δ 7.47 (5H, m, PC_6H_5), 2.35 (2H, m, PC^1H_2), 2.27 (2H, m, $\text{C}^2\text{H}_2\text{CF}_2$). ^{19}F NMR (CD_2Cl_2 , -40 °C): all isomers, δ_F -81.43 (3F, t, J_{FF} 12 Hz, C^8F_3), -116.08 (2F, m, C^3F_2), -122.95 (2F, m, C^4F_2), -123.92 (2F, m, C^6F_2), -124.28 (2F, m, C^7F_2), -127.25 (2F, m, C^5F_2). $^{31}\text{P}\{^1\text{H}\}$

NMR (CD_2Cl_2 , -40 °C): **3a–b**, δ_P -0.97 (s, PPh_3), -5.50 (s, PPh_3), -20.00 (s, PR^F_3), -23.72 (s, PR^F_3); (CD_2Cl_2 , -40 °C): **3c**, δ_P -1.26 (d, J_{PP} 7.0 Hz, PPh_3), -21.27 (d, J_{PP} 7.0 Hz, PR^F_3).

Compound 4. Anal. Calcd. for $C_{69}H_{42}F_{39}O_9Os_3P_3$: C, 34.25; H, 1.75. Found: C, 34.16; H, 1.72. IR (cyclohexane): $\nu(\text{CO})$, 2057 (w), 2003 (sh), 1993 (sh), 1980(vs), 1945 (m), 1931 (w) cm^{-1} . Mass Spec. (FD): m/z 2420 $[M^+]$. ^1H NMR (CD_2Cl_2 , -20 °C): δ 7.44 (5H, m, PC_6H_5), 2.30 (2H, m, PC^1H_2), 2.24 (2H, m, $\text{C}^2\text{H}_2\text{CF}_2$). ^{19}F NMR (CD_2Cl_2 , -20 °C): δ_F -81.47 (3F, t, J_{FF} 12 Hz, C^8F_3), -115.90 (2F, m, C^3F_2), -122.82 (2F, m, C^4F_2), -123.79 (2F, m, C^6F_2), -124.05 (2F, m, C^7F_2), -127.11 (2F, m, C^5F_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -40 °C): δ_P -1.39 (s, PPh_3), -3.65 (s, PPh_3), -24.49 (s, PR^F_3).

2.5. Preparation of $(\mu\text{-H})_2Os_3(\text{CO})_9(\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3)$ (**5**)

In a 25 mL Schlenk tube containing a magnetic stir bar, 2.0 mL of chloroform was added to 40.0 mg, 0.0469 mmol, of $H_2Os_3(\text{CO})_{10}$ forming a purple solution, 55.6 mg, 0.0518 mmol of $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ was then added, resulting in a yellow solution attributed to the formation of $(\mu\text{-H})(\text{H})Os_3(\text{CO})_{10}(\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3)$. The chloroform was removed under vacuum, and the residue was re-dissolved in hexane. Infrared bands, $\nu(\text{CO})$, at 2108 (m), 2068 (s), 2055 (s), 2028 (vs), 2024 (sh), 2009 (m), 1990 (w), 1978 (w) cm^{-1} were observed for the hexane solution; the observed pattern is consistent with that of other reported clusters: $(\mu\text{-H})(\text{H})Os_3(\text{CO})_{10}\text{PR}_3$ [22]. The Schlenk tube was heated in an oil bath for 4.5 h under N_2 with solvent reflux to provide a deep green solution. Decarbonylation to **5** was confirmed by infrared spectroscopy, and the hexane was removed under vacuum. The residue was dissolved in benzotrifluoride and subjected to TLC separation. Dichloromethane was employed as the eluent. Compound **5**, $R_f = 0.85$, was isolated as a viscous, dark green liquid after extraction from the silica gel with dichloromethane. Anal. Calcd. for $C_{33}H_{14}F_{39}O_9Os_3P$: C, 20.89; H, 0.74. Found: C, 21.57; H, 1.08. IR (hexane): $\nu(\text{CO})$, 2097 (m), 2059 (s), 2021 (vs), 2015 (s,sh), 1997 (m), 1989 (m), 1982 (m), 1963 (w) cm^{-1} . Mass Spec. (FD): m/z 1898 $[M^+]$. ^1H NMR (CDCl_3): δ -11.44(2H, d, J_{PH} 8.0 Hz), 2.45 (6H, m, PC^1H_2), 2.35 (6H, m, $\text{C}^2\text{H}_2\text{CF}_2$). ^{19}F NMR (CDCl_3): δ_F -81.15 (3F, t, J_{FF} 12 Hz, C^8F_3), -114.98 (2F, m, C^3F_2), -122.16 (2F, m, C^4F_2), -123.22 (2F, m, C^6F_2), -123.61 (2F, m, C^7F_2), -126.52 (2F, m, C^5F_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ_P 18.47 (1P, s).

2.6. Formation of **5** by reaction of **1** with H_2

In a 3-neck 50 mL round bottom flask with condenser, gas inlet, thermometer adapter, and magnetic stir bar, 40.0 mg, 0.0205 mmol, of **1** were dissolved in 15.0 mL of perfluoromethyldecalin, and the yellow solution was sparged with H_2 for 30 min. The flask was placed in an oil bath and maintained under an H_2 atmosphere at an internal temperature of 102 °C for 135 min. Infrared and ^{31}P NMR spectra of samples from the reaction mixture revealed the presence of both **1** and **5**. The solvent was removed under vacuum, and preparative TLC was performed on reversed phase, octadecylsilane-coated plates (J.T. Baker) with acetonitrile as the eluent. Green, $R_f = 0.55$, and yellow bands moved and separated. Extracting with dichloromethane, compound **1** was isolated from the yellow band (159 mg), and compound **5** was isolated from the green band as a viscous, dark green liquid (105 mg, 45% yield based on the amount of **1** converted).

Longer reaction times or higher temperatures (in octane as solvent) did not result in higher yields of **5**. In the latter case a red precipitate formed as the solution cooled to room temperature. From spectroscopic evidence this material is formulated as largely $H_4Os_4(\text{CO})_{10}(\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_2)$. The ^1H NMR spectrum of the

precipitate possessed four resonances in the high field portion of the spectrum at -20.18 ppm, -20.52 ppm, -20.98 ppm, and -21.01 ppm assignable to bridging hydrides. The hydride signals did not integrate to whole numbers. The ^{31}P NMR spectrum of the precipitate contained two singlets at 5.85 ppm and 39.85 ppm. The field desorption mass spectrum of the precipitate featured two main signals at 3191 and 2916 amu. The former peak was attributed to the presence of $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{10}\{\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3\}_2$.

2.7. Preparation of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\{\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3\}$ (**6**)

In a 100 mL Schlenk tube containing a magnetic stir bar, 20.0 mL of hexanes was added to 75.0 mg, 0.0879 mmol, of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ to give a purple solution, 168 mg, 0.105 mmol, of $\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3$ was then added, resulting in a cloudy yellow suspension attributed to the formation of $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3\}$. After 90 min of stirring, infrared bands, $\nu(\text{CO})$, at 2106 (m), 2067 (s), 2052 (s), 2025 (vs), 2018 (sh), 2008 (m), 2001 (sh), 1984 (m), 1978 (m) cm^{-1} were observed for the supernatant; the observed pattern is consistent with that of other reported clusters: $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}\text{PR}_3$ [22]. Decarbonylation to **6** was achieved by heating the suspension under N_2 to solvent reflux for 2.5 h, during which period the color of the supernatant turned deep green. The hexanes were removed under vacuum, and the residue was dissolved in CFC-113 and subjected to TLC separation. A mixture of hexanes/toluene, 6:1, was employed as the eluent. Compound **6** was isolated, $R_f = 0.65$, as a very pale, purple solid after extraction from the silica gel with CFC-113. Anal. Calcd. for $\text{C}_{57}\text{H}_{26}\text{F}_{51}\text{O}_9\text{Os}_3\text{P}$: C, 28.23; H, 1.08. Found: C, 28.37; H, 1.19. IR (hexane): $\nu(\text{CO})$, 2092 (m), 2054 (s), 2014 (vs), 2005 (m,sh), 1990 (m), 1978 (w), 1962 (w) cm^{-1} . Mass Spec. (FD): m/z 2426 $[\text{M}]^+$. ^1H NMR (C_6D_6): δ -9.84 (2H, d, $J_{\text{P-H}}$ 7.0 Hz), 7.40 (2H, dd), 6.64 (2H, dd), 2.46 (2H, m, PC^1H_2), 1.91 (2H, m, $\text{C}^2\text{H}_2\text{CF}_2$). ^{19}F NMR (C_6D_6): δ_{F} -81.4 (3F, t, J_{FF} 11 Hz, C^{10}F_3), -114.7 (2F, m, C^3F_2), -122.0 (2F, m, C^5F_2), -122.3 (4F, m, $\text{C}^6\text{F}_2\text{C}^7\text{F}_2$), -123.2 (2F, m, C^8F_2), -123.7 (2F, m, C^4F_2), -126.6 (2F, m, C^9F_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ_{P} 26.7 (1P, s).

2.8. Crystallographic analysis of **4**

Diffraction quality, yellow crystals of compound **4** were formed as a saturated dichloromethane solution diffused into a layer of ethanol at ambient temperature. The structure was solved by employing direct methods within the SHELXTL software package [23]. The correct positions for the osmium and phosphorus atoms were deduced from direct methods E-maps; subsequent least squares refinement and difference Fourier calculations established the positions of the remaining non-hydrogen atoms, which were refined with independent anisotropic displacement parameters. Hydrogen atoms were fixed in idealized positions and their displacement parameters were tied to those of the attached non-hydrogen atom. Successful convergences were indicated by maximum shift/error values that approached 0.002 for the last cycle(s) of the least squares refinements. In the final Fourier difference map, the largest peak, $2.07 \text{ e}\text{\AA}^{-3}$, was located 1.03 \AA from the fluorine atom F48A. Final analyses of variance between calculated and observed structure factors exhibited no perceptible errors.

For every molecule of **4** there existed one-half molecule of solvate, dichloromethane, possessing two disordered sites that have occupancy factors of 32% and 18%, respectively. In the solid state, **4** exhibited thermal movement along the ponytail C41 to C48, including the associated fluorine and hydrogen atoms, resulting in the disorder of this particular phosphine substituent. Accordingly, our model provides two sets of positions for each of these 25 atoms,

with an average site occupancy for each set of 64% and 36%, respectively.

Crystallographic data for **4**, $\text{C}_{69}\text{H}_{42}\text{F}_{39}\text{O}_9\text{Os}_3\text{P}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$: $M = 2462.10$, Monoclinic, space group $\text{P}2_1/c$, $a = 33.17(2) \text{ \AA}$, $b = 22.38(2) \text{ \AA}$, $c = 10.996(8)$, $\beta = 98.04(1)^\circ$, $V = 8083(10) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.023 \text{ g/cm}^3$, $\mu(\text{Mo K}\alpha) = 4.940 \text{ mm}^{-1}$, $T = 193(2) \text{ K}$, 14 851 independent reflections, psi-scan absorption correction ($\mu = 4.940 \text{ mm}^{-1}$), R_1 (all data) = 0.0982, wR_2 (all data) = 0.1511, 9574 independent observed reflections ($I > 2.0\sigma(I)$), R_1 ($I > 2.0\sigma(I)$) = 0.0531, wR_2 ($I > 2.0\sigma(I)$) = 0.1333, restraints/parameters = 1175/1330.

2.9. Measurement of partition coefficients

For each complex a 4 mL vial was tared and *circa* 10 mg of the compound (**1–4**, **6**) was placed in the vial, $\text{C}_6\text{F}_{11}\text{CF}_3$ (1.00 mL) and $\text{C}_6\text{H}_5\text{CH}_3$ (1.00 mL) were then added. At ambient temperature, compounds **1**, **2**, and **6** dissolved in the fluororous phase. With agitation, compounds **3** and **4** dissolved in both phases, but **3** favored perfluoromethylcyclohexane, whereas **4** preferred toluene. The vials were sealed, placed in an oil bath, and the bath temperature was increased until a homogeneous solution ($95\text{--}100^\circ\text{C}$) resulted. This temperature was maintained for 30 min. The mixtures became opalescent before achieving homogeneity. After cooling to ambient temperature, the hydrocarbon phase was separated by syringe and was placed in a separate, tared vial, all solvents were removed under vacuum, and the amount of compound in each vial was determined gravimetrically [21]. The partitioning percentages, fluorocarbon/hydrocarbon, for compounds **1** and **2** were 94.2/5.8 and 96.2/3.8, respectively; percentages for compounds **3** and **4** were 33.2/66.8 and 8.9/91.1, respectively. The fluorocarbon/hydrocarbon ratio for **6** was 94.8/5.2.

2.10. Polymerization of norbornene in the presence of **6**

(A) *Toluene*. In a 20 mL screw cap vial with stir bar, 8 mL of toluene was added to 11.92 mg, 4.915 μmol , of **6**, then 3100 equivalents, 1417.81 mmol, of norbornene were added to the vial. The vial was sealed with a thin pad of 1.0 inch wide PTFE tape, flushed with N_2 , capped, and placed in an oil bath held at 70°C . After 40 h, free movement of the stir bar was visibly hindered by the viscosity of the solution. The toluene and the remaining norbornene were removed under vacuum providing 238.80 mg of polymer film. The polymer film was washed with $6 \times 2.0 \text{ mL}$ aliquots of benzotrifluoride until the washings were colorless. The film was then washed with $2 \times 2.0 \text{ mL}$ aliquots of CFC-113. The CFC-113 washings also appeared to be colorless. All washings were combined and the solvents were removed under vacuum to provide 5.84 mg of green/yellow residue. The remaining polymer film was also a green/yellow color.

Polymer. An infrared spectrum of the film was consistent with previously published results, and indicated that ring-opening metathesis polymerization of norbornene had occurred [12]. The ^1H and ^{13}C NMR spectra, in benzene- d_6 (yellow solution), confirmed the ROMP of norbornene [24,25]. *Polynorbornene*, ^1H NMR (C_6D_6): δ 5.50 (s, br), 5.35 (s, br), 2.90 (s, br), 2.51 (s, br), 2.02 (s, br), 1.83 (s, br), 1.42 (s, br), 1.17 (s, br). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 134.2 (m), 133.4 (m), 43.9 (s), 43.6 (s), 43.1 (s), 42.4 (s), 41.7 (s), 39.1 (s), 38.8 (s), 33.4 (s), 33.2 (s), 32.7 (s), 32.5 (s).

Recovered osmium. The collected green/yellow residue from the fluororous solvent washings was dissolved in benzene- d_6 and proton and phosphorus-31 NMR spectra were obtained. The residue was also analyzed by field desorption mass spectroscopy. The δ 1.0–5.5 region of the ^1H NMR spectrum was dominated by broad signals

attributable to polynorbornene, these signals masked those of the methylene groups of **6**. Additional signals, not assignable to either **6** or polynorbornene, were observed in the δ 2.0–5.0 and δ 6.5–7.5 regions. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the residue showed the signal of **6** at δ 26.7. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also exhibited an additional five singlets. *Green/yellow residue*, signals not attributable to **6** or to the polymer: ^1H NMR (C_6D_6): δ 4.82 (s), 4.04 (t), 2.97 (t), 2.56 (t); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): 20.6 (s), 20.7 (s), 18.7 (s), -2.0 (s), -18.3 (s). The mass spectrum of the residue exhibited six major signals in the range 2398–2670 amu. Five signals were assigned as triosmium clusters related to $[\mathbf{6}]^+$, m/z 2426. The signal at m/z 2670 remained unassigned. Assigned peaks: m/z 2398 $[\text{M} - \text{CO}]^+$, 2426 $[\text{M}]^+$, 2492 $[\text{M} - \text{CO} + \text{C}_7\text{H}_{10}]^+$, 2520 $[\text{M} + \text{C}_7\text{H}_{10}]^+$, 2586 $[\text{M} - \text{CO} + 2\text{C}_7\text{H}_{10}]^+$.

(B) *Benzotrifluoride*. In a 20 mL screw cap vial (Vial 1) with stir bar, 8 mL of $\text{CF}_3\text{C}_6\text{H}_5$ was added to 11.0 mg, 4.54 μmol , of **6**, then ca. 1900 equivalents, 812.9 mg, 8.634 mmol, of norbornene were added to the vial. The vial was sealed as noted above, and placed in an oil bath held at 70 °C. After 72 h, the bottom and walls of the vial were coated with a polymer film and polymer filaments were visible in the green/yellow supernatant. The supernatant was decanted into Vial 2. (The polymer coating and the yellow supernatant suggested that the substituted triosmium cluster was preferentially soluble in the benzotrifluoride.) The benzotrifluoride and the remaining norbornene were removed from both vials under vacuum. Vial 1 contained 54.7 mg of reaction residue, and Vial 2 (supernatant) provided an additional 42.3 mg of reaction residue for a total of 97.0 mg.

Polymer. A sample of polymer film from Vial 1 was dissolved in benzene- d_6 and ^1H and ^{13}C NMR spectra were obtained. The spectra were consistent with the spectra obtained from the polymers produced in toluene. The contents of Vial 2 were divided into two parts: 25.8 mg of reaction residue in Vial 2, and 16.5 mg of reaction residue in Vial 3. In Vial 2, the residue was re-dissolved in 4 mL of $\text{CF}_3\text{C}_6\text{H}_5$, and 681.9 mg, 7.242 mmol, of norbornene were added to the vial. Vial 2 was sealed as noted above, and placed in an oil bath held at 70 °C. After 30 h, the solvent was removed under vacuum and Vial 2 contained a total of 62.9 mg of polymer film, an additional 37.1 mg of polynorbornene. The contents of Vial 3 were examined by ^1H NMR spectroscopy, which showed only the broad peaks associated with polynorbornene. The residue was then dissolved in a 1:1 mixture of $\text{CF}_3\text{C}_6\text{H}_5$ and toluene, and subjected to TLC separation. A 6:1 mixture of hexanes and toluene was employed as eluent. A single yellow band moved, and 2.1 mg of viscous, yellow material were recovered after extraction from the silica gel with dichloromethane. The yellow material was examined by field desorption mass spectroscopy, and also IR, ^1H NMR, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies. The infrared spectrum, in CH_2Cl_2 , did not exhibit those peaks characteristic of **6**. However, the overall pattern suggested a triosmium cluster. The $^{31}\text{P}\{^1\text{H}\}$ spectrum showed three unidentified singlets at δ 20.6, 20.4, and -2.0 . The ^1H NMR spectrum exhibited some signals consistent with the substituted triphenylphosphine ligand. In contrast to the spectrum of **6**, the signals in the δ 6.5–8.0 region were 0.10 ppm downfield and both signals were multiplets as opposed to doublets of doublets. The ponytail methylene signals remained unchanged. Additionally, there were two doublets at δ -12.61 , and -12.65 . The mass spectrum showed two major and six minor peaks in the region 2398–2674 amu. Five signals were assigned as triosmium clusters related to $[\mathbf{6}]^+$, m/z 2426. The signals at m/z 2460, 2478, and 2674 remained unassigned. Assigned peaks: m/z 2398 $[\text{M} - \text{CO}]^+$, 2426 $[\text{M}]^+$, 2492 $[\text{M} - \text{CO} + \text{C}_7\text{H}_{10}]^+$, 2520 $[\text{M} + \text{C}_7\text{H}_{10}]^+$, 2548 $[\text{M} + \text{CO} + \text{C}_7\text{H}_{10}]^+$.

(C) *Benzotrifluoride/toluene*. In a 20 mL screw cap vial with stir bar, 4 mL of $\text{CF}_3\text{C}_6\text{H}_5$ and 4 mL of $\text{CH}_3\text{C}_6\text{H}_5$ were added to 13.87 mg,

5.718 μmol , of **6**, then, ca. 3400 equivalents, 1817.7 mg, 19.305 mmol, of norbornene were added to the vial. The vial was sealed as noted above and placed in an oil bath held at 95 °C. After 40 h, 2 mL of perfluoromethylcyclohexane and 5 mL of toluene were added to the vial, which was placed in a 70 °C oil bath for an addition 30 min with stirring. Separation into two phases began after the cessation of stirring. After resting for 120 min, a clear, green fluorocarbon phase was removed by syringe. A second 2 mL aliquot of $\text{CF}_3\text{C}_6\text{F}_{11}$ was added to the vial and the 30 min oil bath immersion with stirring was repeated. After phase separation, a colorless fluorocarbon phase was removed by syringe. The organic phase remained a yellow color throughout. After resting an additional 180 min, the polymer strands settled and a clear, yellow supernatant was removed by syringe. All solvents were removed under vacuum. The perfluoromethylcyclohexane extracts provided 9.21 mg of viscous, green residue – Part A. A yellow polymer film was obtained by removal of the solvents from the supernatant – Part B. Finally, a yellow polymer film remained in the vial – Part C. In total, 122.92 mg of polymer film and residual (osmium) material were collected from Parts A, B, and C.

Polymer. A sample of polymer film, from Part B, was dissolved in benzene- d_6 and ^1H and ^{13}C NMR spectra were obtained. The spectra were consistent with those of the polymers produced in toluene.

Recovered osmium. The green residue, Part A, was examined by field desorption mass spectroscopy and by ^1H NMR, ^{19}F NMR, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies. The results of all four spectroscopic experiments clearly identified **6** as the major component of the green residue. However, in addition to the singlet of **6** at δ 26.7, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited singlets at δ 18.6 and -2.0 . In the δ 6.5–8.0 region of the proton spectrum, there was one multiplet of lesser intensity downfield of each of the two doublet of doublets assigned to **6**. (This suggests that the perfluoroalkyl-substituted phosphine is in a different environment from that of **6**.) The major signal in the mass spectrum at m/z 2426 was characteristic of **6**. Additional signals of lesser intensity were featured at m/z 2398 $[\text{M} - \text{CO}]^+$, m/z 2492 $[\text{M} - \text{CO} + \text{C}_7\text{H}_{10}]^+$, and m/z 2548 $[\text{M} + \text{CO} + 2\text{C}_7\text{H}_{10}]^+$.

3. Results and discussion

3.1. Preparation of the fluororous ligand–triosmium complexes **1** and **2**

The lightly stabilized complexes $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ and $\text{Os}_3(\text{CO})_{11}\text{MeCN}$ react with $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ in hot benzotrifluoride to produce the compounds $\text{Os}_3(\text{CO})_{11}\text{L}$ (**1**) and $\text{Os}_3(\text{CO})_{10}\text{L}_2$ (**2**). Preparative thin-layer chromatography workup of the reaction residues on normal silica gel plates but mixing some benzotrifluoride into the eluting solvent provided sufficient separation to allow isolation of the derivatives **1** and **2** in moderate yields as air-stable, viscous yellow liquids. All attempts to crystallize these derivatives were fruitless, but elemental analysis (C, H) and mass spectral molecular ions established the composition and purity of the compounds. To our knowledge, compounds **1** and **2** are the first reported transition metal cluster compounds bearing fluororous substituted aliphatic tertiary phosphine ligands.

The infrared spectrum of **1** in the carbonyl stretching region exhibits a pattern comparable to $\text{Os}_3(\text{CO})_{11}\text{PPh}_3$ [19a,26]. The carbonyl stretching frequencies of **1** are, generally but not exclusively, 3 to 5 wavenumbers higher than those of $\text{Os}_3(\text{CO})_{11}\text{PPh}_3$. The infrared spectrum of **2** in the carbonyl stretching region displays a pattern similar to $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ [26]. All carbonyl stretching frequencies of **2** are at consistently higher wavenumbers than those of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$. These data suggest the fluoro ponytail phosphine $\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ is a better π -acceptor than PPh_3 . This ranking of π -accepting ability agrees with the results of our studies

of compounds $W(CO)_5L$, where L is a tertiary fluoroonytail phosphine ligand [27]. The ^{31}P NMR spectra of **1** consists of one broad singlet. The ^{31}P NMR spectrum of **2** exhibits three singlets corresponding to two isomers: **2a** and **2b**, Fig. 1. The equally intense, broad signals at -21.38 and -25.54 ppm are due to **2a**, and the resonance at -27.42 ppm is due to **2b**. As with the infrared, the ^{31}P NMR spectrum of **2** is comparable to that of $Os_3(CO)_{10}(PPh_3)_2$ [28]. The ^{31}P NMR spectrum of $Os_3(CO)_{10}(PPh_3)_2$ also possesses three singlets attributable to two solution state isomers. Regarding the ^{31}P NMR spectra, one interesting difference between **2** and $Os_3(CO)_{10}(PPh_3)_2$ is the three singlets of **2** were broad but visible at ambient temperature, whereas those of $Os_3(CO)_{10}(PPh_3)_2$ were apparent at -80 °C and coalesced at *circa* 30 °C [28]. The structural fluxionality of $Os_3(CO)_{12-x}(L)_x$, where $x = 1-3$, that accounts for both the broad ^{31}P NMR signals of **1** and **2** and, the isomerization of **2** and $Os_3(CO)_{10}(PPh_3)_3$ has also been observed in compounds **3** and **4** and will be discussed below. Both the fluorine-19 and proton NMR spectra of compounds **1** and **2** display the occurrence of slight, random coordination chemical shifts versus the free ligand.

3.2. Preparation of triphenylphosphine derivatives **3** and **4**

In octane at reflux, compound **1** plus *circa* one equivalent of PPh_3 reacted to provide both the mono-substitution product $Os_3(CO)_{10}(PPh_3)P(CH_2CH_2(CF_2)_5CF_3)_3$ (**3**) and a small amount of the di-substitution product $Os_3(CO)_9(PPh_3)_2(P(CH_2CH_2(CF_2)_5CF_3)_3)$ (**4**). In the presence of excess PPh_3 , the formation of **4** was favored. Additional side and/or decomposition products, observed after preparative thin-layer chromatography, were formed in these reactions. Preparative thin-layer chromatography workup of the reaction residues provided the air-stable derivatives **3** and **4**, in adequate yields. Elemental analysis (C, H) and mass spectral molecular ions established the composition and purity for all four compounds.

$Os_3(CO)_{12}$ reacts thermally with tertiary phosphines, L, to form the substitution products $Os_3(CO)_{12-x}(L)_x$, where $x = 1-3$. The extent of substitution, and the formation of side products, can be partially controlled via reaction temperatures. In toluene at reflux (111 °C), $Os_3(CO)_{12}$ plus an excess of PEt_3 produced all 3 adducts. With reactants in similar proportions in xylene at reflux (*ca.* 139 °C), only $Os_3(CO)_9(PEt_3)_3$ was recovered [29]. In nonane at reflux (151 °C), both $Os_3(CO)_{11}PMe_3$ and $Os_3(CO)_{11}PEt_3$ underwent intramolecular C-H bond activation at an α -carbon-hydrogen position to create four-centered, Os-P-C-Os, metallocycles [30]. In xylene at reflux (*ca.* 139 °C), $Os_3(CO)_{12}$ plus 2 equivalents of PPh_3 provided all 3 adducts. However, beyond the expected adducts, six additional derivatives were isolated. Spectroscopic and structural characterization revealed the occurrence of significant intramolecular C_{aryl} -H bond activation at the carbon-hydrogen bond *ortho* to the phosphorus-aryl bond (*ortho*-metallation) [31].

The infrared spectra of **3** and **4** in the carbonyl stretching region exhibit patterns comparable to $Os_3(CO)_{10}(PPh_3)_2$ and $Os_3(CO)_9(PPh_3)_3$, respectively [26]. The carbonyl stretching frequencies of **3** are, with

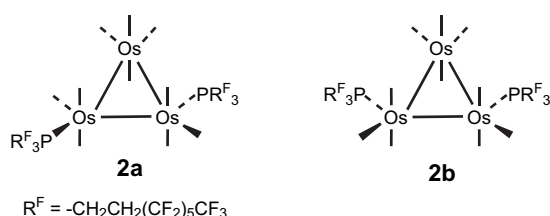


Fig. 1. Isomers of **2**.

one exception, at wavenumbers between the equivalent peaks displayed in the infrared spectra of **2** and $Os_3(CO)_{10}(PPh_3)_2$. The peaks in the infrared spectrum of **4** are at consistently higher wavenumbers than those of $Os_3(CO)_9(PPh_3)_3$. The phosphorus-31 NMR spectra of **3** and **4** at ambient temperature exhibit six and three phosphorus environments, respectively. The nine signals are broad but sharpen rapidly as the temperature is lowered. Our reported chemical shifts for **3** and **4** are from spectra obtained at -40 °C. The ^{31}P NMR spectra of compounds **1** and **2** both display modest coordination chemical shifts for $P(CH_2CH_2(CF_2)_5CF_3)_3$. The ^{31}P NMR spectra of compounds **3** and **4** also exhibit limited coordination chemical shifts for both $P(CH_2CH_2(CF_2)_5CF_3)_3$ and PPh_3 . Thus, there exists a distinct “ PR^F_3 region” and a distinct “ PPh_3 region” to the phosphorus-31 NMR spectra of **3** and **4**.

In general, a phosphine ligand will occupy one of six equatorial positions available on the triosmium triangle. However, it is unusual for two phosphines to be coordinated to the same osmium atom. Also, with the exception of bidentate phosphine ligands, it is unusual for two tertiary phosphine ligands to coordinate to one edge of the trigonal planar triosmium cluster [1b]. The ^{31}P NMR spectrum of **3** exhibits three unique PR^F_3 environments and three unique PPh_3 environments. In light of the aforementioned preferences regarding phosphine coordination to the triosmium triangle, we propose the six ^{31}P NMR resonances of **3** are due to the existence of three isomers in solution: **3a**, **3b**, and **3c**, Fig. 2. Each isomer possesses a unique PR^F_3 and PPh_3 environment with respect to the other two isomers. Two of the six signals in the ^{31}P NMR spectrum of **3**, are barely discernible as doublets, $^3J_{PP} = 7.0$ Hz, one doublet each in the PR^F_3 and PPh_3 regions. We believe this weak coupling identifies **3c** as the source of these resonances. Finally, there is only one “most likely” configuration for **4**. In this configuration, there are two different PPh_3 positions and the position for PR^F_3 accounts for all three singlets in the phosphorus-31 NMR spectrum of **4**. This configuration is also achieved in the solid state, *vide infra*, Fig. 3. As observed in the various ^{31}P NMR spectra, the broad, ambient temperature signals and the isomerization evinced by multiple phosphorus environments are indicative of the nonrigidity of compounds **1**, **2**, **3**, and **4**.

The structural fluxionality of $Os_3(CO)_{12-x}(L)_x$, where L is a tertiary phosphine or phosphite ligand and $x = 1-3$, has been thoroughly studied [32]. There have been two conclusions, regarding phosphine and phosphite ligands, based on NMR evidence. The first is that phosphine or phosphite ligands do not migrate about the triosmium framework [32d]. This conclusion supports earlier positions of isomerization based on limited turnstile rotations at those osmium atoms possessing phosphine or phosphite ligands [32a–c]. However, there has been a recent report regarding the isomerization of $Os_3(CO)_{10}(P-P)$, where P–P is an

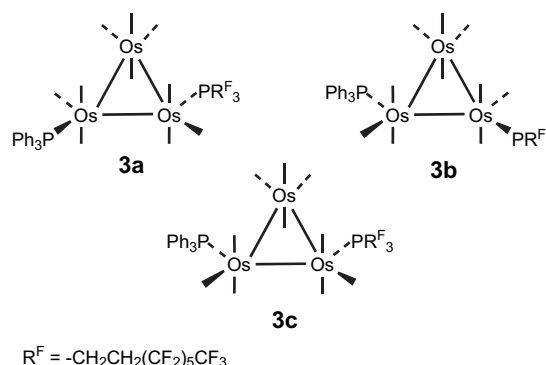


Fig. 2. Isomers of **3**.

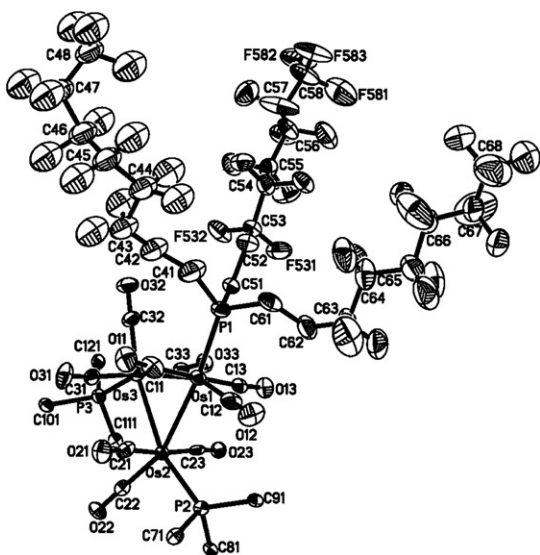


Fig. 3. ORTEP diagram (35%) of complex **4**, all hydrogen, and thirty phenyl carbon, atoms removed.

unsaturated derivative of diphenylphosphinoethane, (*Z*)-Ph₂PCH=CHPh₂ [33]. This cluster exhibited reversible diphosphine isomerization from a bridged configuration, along one edge of the osmium triangle, to a chelated configuration. The analogous isomerization of Os₃(CO)₁₀(dppe) is not known to occur. The authors attribute this unusual behavior to the “*Z*” configuration and the rigid backbone of the bidentate phosphine ligand. Two possible mechanisms are discussed; both mechanisms feature “terminal-bridge-terminal” migration of one phosphorus moiety with simultaneous involvement, and analogous behavior, of at least one carbonyl group. The “terminal-bridge-terminal” migration of carbonyl groups about triangular, Group 8 transition metal frameworks has long been an accepted phenomenon [34].

3.3. Crystal structure of Os₃(CO)₉(PPh₃)₂{P(CH₂CH₂(CF₂)₅CF₃)₃} (**4**)

Compound **4** has been characterized by single crystal X-ray diffraction. The crystal structure of compound **4** is presented in Fig. 3 and a view of the molecular structure of **4** is shown in Fig. 4. The solid state packing appears to be controlled by the fluoro-ponytail moieties. However, the partition coefficients indicate complex **4** prefers organic phases. Thus, it is also appropriate to state that the solid state packing appears to be controlled by the organic moieties. The osmium triangles align side-by-side, in an orientation creating a “fluorous plane” (ponytail-to-ponytail-to-ponytail) and an “organic plane” (phenyl-to-phenyl-to-phenyl). These fluorous and organic planes then stack in a like-to-like manner, thus constructing explicit, alternating (-fluorocarbon-hydrocarbon-)_n layers. Another interesting feature is the conformation of the fluoro-ponytail chains. None of the three fluoro-ponytails can be described as fully trans-extended, as each chain displays some twisting and/or kinking. Also, the ellipsoids reveal considerable thermal motion that increases along the length of the chain. The twisting, flexing, or kinking of the fluoro-ponytail chains has been consistently observed in the few existing structures of transition metal compounds ligated by tertiary fluoro-ponytail phosphines [27,35], including the five known structures of transition metal complexes bearing the P(CH₂CH₂(CF₂)₅CF₃)₃ ligand [27,35a–e]. The increasing thermal motion exhibited toward the ends of any given fluorocarbon chain is another trait generally shared by known structures.

The osmium atoms reside in a planar, triangular array approaching an equilateral triangle. The three osmium–osmium bond distances of **4** are 2.899 (2) Å, 2.910 (2) Å, and 2.919 (1) Å, an average of 2.909 Å. The average osmium–osmium bond lengths of Os₃(CO)₉(PPh₃)₃ and Os₃(CO)₁₂ are 2.910 Å and 2.877 Å, respectively [36,37]. Individual osmium atoms achieve a distorted octahedral coordination sphere as the remaining two osmium atoms each occupy an equatorial position in the coordination sphere of the osmium under consideration. Thus, two axial and two equatorial coordination sites are available, and filled, on each osmium

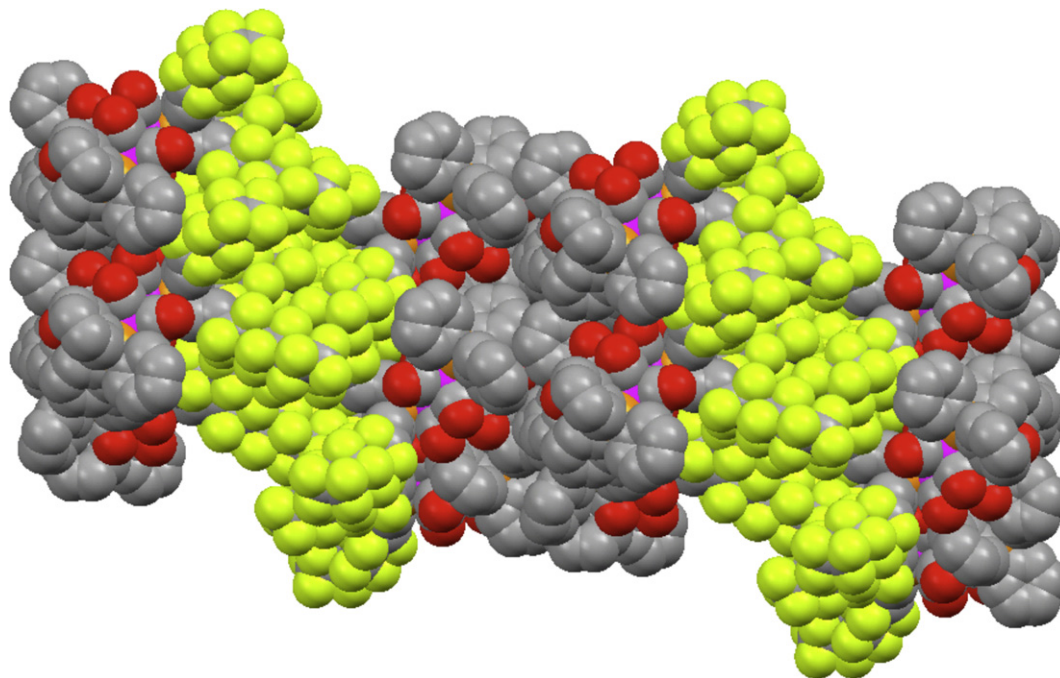


Fig. 4. Solid-state packing of complex **4**.

atom of **4**. There is one phosphine ligand per osmium atom, with the phosphines occupying every other equatorial site in a staggered arrangement. This arrangement places one phosphine on each triangular edge and maximizes the distance between the phosphine ligands.

Phosphine substitution generally results in a distortion away from D_{3h} symmetry by the entire molecule. To relieve steric interaction, each $\text{Os}(\text{CO})_3\text{L}$ and $\text{Os}(\text{CO})_4$ unit sympathetically rotates on the twofold axis passing through each osmium atom. That is, all axial carbonyl ligands are no longer strictly perpendicular to the plane of the osmium triangle and all equatorial ligands are no longer strictly in the plane of the osmium triangle. The average dihedral angle of the axial carbonyl ligands, $C_{\text{axial}} - \text{Os} - \text{Os} - C_{\text{axial}}$, in reference to the triosmium plane, is used to measure and report this rotation [28,36,38]. The average dihedral angle for **4** is 13.3° . The average distortion for $\text{Os}_3(\text{CO})_{11}\text{PPh}_3$ is 11.3° [38a]. The average dihedral angle of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ depends on the isomer (see Fig. 1 for the analogous isomers of **2**). The distortions of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ are 9.7° for the “*trans*” isomer and 21.7° for the “*cis*” isomer [28].

3.4. Preparation of the unsaturated dihydrido complexes **5** and **6**

The parent compound $\text{Os}_3(\text{CO})_{12}$ reacts with H_2 at atmospheric pressure in hot octane initially to form the unsaturated dihydrido complex $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$, but prolonging the reaction results in the formation of $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{12}$ [19c]. In both hot octane and hot perfluoromethyldecalin, **1** reacted with H_2 at atmospheric pressure to provide $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ (**5**), in low yield, and prolonged exposure of **1** to H_2 in hot octane produced a viscous, red precipitate that spectroscopic data suggest contained $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{10}(\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_2)_2$. The field desorption mass spectrum of the precipitate featured two main signals at 3191 and 2916 amu. The peak at 3191 amu is attributed to M^+ and the peak at 2916 amu can be considered $[\text{M}-\text{Os}(\text{CO}_3)]^+$. The ^{31}P NMR spectrum of the precipitate contained two singlets at 5.85 ppm and 39.85 ppm. The proton NMR spectrum of the precipitate possessed four resonances in the high field portion of the spectrum assignable to bridging hydrides at -20.18 ppm, -20.52 ppm, -20.98 ppm, and -21.01 ppm. The hydride signals do not integrate to rational numbers. A number of tetraosmium clusters of the general formula $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{10}(\text{L}-\text{L})$, where L–L are chelating, bidentate phosphine ligands, have been synthesized and both structurally and spectroscopically characterized [39]. The ^{31}P NMR spectra of these tetraosmium clusters exhibit either one or two singlet resonances, while the proton NMR spectra possess either one multiplet (4H) or two multiplets (2H and 2H). The complexes $(\mu\text{-H})_4\text{Os}_4(\text{CO})_{10}(\text{L}-\text{L})$ possessing more flexible chelates exhibit two ^{31}P NMR signals, while those compounds with less flexible chelates display one ^{31}P NMR resonance.

Compounds **5** and **6** have been prepared via a more traditional methodology. Consistent with the results of Deeming et al. and Keister et al. [22], the perfluoroalkyl-substituted tertiary phosphines, $\text{L} = \text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ or $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3$, add to $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ in solution to generate the cluster $\text{H}(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{L}$. At the temperature of refluxing hexane, CO is lost to provide the substitution product $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$ (**5**) or $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3$ (**6**), respectively. Preparative thin-layer chromatography of the reaction residues, using silica-gel plates and a mixture of hexanes and toluene as eluent, provided the air-stable compound **6** in good yield. Elemental analysis (C, H) and the mass spectral molecular ion established the composition and purity for **6**.

3.5. Solubility properties of compounds **1–4** and **6**, partition coefficients

Compounds **1** and **2** are slightly soluble in short-chain and cyclic hydrocarbon solvents such as pentane, hexane, and toluene, whereas both **3** and **4** are fully soluble in these solvents. All four compounds are soluble in ether, THF, acetone, dichloromethane, chloroform, and the partially fluorinated solvents 1,1,2-trichlorotrifluoroethane, and benzotrifluoride. Compounds **1** and **2** are fully soluble in perfluoromethylcyclohexane and perfluorodecalin, whereas **3** is just partially soluble, and **4** is only slightly soluble in these perfluorinated solvents. Compound **6** is moderately soluble in short-chain and cyclic hydrocarbon solvents such as hexanes, benzene, and toluene, slightly soluble in ether, dichloromethane, and chloroform, and fully soluble in the partially fluorinated and perfluorinated solvents 1,1,2-trichlorotrifluoroethane (CFC-113), benzotrifluoride, and perfluoromethylcyclohexane.

Partition coefficients for compounds **1**, **2**, **3**, **4**, and **6** were established within the fluorous biphasic solvent system of toluene:perfluoromethylcyclohexane. These two solvents are miscible at temperatures above 88.6°C , and are the most commonly used pair in the determination of partitioning percentages [40]. The partitioning percentages, hydrocarbon/fluorocarbon, for **1** and **2** were 5.8/94.2 and 3.8/96.2, respectively. The corresponding values for **3** and **4** were 66.8/33.2 and 91.1/8.9, respectively. The partitioning percentages, hydrocarbon/fluorocarbon, for compound **6** were 5.8/94.8. For $\text{L} = \text{P}(\text{CH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3)_3$, partitioning percentages for a number of mono- and bis-substituted compounds have been reported. Specifically, hydrocarbon/fluorocarbon partitioning percentages for $\text{W}(\text{CO})_5\text{L}$, and $[\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2(\text{CF}_2)_9\text{CF}_3]\text{Rh}(\text{CO})\text{L}$ are 3.6/96.4 and 3.3/96.7, respectively [27,41]. The latter complex possesses a cyclopentadienyl ring bearing a single fluoroonyl substituent in addition to ligation by a perfluoroalkyl-substituted tertiary phosphine. The compounds *trans*- $\text{Ir}(\text{CO})(\text{Cl})\text{L}_2$, *trans*- $\text{Ni}(\text{Cl})_2\text{L}_2$, and $[\text{Ru}(\mu\text{-MeCO}_2)(\text{CO})_2\text{L}]_2$ possess partitioning percentages of 1.2/98.8, 0.3/99.7, and 0/100, respectively [35a,41,35e]. The partitioning percentages for **1** and **2** are consistent with reported percentages insofar as the bis-substituted cluster exhibits the greater retention in a fluorocarbon phase. However, it is clear that clusters **1** and **2** have lower fluorocarbon retentions than mononuclear compounds. The substitution of triphenylphosphine for carbon monoxide, creating **3** and **4** from **1**, resulted in large changes to the partitioning percentages, to the extent that the partitioning of **4** is approximately the reverse of **1**. The compounds $\text{W}(\text{CO})_5\text{L}$ and $[\text{Ru}(\mu\text{-O}_2\text{CCH}_3)(\text{CO})_2\text{L}]_2$, where $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3$, possess toluene/PFMCH partitioning percentages of 9.8/90.2 and 7.3/92.7, respectively [27,35e]. No other partitioning data has been reported for transition metal complexes ligated by $\text{P}(\text{C}_6\text{H}_4\text{-4-CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3)_3$.

3.6. ROMP polymerization of norbornene

The unsaturated cluster compound $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was reported to be an active norbornene ROMP catalyst (or pre-catalyst) in CH_2Cl_2 at ambient temperature [17]. Norbornene also is polymerized in the presence of **6**. Compound **6** was treated with excess norbornene, ca. 2000–3000 equivalents, in a variety of solvents and at bath temperatures of 70°C or 95°C . Examination of the resulting polymer films provided ^1H and ^{13}C NMR (Fig. 5) spectra exhibiting features consistent with ring-opening metathesis polymerization. The results of the polymerizations are summarized in Table 1.

In toluene, a yield of 46.2 g of polymer/mmol of catalyst precursor was achieved in the presence of **6** at a bath temperature of 70°C . A viscosity change was noticed approximately 12 h after placing the vial in the oil bath. Also, for the duration of the

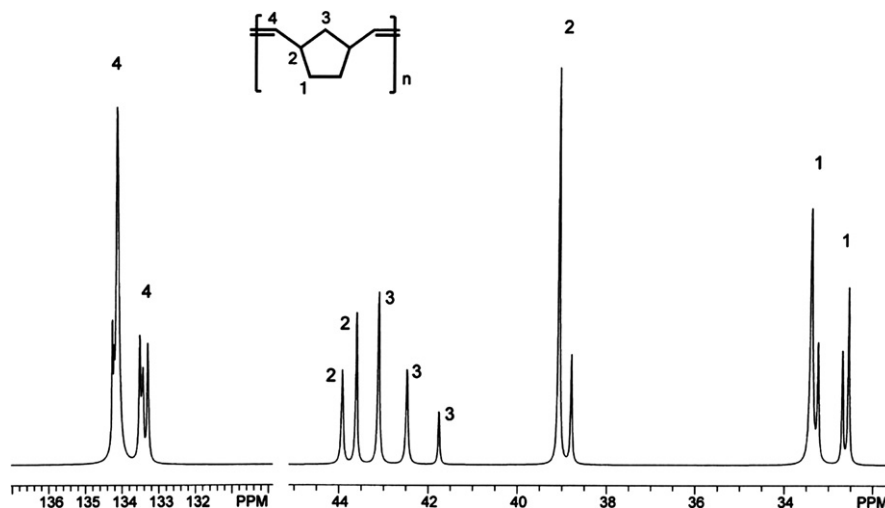


Fig. 5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polynorbornene generated with **6** as catalyst.

polymerization, the reaction mixture stayed clear, indicating that the polymer strands remained swelled by toluene throughout the process.

In benzotrifluoride, the polymerization was markedly different in that polymer strands were visible from the onset of heating. Over a period of time, the strands began to coat the sides of the reaction vessel indicating that the polymer strands would not remain swelled by the benzotrifluoride. Even after a longer exposure of **6** to the monomer at 70 °C bath temperature, the yield was 19.0 g of polymer/mmol of catalyst precursor. The lower yield combined with polymer deposition suggest some active metal centers had been incorporated into the film coating the vial and were thus isolated from contact with the monomer.

In an attempt to prevent the deposition of a polymer film, a 1:1 mixture of toluene and benzotrifluoride was employed in the polymerization of norbornene in the presence of **6** in a 95 °C bath. Again, polymer strands were visible throughout the polymerization, however, the strands did not build up a film on the walls of the reaction vessel. The yield was 19.1 g of polymer/mmol of catalyst precursor for a polymerization conducted over 40 h as opposed to 72 h.

Truett et al. described their product (provided by a catalytic system of TiCl_4 with co-catalyst $\text{Li}[\text{Al}(n\text{-C}_7\text{H}_{15})_4]$) as “remarkably stereospecific” and that the ring-opening reaction gave polymer chains composed of cyclopentane rings linked in a *cis*-1,3-fashion by *cis*- and *trans*-CH=CH groups [12]. Infrared spectra of the polymer films were obtained for the polymer produced by **6** in toluene at 70 °C (bath), and the spectra display those features associated with polynorbornene produced by ROMP [12,14,17]. Specifically, the spectra show a broad band at ca. 2900 cm^{-1} due to C–H bond stretching and three bands at 1778, 1712, and 1653 cm^{-1} assigned to C=C bond stretching. In the fingerprint region, the band at 967 cm^{-1} is attributed to *trans*-disubstituted C=C bending

and the band at 736 cm^{-1} is assigned to *cis*-disubstituted C=C bending.

A ^1H NMR spectrum of the polymer film was obtained for each polymerization. All spectra were identical and the signals matched those reported, and illustrated, by Gilliom and Grubbs [24]. In the olefinic proton region, discrete signals at δ_{H} 5.50 and 5.35 have been assigned to the *trans*- and *cis*-CH=CH units, protons at positions 2 and 3 of the polymer, respectively [42]. The protons at positions 1 and 4 also display discrete signals attributed to linkage to *cis*- or *trans*-CH=CH units at δ 2.90 and 2.51, respectively. The *cis*-1,3 linkage of the cyclopentane rings gives two unique faces to every ring in the polymer chain. Thus, the hydrogen atoms at positions 5, 6, and 7 are in a different environment from those at positions (5'), (6'), and 7'. In the proton NMR spectrum of the polymer, two peaks, at δ 1.83 and 1.42, are due to the protons at positions 5,6 or 5',6'. Similarly, two peaks, at δ 2.02 and 1.17, are assigned to the protons at positions 7 or 7'. These four signals integrate 1:2:2:1.

A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the polymer film was obtained for each polymerization, Fig. 5. All spectra were identical and the signals matched those reported, and illustrated, by Rooney et al. [25]. Unlike the proton-NMR spectra, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are rich in detail; the signals associated with each of the polymer's four carbon positions possess considerable fine structure. Relative peak areas can be employed to generate information about the microstructure of the polynorbornene: information regarding the percentage of *cis* double bonds, and information regarding the “blockiness” of the polymer. In a seminal work appearing in 1977 [25], Rooney et al. proceeded upon the assumption that the fine structure was the result of the geometric isomerization possible along the polymer chain and assigned a three digit (alphameric) code to each signal based on the four possible dyad structures, Table 2. For example, **1tc** refers to the peak assigned to a carbon in position 1 where the nearest double bond has a *trans* configuration and the next-nearest double has a *cis* configuration. The availability of all *trans* [12], and all *cis* polynorbornene [25], each with four, unique ^{13}C NMR signals supported their original assumption and aided the assignment of the majority of signals. For the vinylic carbons, C-4, the fine structure has yet to be fully resolved and the two broad resonance envelopes are simply assigned to *cis* and *trans* environments. For the bridging carbon, C-3, a **3tc** assignment is equivalent to a **3ct** assignment. Thus, only three C-3 signals appear in polynorbornene $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. Finally, four separate C-1 and C-2 resonances can be observed.

Table 1
Characteristics of polynorbornene formation in the presence of compound **6**.

Solvent	Temp °C	Time h	Yield ^a	TON ^b	% <i>cis</i>	r_c	r_t
Toluene	70	40	46.2	490	65.9	3.8	1.4
$\text{CF}_3\text{C}_6\text{H}_5$	70	72	19.0	201	70.2	3.5	1.8
$\text{CF}_3\text{C}_6\text{H}_5/\text{toluene}$	95	40	19.1	203	65.2	3.7	1.0

^a g polymer/mmol catalyst.

^b mmol monomer polymerized/mmol pre-catalyst.

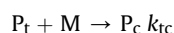
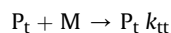
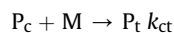
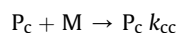
Table 2
Assignment of $^{13}\text{C}\{^1\text{H}\}$ NMR fine structure to specific polymer chain environments.

C-13 shift (ppm)	Geometric isomerization ^a	C-13 shift (ppm)	Geometric isomerization ^a
32.54	1tt	42.46	3tc = ct
32.68	1tc	43.11	3cc
33.23	1ct	43.60	2tt
33.38	1cc	43.92	2tc
38.78	2ct	133.43	4t
39.07	2cc	134.19	4c
41.76	3tt		

^a The first letter specifies the *cis* or *trans* structure at the nearest double bond; the second letter specifies the *cis* or *trans* structure at the next nearest double bond [25].

Peak fitting of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, to acquire relative peak areas, allows for the calculation of the fraction of *cis* double bonds in the polymer [25]. The *cis* fractions were calculated four times, using the peak area information for each carbon position (see Table 2). The polymers produced in the presence of **6** possess 65–70% *cis* double bond content. For $\text{H}_2\text{Os}_3(\text{CO})_{10}$ as a catalyst precursor, long reaction times (5 days) led to higher *trans* content (up to 1:12, *cis*:*trans*) [17].

The relative areas obtained by peak fitting can also be utilized to develop information regarding the “blockiness” of the polymer chain. Any departure from a random distribution of *cis* and *trans* double bonds is considered a movement toward polynorbornene blockiness [43]. Blockiness is defined as the frequency of *cc* or *tt* double bond repetition relative to *ct* or *tc* double bond repetition. Rooney et al. developed the following rate constants and formulae with regard to the active species P_c or P_t and monomer (M) [43]. P_c is defined as a metal bound polymer chain with a *cis*-C=C double bond adjacent to the active center. There are four possible outcomes, and rate constants, regarding monomer addition to P_c or P_t .



Thus, for example, the rate constant k_{cc} characterizes the rate of monomer insertion resulting in a *cis*-*cis* linkage. Therefore the ratios $k_{cc}/k_{ct} = r_c$ and $k_{tt}/k_{tc} = r_t$ are measures of polymer blockiness. If both ratios equal zero, then *cis* and *trans* double bonds alternate along the polymer chain -*cis*-*trans*-*cis*-*trans*-. If both ratios equal 1, then *cis* and *trans* double bonds occur randomly along the polymer backbone. As either ratio increases, the polymer chain consists of long -*cis*-*cis*-*cis*-*cis*- or -*trans*-*trans*-*trans*-*trans*- sequences. The blockiness ratios appearing in Table 2 are average ratios calculated from peak areas ($r_c = I_{cc}/I_{ct}$, $r_t = I_{tt}/I_{tc}$) for C-1 and C-2. For entry four, polynorbornene produced in a 1:1 mixture of benzotrifluoride and toluene, $r_c = 3.7$ and $r_t = 1.0$. Thus for this particular polymer, a *cis*-C=C double bond is 3.7 times as likely to be followed by a *cis*-C=C double bond than by a *trans*-C=C double bond, and a *trans*-C=C double bond is equally likely to be followed by a double bond of either geometry.

The attempts to recover the triosmium cluster, **6**, were not completely successful. In every instance the polymer retained color, and the total mass of the recovered residues was less than the initial mass of added **6**. After examination by ^1H NMR spectroscopy,

it was clear the recovered residues also contained polynorbornene. Interestingly, the ^1H NMR spectra of the recovered residues from the polymerization in toluene at 70 °C show a singlet and three triplets in the δ 5.0–2.0 range. We believe these resonances are associated with a cluster-norbornene addition product. Furthermore, since these resonances are visible in residues from low(er) temperature polymerizations, they may be associated with the initiating species. Unfortunately, signals attributed to the polymer or to the methylene spacers of the fluororus-substituted phosphine also appear in the δ 3.0–2.0 range.

The reactions of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ with norbornene were studied by Johnson et al. [44]. There is no significant match between the ^1H NMR signals observed in our residues, and the ^1H NMR signals reported for those compounds isolated by Johnson et al. In particular, we did not see strong evidence for hydride ligands.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the residues recovered after polymerization in the presence of **6** all show multiple phosphorus environments, and the proton spectra often display a downfield shift in those signals assigned to the substituted phosphine ligand, or a second set of phenyl resonances attributable to the substituted phosphine being in a different environment from that of **6**. The mass spectra of the residues, after polymerization in benzotrifluoride, then thin-layer chromatography, often exhibit signals attributable to **6** (at 2426 amu) and/or to triosmium clusters related to **6**. A signal at 2520 amu, assigned to $[\mathbf{6} + \text{C}_7\text{H}_{10}]^+$, has been observed. A signal at 2492 amu is present in all four residues. We attribute this signal to $[\mathbf{6} - \text{CO} + \text{C}_7\text{H}_{10}]^+$. In one residue, a signal at 2586 amu, assigned to $[\mathbf{6} - \text{CO} + 2\text{C}_7\text{H}_{10}]^+$, was present. Finally, signals at 2670 and 2674 amu have been observed and these clusters approximate $[\mathbf{6} - \text{CO} + 3\text{C}_7\text{H}_{10}]^+$ at 2680 amu.

The spectroscopic evidence suggests that the triosmium framework with the substituted-phosphine ligand survives the polymerizations (and also TLC) intact and thus it is possible that the active metal center(s) resides on a substituted-phosphine ligated triosmium cluster. The presence of a signal for **6**, at 2426 amu, in three of four recovered residues suggests that a fraction of the clusters become catalytically active and/or that **6** is regenerated.

4. Conclusions

The syntheses of compounds **1** and **2** are comparable to their non-fluoropolytailed phosphine analogs. The reactivity of compound **1** with H_2 and PPh_3 corresponds broadly to that of $\text{Os}_3(\text{CO})_{12}$. While the syntheses of **1**–**6** were reasonably straightforward, the separation and purification of these compounds was demanding. However, transition metal complexes bearing fluoropolytail phosphine ligands can be purified using preparative TLC on standard silica gel plates with common organic solvents as eluents.

The partitioning of **3** and **4**, relative to **1**, in fluororus and organic phases suggests troublesome consequences regarding the application of FBS in catalysis. The addition of one or two triphenylphosphine ligands to **1** dramatically altered the propensity of **3** or **4** to remain solvated in the fluororus phase. This behavior evokes the possibility that substrate coordination/activation may profoundly alter the solubility of fluoropolytail bearing catalysts, or catalyst precursors, in fluororus media.

In the presence of **6**, polynorbornene is produced from norbornene by ring-opening metathesis polymerization. After 40 h reaction times, the polymer produced is constructed of 66% *cis* double bonds. In the context of Fluororus Biphasic Catalytic Systems, benzotrifluoride is regarded as a universal solvent, and in the context of ring-opening metathesis polymerization by **6**, both norbornene and **6** are soluble in BTF. However, we believe the lower yields of polynorbornene produced in BTF are due to the

insolubility of polynorbornene in benzotrifluoride. This insolubility causes the active species to become isolated from the monomer. Attempts to reclaim **6**, and other osmium moieties, from reaction mixtures by immobilization in fluoros media resulted in only partial recoveries. The recovered residues generally contained **6** and always contained triosmium clusters ligated by the per-fluoroalkyl substituted phosphine. This result suggests that the active species is a triosmium cluster but that only a fraction of precursor **6** becomes active.

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Appendix A. Supplementary material

CCDC 747663 contains the supplementary crystallographic data for $Os_3(CO)_9(PPh_3)_2\{P(CH_2CH_2(CF_2)_5CF_3)_3\}$ (**4**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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