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Journal of Organometallic Chemistry 691 (2006) 3874–3880

Journal of Organo metallic Chemistry

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Synthesis, characterization, and crystal structures of the osmium triflate complexes $Cp^*Os(P–P)(OTf)$ and $[Cp^*Os(P–P)(OH_2)][OTf]$

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Received 15 April 2006; received in revised form 18 May 2006; accepted 18 May 2006
Available online 3 June 2006

Abstract

Treatment of the osmium(II) hydrides $Cp^*Os(P–P)H$ (Cp^* = pentamethylcyclopentadienyl) with methyl trifluoromethanesulfonate (MeOTf) affords osmium(II) triflate complexes with the general formula $Cp^*Os(P–P)(OTf)$, where P–P = bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)methane (dppm), or 1,2-bis(dimethylphosphino)ethane (dmpe). The aqua complexes $[Cp^*Os(dmpm)(OH_2)][OTf]$ and $[Cp^*Os(dppm)(OH_2)][OTf]$ are synthesized by the addition of water to the corresponding anhydrous triflates. The complexes $Cp^*Os(dppm)(OTf)$ and $[Cp^*Os(dmpm)(OH_2)][OTf]$ have been examined crystallographically, and all compounds have been characterized by NMR spectroscopy.

Keywords: Osmium; Trifluoromethanesulfonate; Triflate; Hydride; Alkylation; Aquo; Crystal structure; NMR

1. Introduction

Transition metal complexes containing coordinated trifluoromethanesulfonate (OTf) ligands are useful starting materials because the weakly bound triflate ligand is displaced readily [1]. For late transition metals, such complexes are commonly synthesized by the addition of silver triflate to a metal halide or metal alkyl complex. A particularly clean method is the addition of triflic acid to a transition metal alkyl complex, with loss of alkane. For the platinum metals, this route has been used to prepare triflate complexes of Ru [2–4], Os [5,6], Rh [7], Ir [8], and Pt [9–11]. Formation of triflate complexes by addition of triflic acid to metal hydrides (with loss of H_2) is also possible; all the examples of this approach of which we are aware involve the element Ru [12–14].

We now describe the synthesis of transition metal triflate complexes by a method that is in one sense the reverse of the above approaches: instead of protonating a metal alkyl, the method entails alkylating a metal hydride. Only a few compounds have previously been prepared by this route: Malisch and co-workers [12] used this method to obtain $CpMo(CO)_2(PR_3)(OTf)$, $CpW(CO)_2(PR_3)(OTf)$, $Cp^*Fe(CO)L(OTf)$, and $Cp^*Ru(CO)L(OTf)$, where L = CO or PMe_3, and Bleeke and Behm [15] employed it to generate the iridacycle $(C_5H_4Me_2)Ir(PEt_3)_3(OTf)$. In the current paper, we find that the osmium(II) hydride complexes $Cp^*Os(P–P)H$ react with methyl trifluoromethanesulfonate (MeOTf) to form bound triflate complexes with the general formula $Cp^*Os(P–P)(OTf)$, where P–P = bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)methane (dppm), or 1,2-bis(dimethylphosphino)ethane (dmpe). The syntheses of the aqua complexes $[Cp^*Os(dppm)(OH_2)][OTf]$ and $[Cp^*Os(dmpm)(OH_2)][OTf]$ will also be discussed.

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doi:10.1016/j.jorganchem.2006.05.040

2. Results and discussion

2.1. Synthesis of triflate compounds

We have previously described the conversion of the bromo complexes $Cp^*Os(P–P)_2Br$ to their corresponding hydrides $Cp^*Os(P–P)H$, where P–P = bis(dimethylphosphino)methane (dmpm), dppm = bis(diphenylphosphino)methane (dppm), or 1,2-bis(dimethylphosphino)ethane (dmpe) [16]. Treatment of these hydride complexes with one to two equivalents of methyl trifluoromethanesulfonate in pentane results in loss of methane and generation of the triflate compounds $Cp^*Os(dmpm)(OTf)$ (**1**), $Cp^*Os(dppm)(OTf)$ (**2**), and $Cp^*Os(dmpe)(OTf)$ (**3**), in 59%, 69%, and 86% yield, respectively. To obtain high yields of these compounds, it is important to limit the amount of MeOTf added and to isolate the reaction products promptly (i.e., after at most a few hours). If more than two equivalents of MeOTf are added and the reaction solutions are permitted to stir for more than a few hours, other species are generated – the methylidene complexes $[Cp^*Os(P–P)({=}CH_2)][OTf]$ and the ethylene complexes $[Cp^*Os(P–P)(CH_2{=}CH_2)][OTf]$ – as we have shown elsewhere [17].

$$\begin{aligned} Cp^*Os(P–P)H + MeOTf \rightarrow \quad & Cp^*Os(P–P)(OTf) + CH_4 \\ & \mathbf{1}, P–P = dmpm \\ & \mathbf{2}, P–P = dppm \\ & \mathbf{3}, P–P = dmpe \end{aligned}$$

Complexes **1**–**3** are readily soluble in aromatic hydrocarbons, which suggests that the complexes are not salts, but contain an osmium-bound OTf ligand. As would be expected, these compounds are sensitive to both oxygen and water. The related osmium(II) complex $CpOs(PPh_3)_2(OTf)$ has also been synthesized by treating $CpOs(PPh_3)_2Br$ with AgOTf in toluene [18].

Diagnostic for the coordinated triflate anion are strong bands in the infrared spectra near 1310, 1230, 1210, and 1020 cm^{-1} [1]. The ^1H NMR spectrum of the dmpm compound **1** in C_7D_8 features two triplets for the phosphine methyl protons, and the methylene unit in the phosphine backbone gives rise to two doublets of triplets. Two PMe_2 and two PCH_2 environments are seen in **1** because these groups can either be proximal or distal with respect to the Cp^* ligand. Similarly, the ^1H NMR spectrum of **2** in C_6D_6 shows two different doublets of triplets for the backbone of the dppm ligand. The ^1H NMR spectrum of the dmpe compound **3** in C_6D_6 features two doublets for the inequivalent phosphine methyl protons. The backbone methylene resonances appear as multiplets at δ 1.07 and ca. 1.5; the latter is mostly obscured by the resonances for the ring and phosphine methyl protons. Interestingly, the $^{13}C\{^1H\}$ NMR resonances for the PCH_2 and PMe_2 groups of the dmpe ligands in **3** appear as four- and six-line patterns. These patterns can be analyzed in terms of ABX spin systems (A, B = ^{31}P, X = ^{13}C), where the phosphorus chemical shifts are different because only one of the two phosphorus atoms bears a ^{13}C-labeled carbon. Simulations show that the one-bond $^{13}C/^{12}C$ secondary isotope effect on the ^{31}P NMR chemical shift is about 0.025 ppm; this value is similar to those seen in other systems [16,19]. Single resonances were seen in the $^{31}P\{^1H\}$ NMR spectrum for all three compounds.

Orange crystals of **2** having the formula $Cp^*Os(dppm)OTf \cdot 0.5C_7H_8$ crystallize in space group $P2_1/n$ with one molecule in the asymmetric unit (Fig. 1). Crystallographic data and selected bond distances and angles for **2** are given in Tables 1 and 2. The Os–O distance to the bound triflate of 2.24 Å can be compared with the Os–OTf distances of 2.15(1), 2.29, 2.33, and 2.22 Å seen for $Os_3(\mu\text{-}H)_2(CO)_9(\mu,\eta^2\text{-}O_2CCH_3)(OTf)$ [20], $[Os(terpy)N(Cl)(OTf)][OTf]$ (terpy = 2,2′:6′,2″-terpyridine) [21], $Os(NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(CH_2CMe_3)_2(OSiMe_3)(OTf)$ [22], and $CpOs(PPh_3)_2(OTf)$ [18], respectively. The Os–P distances in **2** of 2.294(1) and 2.309(1) Å are essentially equivalent. In comparison, the reported Os–P bond distances for the related cation $[Cp^*Os(dppm)H_2]^+$ are both 2.312(1) Å [23]. The crystal structure of the corresponding CpRu(dfepe)(OTf) complex (dfepe = 1,2-bis[bis(pentafluoroethyl)phosphino]ethane) is also known [13].

2.2. Synthesis of aqua compounds

The aqua complex $[Cp^*Os(dppm)(OH_2)][OTf] \cdot 4H_2O$ (**4**) can be prepared by addition of water to the corresponding triflate complex $Cp^*Os(dppm)(OTf)$ in diethyl ether. Yellow crystals of **4** precipitated immediately from solution.

$$\begin{aligned} & Cp^*Os(dppm)(OTf) + 5H_2O \\ & \quad \rightarrow [Cp^*Os(OH_2)(dppm)][OTf] \cdot 4H_2O \\ & \qquad\qquad\qquad\qquad \mathbf{4} \end{aligned}$$

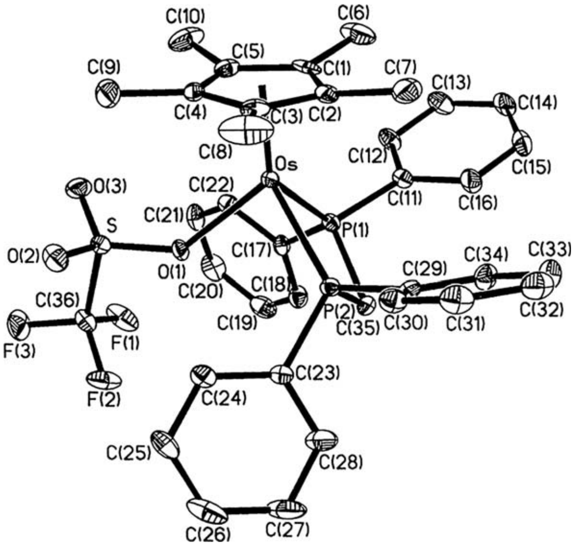

Fig. 1. Molecular structure of $Cp^*Os(dppm)OTf \cdot 0.5C_7H_8$ (**2**). The 30% probability density surfaces are shown. The hydrogen atoms and disordered toluene molecules are omitted for clarity.

Table 1
Crystal data for $Cp^*Os(dppm)OTf \cdot 0.5C_7H_8$ (**2**) and $[Cp^*Os(dmpm)(OH_2)][OTf]$ (**5**)

Chemical formula	$C_{39.5}H_{41}F_3O_3OsP_2S$	$C_{16}H_{31}F_3O_4OsP_2S$
Formula weight	904.96	628.61
Size (mm)	$0.16 \times 0.12 \times 0.04$	$0.36 \times 0.20 \times 0.16$
Color	Orange	Yellow
Habit	Tabular	Platy
Diffractometer	Siemens Smart CCD	Siemens Smart CCD
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	10.3632(4)	22.8835(4)
b (Å)	17.3504(7)	9.7649(2)
c (Å)	21.1034(9)	21.2005(2)
β (°)	94.335(1)	97.991(1)
V (Å^3)	3783.7(3)	4691.4(1)
Z	4	8
T (K)	198(2)	198(2)
λ (Å)	0.71073	0.71073
D_{calc} (Mg m^{-3})	1.589	1.780
μ (mm^{-1})	3.561	5.702
θ Range (°)	1.94–28.28	1.80–28.19
Measured reflections	24517	15016
Independent reflections	9015	5575
Reflections with $[I > 2\sigma(I)]$	5792	1966
Parameters	428	261
Restraints	0	1
R_F $[I > 2\sigma(I)]$[a]	0.0535	0.0594
$R_{wF}2$ (all data)[a]	0.0604	0.0609
$\Delta\rho$ (maximum/minimum) (e Å^{-3})	0.913/−0.561	1.038/−1.061

[a] $R_F = \sum\|F_o| - |F_c\|/\sum|F_o|$, $R_{wF}2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected bond lengths (Å) and bond angles (°) for $Cp^*Os(dppm)(OTf) \cdot 0.5C_7H_8$ (**2**)

Bond lengths (Å)			
Os–O(1)	2.240(3)	S–O(1)	1.460(3)
Os–P(1)	2.2938(11)	S–O(2)	1.428(3)
Os–P(2)	2.3090(11)	S–O(3)	1.434(3)
Os–C(1)	2.177(4)	S–C(36)	1.828(5)
Os–C(2)	2.169(4)	C(36)–F(1)	1.316(5)
Os–C(3)	2.243(4)	C(36)–F(2)	1.330(5)
Os–C(4)	2.270(4)	C(36)–F(3)	1.322(5)
Os–C(5)	2.213(4)		
Bond angles (°)			
O(1)–Os–P(1)	83.72(8)	O(2)–S–O(1)	114.9(2)
O(1)–Os–P(2)	85.22(8)	O(3)–S–O(1)	114.4(2)
P(1)–Os–P(2)	71.30(4)	O(2)–S–C(36)	103.3(2)
S–O(1)–Os	135.5(2)	O(3)–S–C(36)	103.9(2)
O(2)–S–O(3)	116.8(2)	O(1)–S–C(36)	100.6(2)

The corresponding dmpm complex $[Cp^*Os(dmpm)(OH_2)]$-$[OTf]$ (**5**) can be prepared similarly by treatment of $Cp^*Os(dmpm)H$ with MeOTf in the presence of adventitious water. The infrared spectrum of the dppm complex **4** shows a strong O–H stretch at 3275 cm^{-1}, and the ^1H NMR spectrum in CD_3CN shows a resonance at δ 2.13 for the coordinated aqua ligand (in addition to a broad resonance at δ 2.15 due to the four "lattice" water molecules in the molecular formula). Evidently, exchange of bound and free water molecules in **4** is slow on the NMR time scale at this temperature. Similarly, the infrared spectrum of the dmpm complex **5** shows an intense O–H stretch at 3176 cm^{-1}, and the ^1H NMR spectrum of **5** in CD_3CN shows a broad resonance at δ 2.20.

Efforts to distinguish the anhydrous and the aquated triflate complexes from differences in the NMR chemical shifts were thwarted because often there was no solvent in which both kinds of species were soluble without reacting. Thus, it is difficult to find conditions that enable informative comparisons of, for example, the ^{19}F NMR chemical shifts in order to distinguish bound from free triflate groups. Specifically, in aromatic hydrocarbons the anhydrous materials are soluble but the hydrates are not. In chlorinated hydrocarbons such as dichloromethane, the solutions darken upon dissolution and the NMR spectra exhibit peaks due to multiple species, some of which are paramagnetic. This result is consistent with our previous work on similar osmium complexes, which showed that they readily reduce chlorinated hydrocarbons [16].

In coordinating solvents such as tetrahydrofuran and acetonitrile, all the compounds are soluble, but these solvents displace the bound OTf ligands (instantaneously) or water ligands (more slowly) to generate the same $[Cp^*Os(P–P)(solvate)^+]$ species. The rate at which the ligands are displaced depends on the phosphine ligand: $[Cp^*Os(dppm)(OH_2)^+]$ (**4**) is kinetically inert and shows no displacement of the bound water after several hours in acetonitrile, as shown by the persistence of the NMR resonance due to bound water. In only this case, the anhydrous and hydrated forms of the triflate complex can be distinguished by prompt NMR examination of freshly-dissolved samples. In contrast, displacement of the bound water molecule in $[Cp^*Os(dmpm)(OH_2)^+]$ (**5**), by acetonitrile is rapid: over the time needed to prepare a sample and acquire an NMR spectrum, the displacement was complete. The displacement reaction was also evident in the FAB mass spectrum of **5**, which showed peaks due to $[Cp^*Os(dmpm)(MeCN)^+]$ when the sample was introduced as an acetonitrile solution. The faster rates of reactions for the dmpm compound **5** versus the dppm compound **4** is consistent with general trends we have observed for other complexes of the type $Cp^*Os(P–P)X$ (X = Br, H) [16].

In view of the limited ability of NMR spectra to discriminate between the anhydrous and hydrated materials, these compounds are best distinguished by the presence or absence of hydroxyl stretches in their IR spectra, and by their solubility (or lack thereof) in aromatic hydrocarbons.

Compound **5** crystallizes in the space group $C2/c$ with one molecule per asymmetric unit (Fig. 2). Crystallographic data and selected bond distances and angles for **5** are given in Tables 1 and 3. The Os–OH_2 distance of 2.207(4) Å is slightly shorter than the Os–OTf distance of 2.240(3) Å in **2**. The Os–P distances in **5** are equivalent at 2.300 Å; these bonds are somewhat longer than the Os–P distances of 2.25 Å found in $Cp^*Os(dmpm)H$ [23]. This

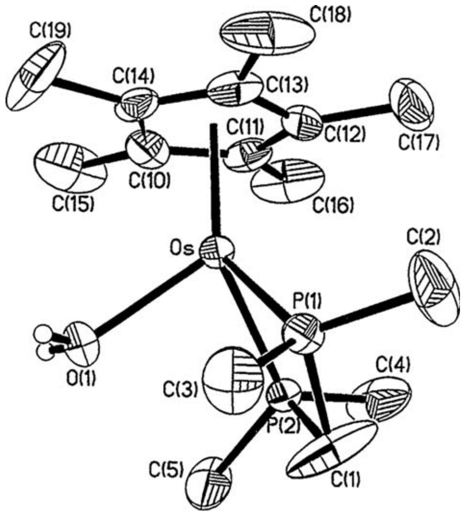

Fig. 2. Molecular structure of the cation in [Cp*Os(dmpm)(OH_2)][OTf] (**5**), showing the 30% probability density surfaces. The carbon-bound hydrogen atoms and the triflate ion have been omitted for clarity; the hydrogen atoms on the aqua ligand are represented by arbitrarily sized spheres.

Table 3
Selected bond lengths (Å) and bond angles (°) for [Cp*Os(dmpm)-(OH_2)][OTf] (**5**)

Bond lengths (Å)			
Os–O(1)	2.207(4)	Os–C(12)	2.169(5)
Os–P(1)	2.3008(12)	Os–C(13)	2.224(5)
Os–P(2)	2.3004(11)	Os–C(14)	2.248(5)
Os–C(10)	2.217(5)	O(1)–H(1)	0.80(1)
Os–C(11)	2.189(5)	O(1)–H(2)	0.79(1)
Bond angles (°)			
C(10)–Os–O(1)	99.6(2)	P(1)–Os–O(1)	86.57(10)
C(11)–Os–O(1)	133.5(2)	P(2)–Os–O(1)	85.25(11)
C(12)–Os–O(1)	158.5(2)	P(1)–Os–P(2)	70.48(4)
C(13)–Os–O(1)	124.8(2)	P(1)–C(1)–P(2)	94.3(3)
C(14)–Os–O(1)	96.6(2)	H(1)–O(1)–H(1)	107.2(8)

difference is somewhat surprising: one might expect that the positive charge and more weakly donating aqua ligand in **5** would lead to stronger donation from phosphorus to osmium. It is unlikely that steric factors would account for this difference in bond lengths between the two compounds. In compound **5**, pairs of cations and pairs of anions are hydrogen bonded to one another to form a cyclic grouping (Fig. 3). The hydrogen atoms of the aqua ligand are hydrogen-bonded to oxygen atoms of the triflate anions with H···O distances of 1.91(1) and 1.99(1) Å. Similar hydrogen bonding interactions between osmium-bound aqua ligands and triflate or tetrafluoroborate counterions have been reported [24,25]. The cyclic hydrogen bonding arrangement in **5** is very similar to that we previously reported for the osmium methallyl compound [Cp*Os(C_4H_7)Me(OH_2)][BF_4] [26] and to that reported by Gemel and co-workers for the tris(pyrazolyl)borate complex [TpRu(COD)(OH_2)][OTf] (COD = 1,5-cyclooctadienyl) [27].

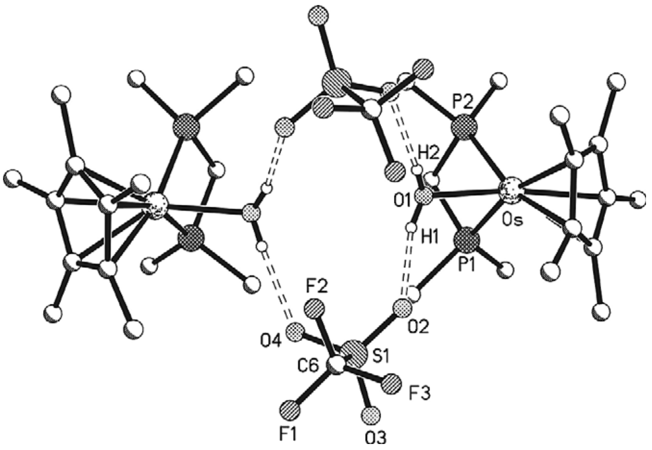

Fig. 3. Hydrogen bonding in [Cp*Os(dmpm)(OH_2)][OTf] (**5**).

2.3. Concluding remarks

The reaction of Cp*Os(P–P)H with MeOTf undoubtedly proceeds by means of the methyl/hydride intermediates [Cp*Os(P–P)H(Me)$^+$], which we have characterized by low-temperature NMR studies [28]. Subsequent loss of methane and ligation of the triflate groups affords the Cp*Os(P–P)(OTf) products. We will show elsewhere that these triflate complexes are useful starting materials for the preparation of other Cp*Os(P–P)X compounds.

3. Experimental

3.1. General details

All experiments were performed under argon or vacuum using standard Schlenk techniques unless otherwise specified. Solvents were distilled under nitrogen from calcium hydride (dichloromethane), sodium (toluene), or sodium benzophenone (pentane, ether, tetrahydrofuran). Methyl trifluoromethanesulfonate (Aldrich) was used as received. Water was deionized before use. The starting materials Cp*Os(dmpm)H, Cp*Os(dppm)H, and Cp*Os(dmpe)H were prepared by literature methods [16].

The IR spectra were obtained on a Nicolet Impact 410 instrument as Nujol mulls between KBr plates. The ^{1}H and ^{13}C{^{1}H} NMR data were recorded on Varian Unity-400 or Unity-500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million (δ) relative to tetramethylsilane; ^{31}P{^{1}H} NMR spectra were externally referenced to H_3PO_4. Positive chemical shifts correspond to resonance frequencies higher than that of the reference. Multiplet designations surrounded by quotation marks (e.g., "t") mean that the multiplet is non-binomial. Field-desorption (FD) and positive-ion fast atom bombardment (FAB) mass spectra were performed on Finnigan-MAT 731 and VG ZAB-SE mass spectrometers, respectively; unless otherwise specified, the samples were loaded as diethyl ether or tetrahydrofuran solutions. The shapes of all peak envelopes correspond with those calculated from the natural abundance isotopic distributions. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

Caution: Methyl trifluoromethanesulfonate is toxic and a suspected carcinogen, and it should be handled in a well-ventilated fume hood.

3.2. (Pentamethylcyclopentadienyl)trifluoromethanesulfonato[bis(dimethylphosphino)methane]osmium(II), Cp*Os(dmpm)(OTf) (1)

To a solution of Cp*Os(dmpm)H (0.27 g, 0.58 mmol) in pentane (30 mL) at −78 °C was added methyl trifluoromethanesulfonate (0.10 mL, 0.88 mmol). The solution was stirred for 15 min at −78 °C and a small amount of a yellow powder and a blue-green oil formed. The colorless solution was filtered while still cold, and upon being warmed to room temperature afforded orange crystals. The crystals were isolated by filtration. Yield: 0.21 g (59%). Anal. Calc. for **1**: C, 31.5; H, 4.8; P, 10.2. Found: C, 31.6; H, 4.9; P, 9.8%. MS (FD): *m/z* 612 [M(OTf)$^+$]. ^{1}H NMR (C_7D_8): δ 1.03 (“t”, $^2J_{PH}+{}^4J_{PH}$ 5.0 Hz, PMe_2), 1.53 (“t”, $^2J_{PH}+{}^4J_{PH}$ 4.9 Hz, PMe_2), 1.67 (t, $^3J_{PH}$ 0.8 Hz, $C_5\mathit{Me}_5$), 3.49 (dt, $^2J_{HH}$ 14.5 Hz, $^2J_{PH}$ 11.0, PCH_2), 4.30 (dt, $^2J_{HH}$ 14.5 Hz, $^2J_{PH}$ 10.2, PCH_2). $^{13}C\{^1H\}$ NMR (C_7D_8): δ 11.1 (s, $C_5\mathit{Me}_5$), 15.7 (t, $^1J_{PC}+{}^3J_{PC}$ 14.7 Hz, PMe_2), 18.4 (t, $^1J_{PC}+{}^3J_{PC}$ 16.6 Hz, PMe_2), 57.1 (t, $^1J_{PC}$ 26.7 Hz, PCH_2), 84.1 (t, $^2J_{PC}$ 2.9 Hz C_5Me_5), 118.0 (q, $^1J_{CF}$ 319.5 Hz, CF_3SO_3). $^{31}P\{^1H\}$ NMR (C_7D_8): δ −62.2 (s). IR (cm^{-1}): 1417 (w), 1311 (s), 1289 (w), 1280 (w), 1232 (s), 1209 (s), 1170 (m), 1125 (w), 1088 (w), 1079 (w), 1016 (s), 940 (s), 877 (w), 850 (w), 758 (w), 740 (w), 709 (m), 664 (w), 633 (s), 581 (w), 518 (w).

3.3. (Pentamethylcyclopentadienyl)trifluoromethanesulfonato[bis(diphenylphosphino)methane]osmium(II), Cp*Os(dppm)(OTf) (2)

To a suspension of Cp*Os(dppm)H (0.45 g, 0.63 mmol) in pentane (30 mL) was added MeOTf (0.15 mL, 1.33 mmol). The mixture was stirred for 1 h and the undissolved solid became orange. The pentane was removed under vacuum, the orange powder was dissolved in toluene (10 mL), and the toluene solution was concentrated to 3 mL. Orange crystals were obtained by layering the toluene solution with pentane (15 mL) and storing at −20 °C. The crystals were collected by filtration and dried under vacuum overnight. Yield: 0.36 g (69%). M.p.: 116 °C (dec). MS (FD): *m/z* 860 [M(OTf)$^+$]. Anal. Calc. for **2**: C, 50.3; H, 4.3. Found: C, 48.8; H, 4.8%. ^{1}H NMR (C_6D_6): δ 1.65 (s, $C_5\mathit{Me}_5$), 4.34 (dt, $^2J_{HH}$ 15.5, $^2J_{PH}$ 11.0 Hz, PCH_2), 6.31 (dt, $^2J_{HH}$ 15.5, $^2J_{PH}$ 9.5 Hz, PCH_2), 6.91 (m, *p*-CH), 7.09 (t, $^3J_{HH}$ 7.0 Hz, *m*-CH), 7.23 (m, *o*-CH), 7.27 (t, $^3J_{HH}$ 7.5 Hz, *m*-CH), 7.64 (d“t”, $^3J_{HH}$ 4.0, $^3J_{PH}+{}^5J_{PH}$ 7.0 Hz, *o*-CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 10.7 (s, $C_5\mathit{Me}_5$), 56.3 (t, $^1J_{PC}$ 25.8 Hz, PCH_2), 84.8 (t, $^2J_{PC}$ 1.0 Hz, C_5Me_5), 127.8 (obscured by solvent, *m*-CH), 128.2 (t, $^3J_{PC}$ 4.6 Hz, *m*-CH), 129.2 (s, *p*-CH), 129.9 (s, *p*-CH), 131.8 (t, $^2J_{PC}+{}^4J_{PC}$ 5.5 Hz, *o*-CH), 132.4 (“t”, $^1J_{PC}+{}^3J_{PC}$ 25.1 Hz, *ipso*-C), 132.7 (t, $^2J_{PC}+{}^4J_{PC}$ 5.5 Hz, *o*-CH), 136.1 (“t”, $^1J_{PC}+{}^3J_{PC}$ 24.9 Hz, *ipso*-C). ^{19}F NMR (C_6D_6): δ −80.0 (s, CF_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −31.0 (s). IR (cm^{-1}): 3047 (m), 2721 (w), 1574 (w), 1437 (s), 1310 (s), 1230 (s), 1211 (s), 1184 (s), 1160 (m), 1097 (m), 1020 (s), 928 (w), 749 (w), 738 (m), 722 (m), 703 (s), 662 (w), 636 (m), 585 (w), 539 (m), 512 (m), 481 (w), 436 (w).

3.4. (Pentamethylcyclopentadienyl)trifluoromethane sulfonato[1,2-bis(dimethylphosphino)ethane]osmium(II), Cp*Os(dmpe)(OTf) (3)

To a solution of Cp*Os(dmpe)H (0.30 g, 0.63 mmol) in pentane (25 mL) at −78 °C was added methyl trifluoromethanesulfonate (0.10 mL, 0.88 mmol). The solution was stirred for 15 min at −78 °C and a small amount of a blue-green oil formed. The pale yellow solution was filtered while still cold, and upon being warmed room temperature afforded orange crystals. The crystals were isolated by filtration. Yield: 0.34 g (86%). Anal. Calc. for **3**: C, 32.7; H, 5.0; P, 9.9. Found: C, 32.1; H, 5.0; P, 9.7%. MS (FD): *m/z* 626 [M(OTf)$^+$]. ^{1}H NMR (C_6D_6): δ 0.84 (d, $^2J_{PH}$ 9.2 Hz, PMe_2), 1.07 (m, PCH_2), ca. 1.5 (m, PCH_2), 1.54 (d, $^2J_{PH}$ 9.6 Hz, PMe_2), 1.60 (t, $^3J_{PH}$ 1.2 Hz, $C_5\mathit{Me}_5$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.1 (s, $C_5\mathit{Me}_5$), 13.9 (4-line pattern, $^1J_{PC}+{}^4J_{PC}$ 29.5 Hz, PMe_2), 18.6 (6-line pattern, $^1J_{PC}+{}^4J_{PC}$ 41.5 Hz, PMe_2), 31.5 (6-line pattern, $^1J_{PC}+{}^3J_{PC}$ 46.0 Hz, PCH_2), 84.0 (t, $^2J_{PC}$ 2.9 Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.9 (s). IR (cm^{-1}): 2177 (w), 2133 (w), 1419 (m), 1404 (w), 1305 (s), 1280 (m), 1266 (m), 1231 (s), 1211 (s), 1170 (s), 1163 (m), 1128 (w), 1080 (w), 1021 (s), 988 (w), 947 (m), 938 (m), 913 (w), 897 (m), 839 (w), 810 (w), 793 (w), 758 (w), 733 (w), 727 (w), 713 (w), 704 (m), 655 (w), 633 (m), 582 (w), 518 (w), 502 (w).

3.5. (Pentamethylcyclopentadienyl)aqua[bis(diphenylphosphino)methane]osmium(II) trifluoromethanesulfonate tetrahydrate, [Cp*Os(dppm)(OH$_2$)][OTf] · 4H$_2$O (4)

To Cp*Os(dppm)(OTf) (0.15 g, 0.17 mmol) in diethyl ether (30 mL) was added water (6.0 μL, 0.33 mmol). The reaction mixture was stirred for 3 h, and yellow microcrystals precipitated from solution. The crystals were collected by filtration and dried under vacuum overnight. Yield: 0.075 g (45%). M.p.: 120 °C (dec). MS (FAB): *m/z* 711 [M$^+$, 100%], 727 [M(H$_2$O)$^+$, 15%]. Anal. Calc. for **4**: C, 45.6; H, 5.0. Found: C, 44.8; H, 4.7%. ^{1}H NMR (CD_3CN): δ 1.62 (t, J_{PH} 1.5 Hz, $C_5\mathit{Me}_5$), 2.13 (s, bound OH_2), 2.15 (br s, free H_2O), 4.97 (dt, $^2J_{PH}$ 16.5, $^2J_{PH}$ 10.5 Hz, PCH_2), 6.21 (dt, $^2J_{HH}$ 16.5, $^2J_{PH}$ 10.5 Hz, PCH_2), 7.37–7.43 and 7.46–7.56 (m, PPh_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 9.79 (s, $C_5\mathit{Me}_5$), 58.3 (t, $^1J_{PC}$ 28.5 Hz, PCH_2), 89.4 (t, $^2J_{PC}$ 2.0 Hz, C_5Me_5), 129.5 (t, $^3J_{PC}$ 5.5 Hz, *m*-CH), 129.6 (t,

$^3J_{PC}$ 4.5 Hz, *m*-CH), 131.2 (“t”, $^1J_{PC} + {}^3J_{PC}$ 23.6 Hz, *ipso*-C), 131.3 (s, *p*-CH), 131.4 (s, *p*-CH), 132.0 (t, $^2J_{PC} + {}^4J_{PC}$ 5.5 Hz, *o*-CH), 133.1 (t, $^2J_{PC} + {}^4J_{PC}$ 5.0 Hz, *o*-CH), 134.0 (“t”, $^1J_{PC} + {}^3J_{PC}$ 24.9 Hz, *ipso*-C). ^{19}F NMR (CD_3CN): δ −81.0 (s, CF_3). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −33.6 (s). IR (cm^{-1}): 3275 (br), 3062 (w), 2731 (w), 1679 (w), 1577 (w), 1438 (m), 1279 (s), 1255 (s), 1228 (m), 1171 (m), 1157 (m), 1095 (m), 1037 (s), 738 (m), 704 (m), 642 (m), 620 (w), 546 (w), 516 (m), 491 (w).

3.6. *(Pentamethylcyclopentadienyl)aqua[bis(dimethylphosphino)methane]osmium(II) trifluoromethanesulfonate, [Cp*Os(dmpm)(OH$_2$)][OTf] (**5**)*

A solution of Cp*Os(dmpm)H (0.40 g, 0.73 mmol) in diethyl ether (30 mL) was cooled to −78 °C. To this solution was added methyl trifluoromethanesulfonate (0.11 mL, 0.97 mmol). The reaction mixture was stirred cold for 15 min and then filtered, leaving a small amount of white precipitate. The resulting orange solution was cooled to −20 °C. Yellow crystals precipitated from solution, and were collected by filtration. Subsequent crops consisted of the unhydrated compound Cp*Os(dmpm)(OTf). M.p.: 79 °C (dec). MS (FAB; introduced as a MeCN solution); *m*/*z* 463 [M^+, 80%], 504 [$M(MeCN)^+$, 100%], 612 [$M(OTf)^+$, 20%]. Anal. Calc. for **5**: C, 30.6; H, 5.0. Found: C, 30.4; H, 4.9%. ^{1}H NMR (CD_3CN): δ 1.51 (“t”, $^2J_{HP} + {}^4J_{PH}$ 5.0 Hz, PMe_2), 1.65 (“t”, $^2J_{PH} + {}^4J_{PH}$ 5.0 Hz, PMe_2), 1.89 (s, C_5Me_5), 3.59 (dt, $^2J_{HH}$ 15.0, $^2J_{PH}$ 11.0 Hz, PCH_2), 4.62 (dt, $^2J_{HH}$ 15.0, $^2J_{HH}$ 11.0 Hz, PCH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 9.7 (s, $C_5\mathit{Me}_5$), 13.7 (t, J_{PC} 25.0 Hz, PMe_2), 16.0 (t, J_{PC} 25.0 Hz, PMe_2), 55.6 (t, $^1J_{PC}$ 28.0 Hz, PCH_2), 87.1 (t, $^2J_{PC}$ 3.0 Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −72.8 (s). IR (cm^{-1}): 3176 (br), 2726 (w), 2664 (w), 1293 (s), 1266 (s), 1240 (s), 1222 (s), 1156 (s), 1080 (m), 1031 (s), 948 (s), 888 (m), 864 (m), 755 (m), 744 (m), 726 (m), 642 (s), 575 (w), 517 (m).

3.7. *Crystallographic studies [29]*

Single crystals of Cp*Os(dppm)(OTf) · 0.5C_7H_8 (**2**), grown from toluene layered with pentane, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. [Single crystals of [Cp*Os(dmpm)(OH$_2$)][OTf] (**5**), grown from diethyl ether, were treated similarly; subsequent comments in brackets will refer to this compound.] Because the crystals of **2** lost solvent readily, they were stored in the supernatant until just before mounting. Standard peak indexing and least squares refinement using 7867 [8162] reflections yielded the cell dimensions given in Table 1.

Data were collected with an area detector by using the measurement parameters listed in Table 1. Systematic absences for 0*k*0 ($k \neq 2n$) and *h*0*l* ($h + l \neq 2n$), were only consistent with space group $P2_1/n$. [For **5**, systematic absences for *hkl* ($h + k \neq 2n$) and *h*0*l* ($l \neq 2n$), were only consistent with space groups *Cc* and *C*2/*c*. The centrosymmetric space group *C*2/*c* was chosen based on the value for average values of the normalized structure factors.] The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, a face-indexed absorption correction was applied, the maximum and minimum transmission factors being 0.863 and 0.586. [For **5**, an absorption correction using the program SADABS was applied, the maximum and minimum transmission factors being 0.928 and 0.612.] Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. The 0 1 1 reflection was deleted because it was occluded by the beam stop. The remaining 9015 unique data were used in the least squares refinement. [For **5**, all 15016 data were used in the least-squares refinement.]

The structure was solved using Patterson and weighted difference Fourier methods (SHELXTL). [The structure of **5** was solved by direct methods.] The correct positions for the osmium, phosphorus, and sulfur atoms were deduced from a sharpened Patterson map [E-map]. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0214P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$ [for **5**, $w = \{[\sigma(F_o^2)]^2 + (0.0240P)^2\}^{-1}$]. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms of the osmium-containing molecule, and the phenyl, methyl, and methylene hydrogen atoms of this molecule were fixed in “idealized” positions with C–H = 0.95, 0.99, and 0.98 Å, respectively. Their isotropic displacement parameters were set equal to 1.2 (for the phenyl and methylene hydrogen atoms) or 1.5 (for the methyl hydrogen atoms) times U_{eq} of the attached carbon atom. Methyl hydrogen atom positions were optimized by rotation about the C–C bonds. [For **5**, the hydrogen atoms on the aqua ligand were located in the difference Fourier map and their locations were independently refined with individual isotropic displacement factors. The two O–H distances were restrained to be equal within 0.03 Å. All other hydrogen atoms were fixed in “idealized” positions.] Two molecules of toluene were present in the unit cell of **4**. These toluene molecules were disordered about inversion centers, and the six aromatic carbon atoms were restrained to conform to a rigid hexagon. All of the toluene carbon atoms were restrained to have identical isotropic displacement parameters. The methyl carbon of the toluene molecule was restrained to lie on the external bisector 1.5 Å from the attached phenyl carbon atom. The hydrogen atoms of the toluene molecule were added as previously described. A correction for secondary extinction was not necessary. Successful convergence was indicated by the maximum shift/error of 0.002 [0.001] for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (0.91 e Å^{-3}) was located 1.11 Å from the osmium atom. [For **5**, the largest peak in the final Fourier difference map (1.04 e Å^{-3}) was located 1.48 Å from *P*2.] A final analysis of variance between observed and calculated structure factors showed no apparent errors.

Acknowledgments

We thank the National Science Foundation (Grant Nos. CHE 00-76061 and CHE 04-20768) for support of this work, and Dr. Scott Wilson and Ms. Teresa Prussak-Wieckowska of the University of Illinois X-ray Diffraction Laboratory for collecting the crystallographic data for **2** and **5**. J.L.B. and C.L.G. thank the University of Illinois for departmental fellowships.

Appendix A. Supporting information

The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 604106 for **2** and 604105 for **5**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.040.

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