Reactivity of the Unsaturated Triosmium Cluster $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}Ph_2PCH_2P(Ph)C_6H_4)(\mu\text{-}H)$ with Benzothiophene: Activation of a P−C Bond in Diphosphine and a C−H Bond in Benzothiophene

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Received February 16, 2005

Treatment of the electronically unsaturated cluster $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}Ph_2PCH_2P(Ph)C_6H_4)(\mu\text{-}H)$ (**1**) with benzothiophene in refluxing *m*-xylene afforded $Os_3(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}PMePh)(\mu_3\text{-}\eta^2\text{-}C_6H_4)$ (**2**), $Os_3(CO)_7(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)(\mu_3\text{-}\eta^3\text{-}SC_8H_5)(\mu\text{-}H)$ (**3**), and $Os_3(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)$ (**4**). Thermolysis of **1** in refluxing toluene for 35 h afforded only **4**, whereas in refluxing *m*-xylene it gave both **4** and **2**. Compound **4** can also be obtained from the thermolysis of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh_2)(\mu\text{-}H)$ (**5**) in refluxing toluene. All the complexes have been structurally characterized. Compound **3** contains a unique example of a μ_3-η^2 benzothienyl ligand coordinated through the sulfur atom and the C−C double bond of the five-membered ring in a σ,π vinyl fashion. This coordination mode results in the rupture of one osmium−osmium bond, whereas the basic triangular metal framework is retained in the case of **2** and **4**, which are derived from the activation of P−C and C−H bonds of **1** and do not contain any benzothiophene-derived ligand.

Introduction

Hydrodesulfurization (HDS) is a heterogeneous reaction of major importance for both industrial and environmental reasons and is performed on a massive scale for the removal of sulfur from organosulfur compounds in petroleum-based feedstocks.[1,2] The sulfur-containing molecule benzothiophene is of special interest because its alkylated derivatives are more difficult to desulfurize than thiophene itself,[3] and thiophene, benzothiophene, and dibenzothiophene are common sulfur-containing contaminants in oil feedstocks.[1f] A variety of organometallic systems have been studied as models for the homogeneous HDS of thiophene.[4−9] Stone and coworkers[6,7a,b] were the first to demonstrate the reactivity of organometallic clusters with thiophenic molecules, such as thiophene and benzothiophene, to produce ring-opened or desulfurized thiophene-containing transition metal complexes. The first homogeneous example of metal-assisted opening and hydrogenation of benzothiophene was reported by Rauchfuss et al.,[8] who

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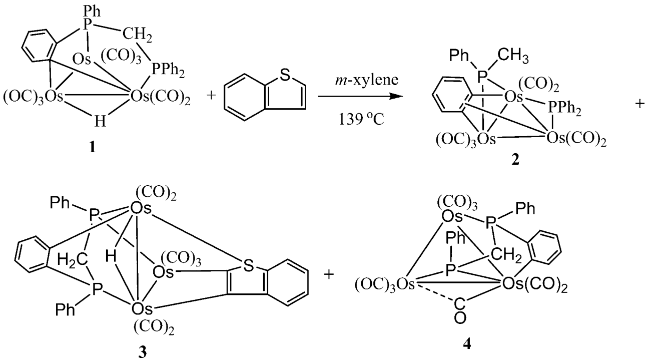
10.1021/om050110k CCC: $30.25

demonstrated its reaction with $Fe_3(CO)_{12}$ to obtain the benzothioferrole compound $Fe_2(CO)_6(\mu\text{-}C_8H_6S)$, which was hydrogenated subsequently to give ethylbenzene. Osmium and ruthenium clusters with sulfur-containing ligands in different binding sites and coordination geometries have been synthesized in an effort to model the early stages of the hydrodesulfurization process. $Ru_3(CO)_{12}$ has been reported to react with thiophene and benzothiophene to afford both ring-opened and desulfurized thiophene-containing complexes.[10-13] For instance, $Ru_3(CO)_{12}$ reacts with benzothiophene in refluxing THF to produce the three complexes $Ru_3(CO)_8(\mu\text{-}C_8H_6)$, $Ru_2(CO)_6(\mu\text{-}C_8H_6S)$, and $Ru_2(CO)_6(\mu\text{-}C_8H_6)$, all of which contain ring-opened or desulfurized benzothiophene ligands.[10a] Recently, García et al. have demonstrated that $Ru_3(CO)_{12}$ reacts with dibenzothiophene at 98 °C to give the dinuclear complex $Ru_2(C_{12}H_8)(\mu\text{-}CO)(CO)_5$, by a double C−S bond activation−desulfurization process.[7d] The lightly stabilized osmium cluster $Os_3(CO)_{10}(MeCN)_2$ reacts with thiophenes and benzothiophenes to give a series of Os-thiophene complexes in which the thiophene has undergone bond cleavage to give C−S and C−H bond-activated products. For example, $Os_3(CO)_{10}(MeCN)_2$ reacts with benzothiophene at ambient temperature to give $Os_3(CO)_{10}(\mu\text{-}C_8H_5S)(\mu\text{-}H)$ and $Os_3(CO)_9(\mu_3\text{-}C_8H_4S)(\mu\text{-}H)_2$, whereas at elevated temperature (80 °C) an additional ring-cleaved complex, $Os_3(CO)_{10}(\mu\text{-}C_8H_6S)$, is also obtained.[10b,13]

In recent years, we have been exploring the chemistry of the unsaturated triosmium cluster $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}Ph_2PCH_2P(Ph)C_6H_4)(\mu\text{-}H)$ (**1**) not only because of its unusual reactivity to give many interesting molecules but also because of the ability of the diphosphine ligand to keep the metal cluster fragment intact during chemical reactions.[14-19] However, there are examples in which diphosphine ligands can also undergo C−H and P−C bond cleavage, forming M−H, M−P, and M−C bonds.[20,21] These types of P−C and C−H bond cleavage reactions represent one of the major deactivation pathways for phosphine complexes used as homogeneous catalysis.[22] In related studies, we have observed that the reaction of $Ru_3(CO)_{12}$ with benzothienyldiphenylphosphine at elevated temperatures leads not only to C−H and C−P bond activation but also, and more importantly, to C−S bond activation/rupture.[23] Following the above observations we were prompted to investigate the reactivity of **1** with benzothiophene, and the results are described in the present paper.

Scheme 1



Results and Discussion

Reaction of **1** with benzothiophene in refluxing *m*-xylene for 4 h resulted in the isolation of three triosmium compounds, $Os_3(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}PMePh)(\mu_3\text{-}\eta^2\text{-}C_6H_4)$ (**2**), $Os_3(CO)_7(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)(\mu_3\text{-}\eta^3\text{-}SC_8H_5)(\mu\text{-}H)$ (**3**), and $Os_3(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)$ (**4**) in 8, 15, and 20% yields (Scheme 1).

Compounds **2**−**4** have been characterized by a combination of spectroscopic data and single-crystal X-ray diffraction studies. The molecular structure of **2** is shown in Figure 1, crystal data are given in Table 1, and selected bond distances and angles are listed in the caption. The molecule consists of a triangular cluster of osmium atoms with three distinctly different Os−Os

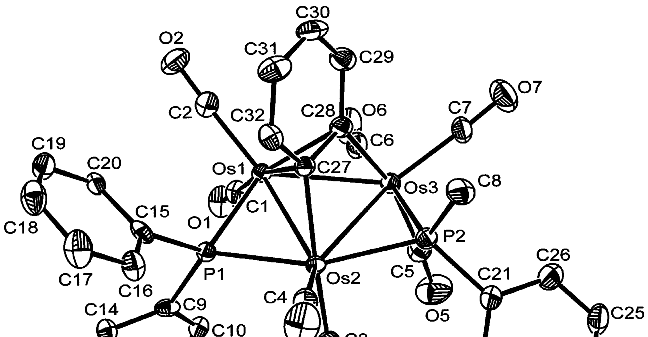


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distance and angles: Os(1)−Os(3) = 2.7480(3), Os(1)−Os(2) = 2.7890(3), Os(2)−Os(3) = 2.9373(3), Os(1)−P(1) = 2.2786(14), Os(2)−P(2) = 2.3259(15), Os(2)−P(1) = 2.3587(14), Os(3)−P(2) = 2.3828(15), Os(1)−C(27) = 2.365(6), Os(1)−C(28) = 2.316(6), Os(2)−C(27) = 2.150(5), Os(3)−C(28) = 2.139(6), C(27)−C(28) = 1.427(8), Os(3)−Os(1)−Os(2) = 64.071(8), Os(1)−Os(2)−Os(3) = 57.287(7), Os(1)−Os(3)−Os(2) = 58.642(7), C(8)−P(2)−Os(2) = 120.4(2), C(8)−P(2)−Os(3) = 118.3(2), Os(2)−P(2)−Os(3) = 77.18(5), Os(1)−P(1)−Os(2) = 73.92(4), Os(2)−C(27)−Os(1) = 76.13(17), Os(3)−C(28)−Os(1) = 76.06(18).

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Table 1. Crystallographic Data and Structure Refinement[a] for 2, 3, and 4

	2$\cdot CH_2Cl_2$	**3**	**4**
formula	$C_{33}Cl_2H_{24}O_7Os_3P_2$.	$C_{34}H_{21}O_7Os_3P_2S$	$C_{28}H_{16}O_9Os_3P_2$
fw	1235.96	1206.11	1128.95
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	*Pbca*	*P*2(1)/*c*
a, Å	9.4478(2)	17.8889(3)	10.6868(6)
b, Å	12. 1148(2)	16.9945(3)	11.9802(7)
c, Å	17.3097(3)	22.0581(5)	23.3066(14)
α, deg	72.1513(7)	90	90
β, deg	78.4997(8)	90	91.099(1)
γ, deg	71.8927(8)	90	90
V, Å^3	1780.58(6)	6705.9(2)	2983.4(4)
Z	2	8	4
D_{calc}, mg m^{-3}	2.305	2.389	2.513
μ(Mo Kα), mm^{-1}	10.963	11.546	12.904
F(000)	1140	4440	2056
cryst size, mm	0.25 × 0.22 × 0.20	0.15 × 0.10 × 0.08	0.44 × 0.16 × 0.16
θ range, deg	2.97 to 27.50	2.93 to 27.49	1.75 to 28.32
limiting indices	$-12 \le h \le 12$	$-23 \le h \le 23$	$-13 \le h \le 14$
	$-15 \le k \le 15$	$-21 \le k \le 22$	$-15 \le k \le 15$
	$-22 \le l \le 22$	$-28 \le l \le 28$	$-31 \le l \le 26$
no. of reflns collected	28 941	30 766	20 340
no. of indep reflns	8117 [*R*(int) = 0.1045]	7654 [*R*(int) = 0.983]	7332 [*R*(int) = 0.0284]
max. and min. transmn	0.2178 and 0.1703	0.4586 and 0.2763	0.2319 and 0.0700
no. of data/ restraints/params	811/0/425	7654/0/424	7332/0/379
goodness-of-fit on *F*^{2}	1.041	1.007	1.062
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0358	R1 = 0.0442	R1 = 0.0276
	wR2 = 0.0867	wR2 = 0.0877	wR2 = 0.0667
R indices (all data)	R1 = 0.0432	R1 = 0.0740	R1 = 0.0313
	wR2 = 0.0904	wR2 = 0.0969	wR2 = 0.0683
largest diff peak and hole, e Å^{-3}	1.883 and −2.951	1.958 and −2.018	3.265 and −1.663

[a] Details in common: X-radiation, Mo Kα (λ = 0.71073 Å), temperature (K) 150(2) except **4**, refinement method: full-matrix least-squares on *F*^{2}.

edges (Os(1)−Os(2) = 2.7890(3) Å, Os(1)−Os(3) = 2.7480(3) Å, Os(2)−Os(3) = 2.9373(3) Å), the longer one being associated with a bridging methylphenyl phosphido group as well as a C_4H_4 moiety, while the shortest edge is bridged by the diphenylphosphido group. As expected, the σ-bonds between osmium atoms and the benzyne moiety (Os(2)−C(27) = 2.150(5) Å and Os(3)−C(28) = 2.139(6) Å) are significantly shorter than the two π-bonds (Os(1)−C(27) = 2.365(6) Å and Os(1)−C(28) = 2.3165(6) Å). These Os−C bond distances are similar to those observed in $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_6H_4)$[24] and $Os_3(CO)_8(\mu\text{-}SbPh_2)(\mu_3\text{-}\eta^2\text{-}C_6H_4)(\mu\text{-}H)$.[25] The C(27)−C(28) bond distance of 1.427(8) Å in the phenylene ligand is also indicative of a μ_3-η^2 bonding mode and loss of aromaticity of the ring.[25] The two phosphido groups lie in the same plane of the Os_3 triangle and the Os−P bond distances are close to the values found in other related phosphido-bridged triosmium clusters.[26] The two Os−P−Os angles 73.92(4)° and 77.18(5)° are nearly the same and comparable to those reported for the phosphido-bridged Os−Os edges in $Os_3(CO)_6(\mu\text{-dppm})(\mu\text{-}PPh_2)_2(\mu\text{-}H)_2$.[26a] A striking feature of **2** is the occurrence of one diphenylphosphido, one methylphenylphosphido, and a benzyne moiety, which can only come from the $Ph_2PCH_2P(Ph)C_6H_4$ ligand in **1**. The spectroscopic data of **2** in solution are consistent with the solid-state structure. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows two doublets at δ 181.1 and 131.1 with a P−P coupling constant of 105.0 Hz, supporting the presence of nonequivalent bridging phosphido ligands, and as expected, the ^{31}P chemical shifts of the μ-PR_2 groups are well downfield of 85% H_3PO_4.[26]

The molecular structure of **3** is depicted in Figure 2, crystal data are given in Table 1, and selected bond distances and angles are listed in the caption. The molecule consists of an open cluster of three osmium atoms with seven linear terminal carbonyl ligands. There are only two metal−metal bonds, Os(1)−Os(2) = 3.0901(4) Å and Os(2)−Os(3) = 2.8604(4) Å. Os(1) and Os(2) are ligated by two CO groups, whereas Os(3) is attached to three CO ligands. An intriguing structural feature of **3** is that the μ_3-η^3-benzothienyl ligand is coordinated through the sulfur atom and the C−C double bond in the five-membered ring in a σ,π-coordination mode. The previously reported compound $Os_3(CO)_{10}(\mu\text{-}C_8H_5S)(\mu\text{-}H)$ contains a μ_2-η^2 (σ,π-vinyl) benzothienyl ligand, but compound **3** appears to be the first example of an S-coordinated μ_3-η^3-benzothienyl ligand. The metal−carbon σ-bonding distance, Os(3)−C(34) = 2.0708(8) Å, and π-bonding distances, Os(2)−C(34) = 2. 259(7) Å and Os(2)−C(33) = 2.326(8) Å are significantly shorter than those of the corresponding distances in $Os_3(CO)_{10}(\mu\text{-}C_8H_5S)(\mu\text{-}H)$ (2.14(1), 2.481(1), and 2.41(1)(1) Å, respectively).[13] In contrast to $Os_3(CO)_{10}(\mu\text{-}C_8H_5S)(\mu\text{-}H)$,[13] where the sulfur points away from the $Os(CO)_4$ grouping, the coordination of the sulfur atom in **3** requires the sulfur to be oriented *syn* to the third metal atom. This *syn* orientation is also adopted by most σ,π-vinyl complexes.[28] The Os(1)−S(1) bond distance of

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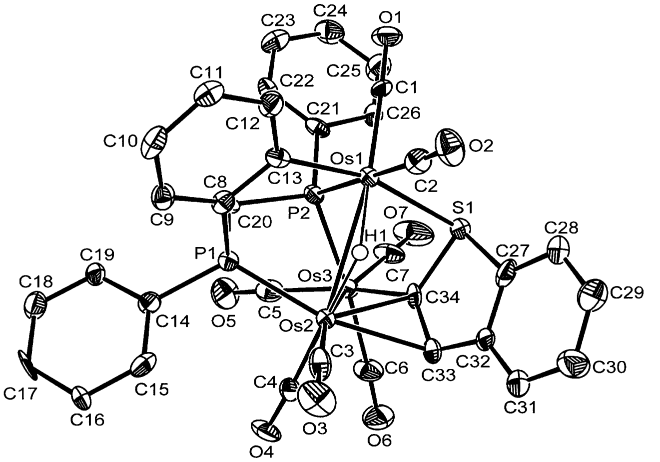

Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distance and angles: Os(1)−Os(2) = 3.0901(4), Os(2)−Os(3) = 2.8604(4), Os(1)−S(1) = 2.435(2), Os(2)−C(34) = 2.259(7), Os(2)−C(33) = 2.326(8), Os(3)−C(34) = 2.070(8), Os(2)−P(1) = 2.319(2), Os(3)−P(2) = 2.422(2), Os(1)−P(2) = 2.440(2), Os(1)−C(13) = 2.141(8), C(32)−C(33) = 1.467(12), C(33)−C(34) = 1.429(11), Os(3)−Os(2)−Os(1) = 84.197(12), Os(3)−C(34)−Os(2) = 82.6(3), P(2)−Os(1)−Os(2) = 68.46(5), S(1)−Os(1)−P(2) = 85.03(7), S(1)−Os(1)−Os(2) = 75.12(5), P(1)−Os(2)−Os(1) = 74.90(5), P(2)−Os(3)−Os(2) = 72.87(5), P(2)−C(20)−P(1) = 101.1(4), P(1)−Os(2)−C(33) = 163.5(2), Os(3)−P(2)−Os(1) = 110.45(8), S(1)−C(34)−Os(3) = 121.9(4), S(1)−C(34)−Os(2) = 113.7(4).

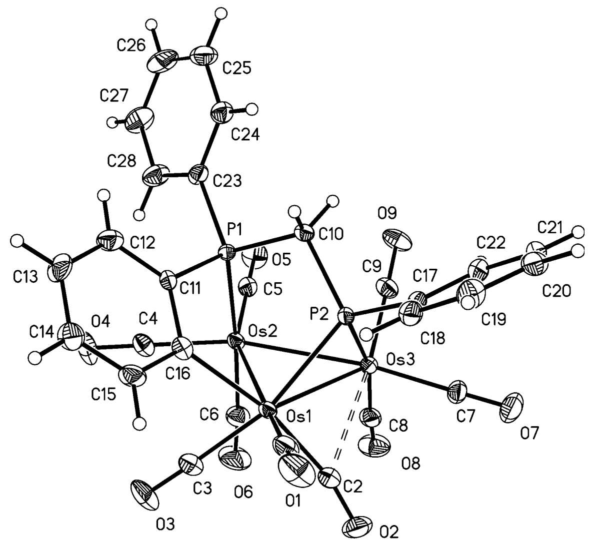

Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distance and angles: Os(1)−Os(3) = 2.9302(3), Os(1)−Os(2) = 2.8827(3), Os(2)−Os(3) = 2.8254(3), Os(2)−P(1) = 2.3775(11), Os(3)−P(2) = 2.3302(12), Os(1)−P(2) = 2.3734(12), C(2)−Os(1) = 1.935(5), C(2) − Os(3) = 2.68(2), C(16)−Os(1) = 2.192(5), C(11)−C(16) = 1.411(6), C(11)−P(1) = 1.811(5), C(10)−P(1) = 1.814(5), C(10)−P(2) = 1.820(4), Os(3)−Os(2)−Os(1) = 61.763(7), Os(2)−Os(1)−Os(3) = 58.156(6), Os(2)−Os(3)−Os(1) = 60.081(6), Os(3)−P(2)−Os(1) = 77.25(4).

2.435(2) Å is typical of the osmium−sulfur bond distances found in $Os_3(CO)_{10}(\mu\text{-}SC_8H_6)(\mu\text{-}Br)$ (2.411(5) Å) and $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2CH_2\text{-})(\mu\text{-}Br)$ (2.37(1) Å).[12]

The benzothienyl ligand forms two bonds to two osmium atoms through C(33) and C(34) of the thiophene ring. As a result, the C(32)−C(33) and C(33)−C(34) bond distances (1.467(12) and 1.429(11) Å, respectively) of the thiophene ring are significantly elongated compared to the average C═C bond distance (av 1.376 Å) in the benzene ring. This elongation of the bond lengths is most probably due to some loss of aromaticity produced by the bonding to the metal center.

The μ_3-η^2-$PPh(C_6H_4)CH_2PPh$ ligand is bonded to three osmium atoms through P(1), P(2), and C(13) atoms (Os(2)−P(1) = 2.319(2) Å, Os(1)−P(2) = 2.440(2) Å, Os(3)−P(2) = 2.422(2) Å, and Os(1)−C(13) = 2.141(8) Å), leading to three five-membered metallacycles, Os(2)−P(1)−C(20)−P(2)−Os(1), Os(2)−P(1)−C(8)−C(13)−Os(1), and Os(2)−P(1)-C(20)−P(2)−Os(3). The terminal Os−P bond distance is significantly shorter than the Os−P−Os bridging bonds. Compound **3** contains a bridging hydride ligand, δ −16.32. It was crystallographically located (not refined) across the Os(1)−Os(2) edge. The Os(1)−Os(2) bond distance of 3.0901(4) Å is significantly longer than the unbridged Os(2)−Os(3) bond distance of 2.8604(4) Å. This elongation of the Os(1)−Os(2) bond is a consequence of the location of the bridging hydride along this edge. The benzothienyl ligand serves as a six-electron donor and the $PPh(C_6H_4)CH_2PPh$ ligand donates five electrons; thus, cluster **3** has a total of 50 valence electrons, and in order for each of the metal atoms to have an 18-electron configuration there can be no more than two metal−metal bonds between the three metal atoms.

The molecular structure of **4** is shown in Figure 3, crystal data are given in Table 1, and selected bond distances and angles are given in the caption. The molecule consists of a triangular cluster of osmium atoms with a triply bridging $PPh(C_6H_4)CH_2PPh$ ligand and eight terminal and one weak semibridging CO ligand. Os(2) and Os(3) are ligated by three CO ligands, while Os(1) is attached to only two CO ligands. The Os(1)−Os(3) edge of the triangle is asymmetrically bridged by a CO group (Os(1)−C(2) = 1.935(5) Å and Os(3)−C(2) = 2.68(2) Å). The tridentate phosphine ligand sits upon the $Os_3(CO)_9$ fragment so that atom Os(2) is bonded to the P(1) atom, Os(1) is bonded to the P(2) atom, and this P atom, along with atom(16) of the C_6H_4 fragment, completes the coordination about Os(3). The capping bonding mode of the diphosphine fragment $PPh(C_6H_4)CH_2PPh$ above the Os_3 plane forces the P(1) atom to be axially oriented along with an axial phenyl group. The Os(2)−Os(3) bond distance of 2.8254(3) Å is significantly shorter than the remaining two Os−Os bonds (Os(1)−Os(3) = 2.9302(3) Å, Os(1)−Os(2) = 2.8827(3) Å). The Os−P bond distances are comparable to those in **3**. Compound **4** is structurally similar to that of $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)$, which was synthesized from the thermolysis of $Ru_3(CO)_{10}(\mu\text{-dppm})$ at 80 °C.[29] The infrared spectrum of **4** in the terminal CO region is similar to that of the ruthenium analogue $Ru_3(CO)_8(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}PPh(C_6H_4)CH_2PPh)$, but it also exhibits a lower energy absorption band at 1869 cm^{-1}, which can be attributed to the semibridging CO ligand.

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In addition to the phenyl proton resonances at δ 8.11, 7.80, 7.51, and 7.40, the ^{1}H NMR spectrum of **4** contains four well-separated equal intensity multiplets at δ 7.10, 6.82, 6.61, 6.12, and 3.56, characteristic of orthometalated phenyl protons. The aliphatic region of the spectrum contains two multiplets at δ 3.56 and 4.75 due to the diastereotopic methylene protons of the orthometalated ligand. As expected, the ^{31}P{^{1}H} NMR spectrum shows two doublets at δ 29.52 and -32.62 ($J = 24.73$ Hz) for the two magnetically nonequivalent ^{31}P nuclei.

It has been demonstrated that the unsaturated compound **1** reacts only sluggishly with benzothiophene at 139 °C to give (μ-H)$Os_3(CO)_7$(μ_3-η^2-PPh(C_6H_4)CH_2PPh)(μ_3-η^3-SC_8H_5)(μ-H) (**3**), containing a novel S-coordinated μ_3-η^3-benzothienyl ligand and the mixed phosphido-bridged compound $Os_3(CO)_7$(μ-PPh_2)(μ-PMePh))(μ_3-η^2-C_6H_4) (**2**) and the tridentate diphosphine compound $Os_3(CO)_8$(μ-CO)(μ_3-η^2-PPh(C_6H_4)CH_2PPh) (**4**). Thermolysis of **1** in refluxing toluene for 40 h afforded only **4**, whereas in refluxing *m*-xylene it gave both **4** and **2**, which are believed to be formed from **1** by independent pathways. Compound **2** is most probably formed from the cleavage of the P−C bonds of the Ph_2PCH_2P(Ph)-C_6H_4 ligand in **1** into three fragments, PPh_2, C_6H_4, and PCH_2Ph, which are retained separately as ligands. Most probably the metal-bound hydride combines with the latter to form the mixed phosphido ligand, PCH_3Ph. Although the formation of μ-PPh_2 and CH_2PPh_2 by the cleavage of the P−C bond of dppm in $Ru_3(CO)_{10}$(μ-η^2-dppm) is known,[30] the formation of μ_2-PPh_2, μ-PMePh, and μ_3-C_6H_4 at a triosmium center from the scission of a diphosphine moiety is unprecedented and the formation of **3** is unique. Compound **4** may be considered as being derived from **1** by the intermediate formation of (μ-H)$Os_3(CO)_9$(μ_3-η^2-PPh(C_6H_4)CH_2PPh_2) (**5**), which in turn was formed from the reaction of **1** with CO (CO probably comes from nonspecific decomposition of **1**) followed by oxidative cleavage of a P−C bond and reductive elimination of benzene via H transfer. In support of this, we have demonstrated that thermolysis of **5** at 110 °C gave exclusively **4** in moderate yield. Taken together, these results show that although the dppm ligand does appear to hold the Os triangle together, its steric bulk, or perhaps its stronger electron donation to the cluster, impedes the reaction with benzothiophene, the major products being the further reaction of dppm with the cluster. The electronic effect could dominate if the reaction rate is controlled only by CO dissociation, which might be slower at a more electron rich cluster, where back-bonding would be expected to strengthen the metal−carbonyl bonds. On the other hand, the bulk of the dppm could impede access of the heterocycle to the CO dissociated sites. In refluxing xylene one would expect CO dissociation to be rapid even in a diphosphine complex.[31] The one thiophene-containing compound obtained reveals what may be an important type of intermediate, **3**, in the early stages of HDS (i.e., coordination of S prior to S−C cleavage). Its isolation is probably due to the paucity of available coordination sites usually obtainable by CO dissociation and brought about by the bulky, less dissociable dppm.

Experimental Section

General Comments. All the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. Benzothiophene was purchased from Aldrich chemical Company, Inc. The starting clusters $Os_3(CO)_8$-(μ_3-η^2-Ph_2PCH_2P(Ph)C_6H_4)(μ-H) (**1**) and (μ-H)$Os_3(CO)_9$(μ_3-η^2-PPh(C_6H_4)CH_2PPh_2) (**5**) were prepared according to the literature method.[32] Infrared spectra were recorded on a Shimadzu FT-IR 8101 spectrophotometer. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on Varian Unity Plus 400 and Bruker DPX 400 spectrometers. Chemical shifts for the ^{31}P{^{1}H} NMR spectra are relative to 85% H_3PO_4. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant.

Reaction of $Os_3(CO)_8$(μ_3-η^2-Ph_2PCH_2P(Ph)C_6H_4)(μ-H) (1) with Benzothiophene. A *m*-xylene solution (25 mL) of **1** (0.100 g, 0.085 mmol) and benzothiophene (0.064 g, 0.477 mmol) was refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (4:1, v/v) developed three bands. The first band gave $Os_3(CO)_7$(μ-PPh_2)-(μ-PMePh)(μ_3-η^2-C_6H_4), (**2**)·CH_2Cl_2 (0.008 g, 8%), as red crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C. Anal. Calcd for $C_{33}H_{24}O_7Os_3P_2$: C, 32.07; H, 1.96. Found: C, 32.29; H, 2.12. IR (νCO, CH_2Cl_2): 2060 s, 2016 s, 1993 vs, 1968 w, 1950 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37−6.24 (m, 19H), 2.21 (d, 3H, $J = 16.5$ Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 181.1 (d, $J = 105.0$ Hz), 131.1 (d, $J = 105.0$ Hz). MS (FAB): *m/z* 1150. The second band gave (μ-H)$Os_3(CO)_7$(μ_3-η^2-PPh(C_6H_4)CH_2PPh)(μ_3-η^3-SC_8H_5)(μ-H) (**3**) (0.015 g, 15%) as yellow crystals from hexane/CH_2Cl_2. Anal. Calcd for $C_{34}H_{21}O_7Os_3P_2S$: C, 33.85; H, 1.76. Found: C, 33.98; H, 1.98. IR (νCO, CH_2Cl_2): 2076 vw, 2062 s, 2031 vs, 2004 vs, 1972 s, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.11−6.12 (m, 19H), 3.48 (m, 1H), 4.65 (m, 1H), 16.31 (dd, 1H, $J = 8.8$, 12.4 Hz). ^{31}P{^{1}H} ($CDCl_3$): δ 34.8 ($J = 35.4$. Hz), −28.6 ($J = 35.4$ Hz). MS (FAB): *m/z* 1205. The third band gave $Os_3(CO)_8$(μ-CO)(μ_3-η^2-PPh(C_6H_4)CH_2PPh) (**4**) (0.019 g, 20%) as red crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C. Anal. Calcd for $C_{28}H_{16}O_9Os_3P_2$: C, 29.79; H, 1.43. Found: C, 29.98; H, 1.55. IR (νCO, CH_2Cl_2): 2076 s, 2039 vs, 2026 vs, 1999 m, 1977 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.11 (m, 3H), 7.80 (m, 2H), 7.51 (m, 2H), 7.40 (m, 3H), 7.10 (m, 1H) 6.82 (m, 1H), 6.61 (m, 1H) 6.12 (m, 1H), 3.56 (m, 1H), 4.75 (m, 1H). ^{31}P{^{1}H} ($CDCl_3$): δ 29.5 ($J = 24.7$ Hz), −32.62 ($J = 24.7$ Hz). MS (FAB): *m/z* 1128 (M^+).

Thermolysis of 1 in *m*-Xylene. A *m*-xylene solution (20 mL) of **1** (0.055 g, 0.047 mmol) was heated to reflux for 4 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (4:1, v/v) gave two bands. The faster moving band gave **2** (0.006 g, 10%). The slower moving band gave **4** (0.014 g, 27%) as red crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C.

Thermolysis of 1 in Toluene. A toluene solution (10 mL) of **1** (0.050 g, 0.042 mmol) was heated to reflux for 40 h. The solvent was removed under reduced pressure, and the residue was chromatographed as above to give **4** (0.019 g, 40%) as red crystals.

Thermolysis of (μ-H)$Os_3(CO)_9$(μ_3-η^2-PPh(C_6H_4)CH_2PPh_2) (5). In a similar thermolysis, a toluene solution (20 mL) of **5** (0.035 g, 0.029 mmol) heated for 30 h followed by similar chromatographic separation gave **4** (0.017 g, 50%).

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X-ray Structure Determination of 2 and 3. Single crystals of **2** and **3** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at −4 °C. Crystallographic data were collected at 150 K, using a FAST area detector diffractometer and Mo Kα radiation (λ = 0.71073 Å). Data collection and processing were carried out using the programs COLLECT[33] and DENZO.[34] Empirical absorption corrections were applied to the data sets using multiple and symmetry-related data measurements via the program SORTAV.[35,36] The unit cell parameters were determined from all observed reflections in a θ range of 3−10° and refined using the entire data set. The structures were solved by direct methods (SHELXS-97)[37] and refined on F^2 by full-matrix least-squares (SHELXL-97)[38] using all unique data. The bridging hydrides in **2** and **3** were located from a difference map but not refined. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions (riding model) with U_{iso} set to 1.2 times the U_{eq} of the parent atom.

X-ray Structure Analysis of 4. Suitable crystals of **4** were coated with Paratone N oil, suspended in a small fiber loop, and placed in a cooled nitrogen gas stream at 173 K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation. A hemisphere of data was measured using a series of combinations of phi and omega scans with 10 s frame exposures and 0.3 frame widths. Data collection, indexing, and initial cell refinements were all carried out using SMART[39] software. Frame integration and final cell refinements were done using SAINT[40] software. The final cell parameters were determined from least-squares refinement on 6692 reflections. The SADABS[41] program was used to carry out absorption corrections.

The structures were solved using direct methods and difference Fourier techniques (SHELXTL, V6.12).[42] Hydrogen atoms were placed in their expected chemical position using the HFIX command and were included in the final cycles of least squares with isotropic U_{ij}'s related to the atoms ridden on. All non-hydrogen atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections are taken from the *International Tables for X-ray Crystallography*.[43] Structure solution, refinement, graphics, and generation of publication materials were performed by using SHELXTL, V6.12 software. Additional details of data collection and structure refinement are given in Table 1.

Acknowledgment. The Swedish International Development Agency (SIDA) and the Swedish Research Council (VR) are gratefully acknowledged for supporting the collaboration between S.E.K. and E.N.

Supporting Information Available: Tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050110K

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