

Stoichiometric and catalytic activation of sp^2 C–H bonds: molecular structure of $Os_3(\mu-H)(\mu_3-{}^nBuOC=CHPEt_2)(CO)_9$ and catalytic properties of this and related Os and Ru clusters

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Abstract

The thermal reaction of ${}^nBuOCH=CHPEt_2$ with $Os_3(CO)_{12}$ gives a new osmium triangular cluster, $Os_3(\mu-H)(\mu_3-{}^nBuOC=CHPEt_2)(CO)_9$ (**1**), which was isolated in 62% yield. The structure of **1** has been determined by X-ray diffraction ($P\bar{1}$, $a = 12.914(3)$, $b = 13.984(4)$, $c = 16.375(4)$ Å, $\alpha = 66.83(2)$, $\beta = 77.82(2)$, $\gamma = 77.97(2)^\circ$, $Z = 4$, $d_{calc} = 2.552$ g/cm³, $R = 0.0399$ for 6636 reflections). The $\mu_3-{}^nBuOC=CHPEt_2$ in **1** acts as a five-electron donor. It forms a σ -bond with one Os atom and coordinates the second and the third Os atoms of the cluster by its olefinic bond and the phosphorus atom, respectively. Both complex **1** and $Os_3(\mu-H)(\mu-CH=CHR)(CO)_{10}$ ($R = {}^nC_6H_{13}$, Ph) catalyze the silylation of terminal olefins with Et_3SiH to yield the corresponding *trans*-triethylvinylsilanes and alkanes in moderate yield *even at ambient temperature*. The proposed mechanism of olefin silylation catalyzed by triangular metal clusters involves the olefin C–H bond activation on the triangular cluster core and formation of an intermediate which has a structure similar to that of cluster **1**. © 1997 Elsevier Science S.A.

Keywords: X-ray diffraction; C–H bonds; Os and Ru clusters

1. Introduction

Dehydrogenative silylation of alkenes (Eq. (1)) [1–11] is a promising method for the preparation of vinylsilanes. Moreover this transformation is one of the alternative pathways of important industrial reaction: olefin hydrosilylation [12].



The photoactivated reaction catalyzed by $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, or $Os_3(CO)_{12}$ was found to yield a mixture of products of both olefin silylation and hydrosilylation [8–10]. However the reaction catalyzed by $Ru_3(CO)_{12}$ at thermal conditions turned out to give only products of dehydrogenative silylation [13,14]. This catalytic silylation was recently shown to be an intrinsic feature of catalytic chemistry of triangular carbonyl clusters of all group VIII metals [15].

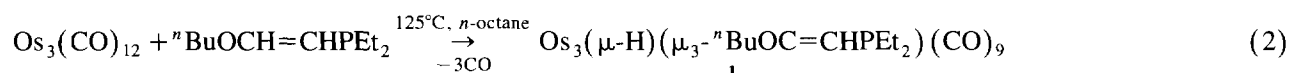
On the other hand olefins $RCH=CHR$ ($R = H$, alkyl, aryl) react readily with $Os_3(CO)_{12}$ to form $Os_3(\mu-H)(\mu-CR=CHR)(CO)_{10}$ clusters [16,17]. Thus, both stoichiometric and catalytic C–H bond activations of olefins are widely

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known general features of triangular clusters of Fe, Ru, and Os. The present work was undertaken with the idea to show that the reactivity of triangular clusters towards olefins is closely related to their catalytic activity. We found that various complexes $\text{Os}_3(\mu\text{-H})(\mu\text{-CR=CHR})(\text{CO})_{10}$ including the compound with a vinylphosphine ligand are very active catalysts of the olefin silylation even at room temperature.

2. Results and discussion

The cluster $\text{Os}_3(\text{CO})_{12}$ reacts with vinylphosphine $n\text{BuOCH=CHPEt}_2$ under reflux in *n*-octane for 14 h to form a mixture of not less than 4 products (TLC). One of them, cluster **1**, has been isolated by TLC in 62% yield and unambiguously identified and characterized (Eq. (2)). More prolonged heating of the reaction mixture results in a considerable decrease of the overall yield of **1** because of its decomposition.



The structure of **1** as determined by X-ray diffraction is shown in the Fig. 1. Bond lengths and selected bond angles are listed in Table 1.

The organic vinylphosphine ligand is coordinated simultaneously by all three osmium atoms. It forms a σ -bond with one Os atom and coordinates the second and the third Os atoms of the metal core by its olefinic bond and the phosphorus atom, respectively.

No examples of complexes with μ_3 -vinylphosphine coordination in clusters have been reported so far. Probably, observed selective activation of the β -C–H bond (relative to the P atom) of vinylphosphine is due to additional coordination of the ligand through the P atom. Obviously this coordination, which follows carbon monoxide elimination from $\text{Os}_3(\text{CO})_{12}$, precedes any further coordination of the olefin fragment. It is noteworthy that similar reactivity and coordination features are manifested by arylphosphines [18,19]. Thus, *ortho*-metallated adducts $\text{Os}_3(\mu\text{-H})(\mu_3\text{-C}_6\text{H}_4\text{PRPh-}o)(\text{CO})_9$ (R = Me, Ph) were isolated after a treatment of $\text{Os}_3(\text{CO})_{12}$ with PPh_2R . The compounds were characterized by X-ray structure analysis. Both these compounds and **1** contain a five-electron-donating C–C–P bridge.

The five-membered ring formed by the Os(2), Os(3), C(10), C(11) and P(1) atoms has an envelope conformation. The Os(2), Os(3), C(10), C(11) atoms are coplanar within 0.03 Å. Angles between this plane and the Os(2)P(1)C(11) and triosmium core planes are 44 and 46° (all geometric parameters are given for two independent molecules in **1**) and 51 and 52°, respectively. The distance Os(2)–Os(3) 3.012(1), 3.021(1) Å in **1** is longer than the two other distances Os(1)–Os(2) and Os(1)–Os(3) (2.780(1)–2.857(1) Å). The hydride atom was objectively located in the X-ray diffraction study and turned out to occupy a bridging position between Os(2) and Os(3) atoms that results in a considerable lengthening of the corresponding metal–metal bond. The presence of a hydride atom is also confirmed by an increase of the Os(3)–Os(2)–C(5) and Os(2)–Os(3)–C(9) bond angles as compared with other similar Os–Os–C(=O) bond angles (see Table 1). The bridging hydrogen atom is displaced from the Os_3 plane towards the

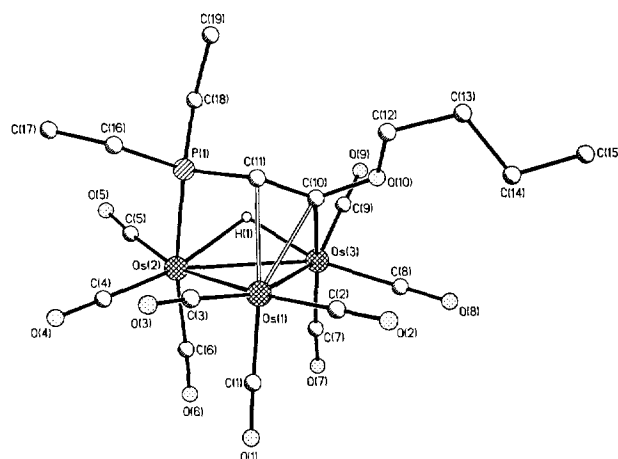


Fig. 1. PLUTO view of **1**.

Table 1
Selected bond lengths (Å) and bond angles (°) in molecule 1

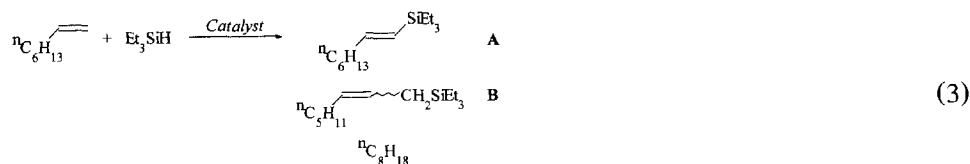
Bond lengths	Bond lengths		Bond angles	Bond angles	
	A	B		A	B
Os(1)–Os(2)	2.840(1)	2.857(1)	Os(2)–Os(1)–Os(3)	64.8(1)	64.9(1)
Os(1)–Os(3)	2.780(1)	2.774(1)	Os(2)–Os(1)–C(10)	85.5(4)	85.3(3)
Os(1)–C(1)	1.86(2)	1.91(2)	Os(3)–Os(1)–C(10)	46.9(3)	46.7(4)
Os(1)–C(2)	1.91(2)	1.90(1)	Os(2)–Os(1)–C(11)	78.2(4)	78.5(3)
Os(1)–C(3)	1.90(1)	1.91(2)	Os(3)–Os(1)–C(11)	75.1(3)	75.3(3)
Os(1)–C(10)	2.36(1)	2.41(2)	Os(1)–Os(2)–Os(3)	56.6(1)	56.2(1)
Os(1)–C(11)	2.28(1)	2.27(2)	Os(1)–Os(2)–P(1)	72.1(1)	72.5(1)
Os(2)–Os(3)	3.012(1)	3.021(1)	Os(3)–Os(2)–P(1)	83.7(1)	83.1(1)
Os(2)–P(1)	2.350(4)	2.336(4)	Os(1)–Os(3)–Os(2)	58.6(1)	58.9(1)
Os(2)–C(4)	1.90(1)	1.89(2)	Os(1)–Os(3)–C(10)	55.8(3)	57.5(4)
Os(2)–C(5)	1.91(2)	1.93(2)	Os(2)–Os(3)–C(10)	86.2(4)	87.2(3)
Os(2)–C(6)	1.96(2)	1.94(2)	Os(2)–P(1)–C(11)	104.1(4)	104.2(5)
Os(3)–C(7)	1.94(2)	1.93(2)	Os(2)–P(1)–C(16)	117.3(5)	117.7(5)
Os(3)–C(8)	1.91(2)	1.88(1)	C(11)–P(1)–C(16)	105.7(7)	105.1(6)
Os(3)–C(9)	1.90(2)	1.89(2)	Os(2)–P(1)–C(18)	116.2(6)	116.4(6)
Os(3)–C(10)	2.08(1)	2.08(2)	C(11)–P(1)–C(18)	107.8(8)	106.5(6)
P(1)–C(11)	1.76(2)	1.79(1)	O(16)–P(1)–C(18)	105.0(6)	105.8(7)
P(1)–C(16)	1.82(1)	1.83(1)	Os(3)–C(10)–O(10)	113.9(7)	117.7(9)
P(1)–C(18)	1.83(1)	1.82(2)	Os(3)–C(10)–C(11)	124.7(11)	123.1(10)
O(10)–C(10)	1.36(2)	1.31(2)	O(10)–C(10)–C(11)	121.3(12)	118.0(13)
O(10)–C(12)	1.44(2)	1.44(2)	P(1)–C(11)–C(10)	120.0(11)	117.4(9)
C(10)–C(11)	1.41(1)	1.43(2)			
C(12)–C(13)	1.49(2)	1.46(2)			
C(13)–C(14)	1.52(3)	1.57(4)			
C(14)–C(15)	1.52(3)	1.32(4)			
C(16)–C(17)	1.49(3)	1.52(2)			
C(18)–C(19)	1.53(3)	1.53(3)			

vinylphosphine ligand. The angle between the Os(2)Os(3)H(1) and triosmium core planes is 147 and 153°.

¹H NMR spectrum of **1** in benzene-*d*₆ reveals the resonance at δ –18.41 (doublet, $J(\text{PH})$ 13.6 Hz) which is attributed to the bridging hydrogen (cf. δ –17.90 and $J(\text{PH})$ 16.6 Hz for Os₃(μ -H)(μ -C₆H₄PMePh-*o*)(CO)₉, δ –17.66 and $J(\text{PH})$ 16.5 Hz for Os₃(μ -H)(μ -C₆H₄PPh₂-*o*)(CO)₉). According to the NMR spectroscopic data cluster **1** exhibits no ligand exchange in benzene at room temperature. However Os₃(μ -H)(μ -CH=CHR)(CO)₁₀ (R = H, alkyl) has been found to display fluxional behavior [16,17]. This means that the rigidity of the former compound (no evidence for a ligand exchange process) may be due to the additional coordination of the organic ligand through phosphorus.

We have found that both complex **1** and Os₃(μ -H)(μ -CH=CHR)(CO)₁₀ (R = ⁿC₆H₁₃, Ph) as well as analogous Ru clusters catalyze silylation of terminal olefins with Et₃SiH to yield the corresponding triethylvinylsilanes of *trans*-configuration and alkanes in high yield even at ambient temperature (Table 2). On the other hand this catalytic reaction in the presence of M₃(CO)₁₂ (M = Ru, Os) proceeds only at high temperature.

The silylation of 1-octene is accompanied by partial isomerization of the product (or an intermediate). This reaction leads to the formation of a mixture of both *trans*-vinylsilane and the corresponding *cis*-/*trans*-allylsilane (Eq. (3)).



The silylation reaction seems to involve the formation of an intermediate product of C–H bond activation with a structure similar to that of complex **1**. This activation suggests the preliminary reversible elimination of CO from M₃(CO)₁₂ on heating of the starting material at 70–80°C for Ru and 110–120°C for Os in a hydrocarbon solution

Table 2

Silylation of olefins $RCH=CH_2$ with Et_3SiH catalyzed by **1** and related Ru and Os clusters

R	T (°C)	Time (h)	Product (yield, %)	Selectivity ^a
$Os_3(CO)_{12}$				
ⁿ C ₆ H ₁₃	120	6	A(66) + B(32)	2.1
Ph	120	1	<i>trans</i> -PhCH=CHSiEt ₃ (91)	
	80	1	no reaction	
$Os_3(\mu-H)(\mu_3-{}^nBuOC=CHPEt_2)(CO)_9$				
ⁿ C ₆ H ₁₃	120	6	A(54) + B(35)	1.5
Ph	80	1	<i>trans</i> -PhCH=CHSiEt ₃ (10)	
$Os_3(\mu-H)(\mu-CH=CHC_6H_{13})(CO)_{10}$				
ⁿ C ₆ H ₁₃	80	6	A(67) + B(27)	2.5
ⁿ C ₆ H ₁₃	30	6	A(23) + B(6)	
$Os_3(\mu-H)(\mu-CH=CHPh)(CO)_{10}$				
Ph	80	1	<i>trans</i> -PhCH=CHSiEt ₃ (51)	3.8
Ph	30	4	<i>trans</i> -PhCH=CHSiEt ₃ (38)	
$Ru_3(CO)_{12}$				
ⁿ C ₆ H ₁₃	80	6	A(57) + B(21)	2.7
Ph	80	1	<i>trans</i> -PhCH=CHSiEt ₃ (67)	
Ph ^b	30	3	<i>trans</i> -PhCH=CHSiEt ₃ (44)	

^a Ratio of A : B.^b $Ru_3(CO)_{12}$ was treated with olefin in toluene for 10 min at 80°C before the reaction with silane.

under argon. For instance, styrene silylation with $Os_3(CO)_{12}$ was not observed at 80°C but proceeded readily at 120°C to form *trans*-PhCH=CHSiEt₃. Moreover the treatment of $M_3(CO)_{12}$ with various α -olefins $RCH=CH_2$ (R = ⁿC₆H₁₃, Ph, Si(OEt)₃) at 80°C (Ru) or 120°C (Os) resulted in catalysts which exhibited high activity *even at ambient temperature*.

C–H bond activation of terminal alkenes proceeds faster than the similar reaction of the studied vinylphosphine. Moreover the silylation of the C–Os bond in vinylphosphine adduct **1** is likely to proceed relatively slowly because of steric reasons. However the relatively low activity of **1** in olefin silylation (see Table 2) seems to result from a specific electron influence of the additional phosphine ligand in the vicinity of the cluster skeleton on separate stages of the overall catalytic reaction.

The proposed mechanism of olefin silylation catalyzed by triangular carbonyl clusters of Ru and Os seems to involve several transformations in the vicinity of the three metal nuclei [20,21] and suggests a C–H bond activation stage similar to reaction **2**.

3. Experimental details

3.1. General procedure

All manipulations have been done using the standard Schlenk technique. $M_3(CO)_{12}$ (M = Ru, Os) [22] and 1-*n*-butoxy-2-dichlorophosphinoethene [23] were prepared by published methods. ¹H, ¹³C, ³¹P spectra were recorded with a Bruker AM 360. Chemical shifts for ¹H and ¹³C were measured relative to TMS. IR spectra were measured with a Perkin-Elmer 457 spectrometer. GLC analysis was carried out with a Tsvet 101 chromatograph using a 3 m × 3 mm column packed with 3% SP-2100 on Chromaton N-Super. The content of products was measured by the internal standard method which required previous calibration on each of the products. C, H microanalyses were done using a set of commercial equipment for CHN microanalysis (Khimlaborpribor, Klin, Russia). MS measurements were carried out on a MX-1321 spectrometer ($E_i = 70$ eV). Electron probe X-ray analysis was done with a scanning electron microscope SEM-505 (Phillips) equipped with a unit for X-ray energy dispersive analysis Edax.

3.2. 1-*n*-butoxy-2-diethylphosphinoethene

0.10 mol of a 2.00M ether solution of EtMgBr was added dropwise under stirring for ~ 15 min at –30°C to a solution of 10.05 g (0.05 mol) of 1-*n*-butoxy-2-dichlorophosphinoethene in ether (30 ml) and hexane (10 ml). The reaction mixture was heated to room temperature and stirred for 2 h. Then, 7.90 g (8.06 ml, 0.10 mol) of pyridine was added, and the mixture was stirred for ~ 30 min. The white precipitate of the MgCl₂–pyridine complex was

separated and washed with hexane (3 × 100 ml). Combined extracts were evaporated at reduced pressure to ~ 50 ml. White crystals precipitated at -5°C were separated. The solution of the crude product was fractionated, b.p. 120–121°C/16 mm. This procedure yielded 7.71 g (83%) of 1-*n*-butoxy-2-diethylphosphinoethene. Anal. calcd for C₁₀H₂₁OP: C, 63.83; H, 11.17; P, 16.49. Found: C, 63.52; H, 11.23; P, 16.16. IR (cm⁻¹): ν(C=C) 1580. ¹H NMR (CDCl₃; δ, ppm): 0.76–0.92 (m, 9H, CH₃), 1.10–1.35 (m, 6H, CH₂CH₃), 1.49 (m, 2H, CH₂CH₂O), 3.59 (t, *J*(HH) = 6.5 Hz, 2H, CH₂O), 4.59 (dd, *J*(HH) = 13.6 Hz, *J*(PH) = 5.4 Hz, 1H, PCH), 6.54 (dd, *J*(HH) = 13.6 Hz, *J*(PH) = 9.5 Hz, 1H, OCH). ¹³C{¹H} NMR (CDCl₃; δ, ppm): 9.28 (d, *J*(PC) = 13.4 Hz; PCH₂CH₃), 13.36 (CH₃CH₂CH₂), 18.75 (CH₃CH₂CH₂), 20.73 (d, *J*(PC) = 6.2 Hz, PCH₂), 30.84 (CH₂CH₂O), 68.59 (CH₂O), 98.82 (d, *J*(PC) = 10.0 Hz; PCH), 157.16 (d, *J*(PC) = 58.7 Hz; OCH). ³¹P{¹H} NMR (CDCl₃; δ, ppm): -27.08.

3.3. 1,1,1,2,2,2,3,3,3-nonacarbonyl-1,2-μ-hydrido-μ₃-{1-*n*-butoxy-2-diethylphosphino-ethene}-[C¹(Os¹)C¹⁻²(Os³)P(Os²)]-triangulo-triosmium, [Os₃(μ-H)(μ₃-ⁿBuOC=CHPEt₂)(CO)₉] (1)

400 mg (0.44 mmol) of Os₃(CO)₁₂ and 83 mg (0.44 mmol) of ⁿBuOCH=CHPEt₂ [5] in 15 ml of *n*-octane were refluxed under argon for 14 h. Removal of the solvent under reduced pressure and separation by TLC (Silpearl UV 254; *n*-hexane:acetone (3:1, v/v)) gave four new bands with *R*_f 0.57, 0.63, 0.69, and 0.78; one of which (main band with *R*_f 0.69) gave 276 mg (62% yield) of **1** as yellow crystals, m.p. 110–111°C. Anal. calcd for C₁₉H₂₁O₁₀Os₃P: C, 22.57; H, 2.08. Found: C, 22.70; H, 2.14. Electron probe microanalysis: Os:P = 3:1. IR (KBr, cm⁻¹) ν 2975m, 2950m, 2934w, 2923w, 2914w, 2885w, 2870wsh, 2091s, 2064s, 2038s, 2020vs, 2003vs, 1981s, 1968s, 1762w, 1615w, 1595wsh, 1471w, 1334m, 1108s, 1051w, 770w, 747w, 713w, 670m, 624w, 590w, 558m, 590wsh, 496w. IR (heptane, cm⁻¹) ν_{CO} 2096s, 2068vs, 2037vs, 2020s, 2007s, 1992vs, 1980m, 1963m. ¹H NMR (C₆D₆; δ, ppm): 5.55 (dd, *J*(PH) 5.7 Hz, *J*(HH) 0.7 Hz; 1H; CH=C), 3.38–3.10 (m; 2H; PCH₂CH₃(1), 1.90–2.45 (m; 2H; OCH₂CH₂CH₂CH₃), 1.27–1.60 (m; 4H; OCH₂CH₂CH₂CH₃), 0.83–1.09 (m; 2H; PCH₂CH₃(2), 0.88 (t; 3H; OCH₂CH₂CH₂CH₃), 0.73 (dt, *J*(PH) 18.0 Hz; 3H; PCH₂CH₃(1), 0.49 (dt, *J*(PH) 15.9 Hz; 3H; PCH₂CH₃(2), -18.41 (dd, *J*(PH) 13.6 Hz, *J*(HH) 0.7 Hz; 1H; μ-H). ¹³C{¹H} NMR (C₆D₆; δ, ppm): 196.66 (d, *J*(PC) 35.9 Hz; CH=C), 181.17 (s; CO(Os¹), 180.84 (d, *J*(PC) 7.0 Hz; CO(Os²), 180.41 (s; CO(Os³), 177.11 (d, *J*(PC) 84.8 Hz; CH=C), 176.01 (s; CO(Os¹), 174.44 (dd, *J*(PC) 8.9 Hz, *J*(CH) 3.4 Hz; CO(Os²), 174.03 (s; CO(Os¹), 173.21 (dd, *J*(PC) 8.9 Hz, *J*(CH) 1.6 Hz; CO(Os²), 170.07 (s; CO(Os³), 69.37 (s; OCH₂CH₂CH₂CH₃), 30.92 (s; OCH₂CH₂CH₂CH₃), 28.90 (d, *J*(PC) 19.4 Hz; PCH₂CH₃(1), 26.15 (d, *J*(PC) 63.9 Hz; PCH₂CH₃(1), 19.48 (s; OCH₂CH₂CH₂CH₃), 18.55 (d, *J*(PC) 42.7 Hz; PCH₂CH₃(2), 13.84 (s; OCH₂CH₂CH₂CH₃), 7.38 (d, *J*(PC) 80.1 Hz; PCH₂CH₃(2). ³¹P{¹H} NMR (C₆D₆; δ, ppm): -20.00 (d, *J*(PH) 13.6 Hz).

3.4. 1,1,1,2,2,2,3,3,3-decacarbonyl-1,2-μ-hydrido-μ₂-*n*-hexylethene-[C¹(Os¹)C¹⁻²(Os³)]-triangulo-triosmium, [Os₃(μ-H)(μ₂-ⁿC₆H₁₃CH=CH)(CO)₁₀]

The reaction was carried out similarly to the preparation of compound **1** starting from 400 mg (0.44 mmol) of Os₃(CO)₁₂ and 81 mg (0.72 mmol) of 1-octene. Yield 321 mg (76%) of yellow crystals of the title compound. Anal. calcd for C₁₈H₁₆O₁₀Os₃: C, 22.45; H, 1.66. Found: C, 22.51; H, 1.70. IR (heptane, cm⁻¹) ν_{CO} 2083vs, 2058vs, 2045s, 2022vs, 2010s, 1982m.

3.5. 1,1,1,2,2,2,3,3,3-Decacarbonyl-1,2-μ-hydrido-μ₂-phenylethene-[C¹(Os¹)C¹⁻²(Os³)]-triangulo-triosmium, [Os₃(μ-H)(μ₂-PhCH=CH)(CO)₁₀]

The reaction was carried out similarly to the preparation of compound **1** starting from 400 mg (0.44 mmol) of Os₃(CO)₁₂ and 67 mg (0.64 mmol) of freshly distilled styrene. Yield 180 mg (43%) of yellow crystals of the title compound. Anal. calcd for C₁₈H₈O₁₀Os₃: C, 22.64; H, 0.84. Found: C, 22.72; H, 0.90. IR (heptane, cm⁻¹) ν_{CO} 2082vs, 2066vs, 2028s, 2018s, 2003m, 1981m.

3.6. Catalytic experiments

Catalytic studies were carried out in a special glass reactor equipped with a thermostated (±0.2°C) water jacket, a teflon stopper and a teflon-covered magnetic stirring bar. This glass reaction vessel was ~ 10 ml in volume. A typical procedure for catalytic experiments is as follows. A mixture of 0.40 mmol of olefin, 0.20 mmol of silane, internal standard (with the exception of some preparative experiments) 0.1 ml of *n*-C₁₂H₂₆ or *n*-C₁₅H₃₂ depending on the olefin under study, and 2.0 ml of toluene was transferred into reaction vessel and thermostated. The catalyst (1.0 × 10⁻⁵ mol) was added into the vessel. Probes of the reaction mixture were taken by a Hamilton syringe (10 μl).

Table 3
Atom coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) in molecule 1

Atom	x	y	z	U_{eq}^a
Os(1A)	-6693(1)	3957(1)	6805(1)	35(1)
Os(2A)	-8131(1)	3023(1)	6350(1)	38(1)
Os(3A)	-8407(1)	5332(1)	6022(1)	43(1)
P(1A)	-8657(3)	2852(3)	7860(2)	38(1)
O(1A)	-5465(10)	4162(9)	4959(7)	75(6)
O(2A)	-5488(10)	5452(10)	7056(8)	83(7)
O(3A)	-5318(9)	2007(9)	7892(8)	74(6)
O(4A)	-6547(9)	1015(8)	6829(8)	74(6)
O(5A)	-10054(12)	2096(12)	6298(11)	113(10)
O(6A)	-7231(9)	3605(8)	4354(7)	66(5)
O(7A)	-8080(17)	5897(12)	3986(8)	152(11)
O(8A)	-7413(11)	7245(9)	5717(8)	87(7)
O(9A)	-10685(11)	6401(10)	6179(9)	97(8)
O(10A)	-8255(8)	5679(6)	7630(5)	42(4)
C(1A)	-5937(13)	4065(10)	5677(10)	51(7)
C(2A)	-5916(12)	4860(14)	6994(11)	62(8)
C(3A)	-5863(12)	2720(12)	7492(10)	52(7)
C(4A)	-7125(12)	1779(11)	6647(9)	49(6)
C(5A)	-9313(14)	2437(13)	6289(10)	62(8)
C(6A)	-7564(13)	3409(12)	5074(11)	58(8)
C(7A)	-8198(17)	5662(14)	4734(11)	90(10)
C(8A)	-7772(15)	6539(13)	5821(9)	66(8)
C(9A)	-9846(16)	5997(13)	6075(11)	67(9)
C(10A)	-8242(10)	4868(9)	7367(8)	36(5)
C(11A)	-8065(9)	3817(9)	7959(8)	33(5)
C(12A)	-8078(12)	5486(10)	8523(8)	48(6)
C(13A)	-8236(15)	6527(12)	8611(10)	66(8)
C(14A)	-7401(19)	7218(14)	8009(14)	109(13)
C(15A)	-7746(23)	8326(16)	8013(16)	145(17)
C(16A)	-8186(12)	1618(10)	8710(9)	50(6)
C(17A)	-8678(17)	704(12)	8798(13)	94(10)
C(18A)	-10099(12)	3090(13)	8220(10)	63(8)
C(19A)	-10387(14)	3140(16)	9160(12)	95(11)
H(1A)	-9416(82)	4302(74)	6327(63)	26(27)
Os(1B)	-1632(1)	-1789(1)	7899(1)	38(1)
Os(2B)	-2628(1)	263(1)	6923(1)	41(1)
Os(3B)	-3677(1)	-1214(1)	8662(1)	39(1)
P(1B)	-2986(3)	-892(2)	6337(2)	35(1)
O(1B)	-718(11)	-821(11)	8908(9)	98(8)
O(2B)	-1051(11)	-4020(10)	9167(9)	100(7)
O(3B)	345(9)	-1826(9)	6513(7)	72(6)
O(4B)	-606(9)	681(9)	5575(8)	71(6)
O(5B)	-4184(12)	2069(10)	5892(9)	121(8)
O(6B)	-2012(14)	1435(12)	7950(10)	130(10)
O(7B)	-3565(13)	281(12)	9587(9)	118(9)
O(8B)	-3568(10)	-3027(10)	10419(7)	82(6)
O(9B)	-6080(10)	-819(10)	8756(8)	82(7)
O(10B)	-3530(8)	-3291(7)	8571(6)	51(4)
C(1B)	-1012(14)	-1200(13)	8524(10)	67(8)
C(2B)	-1261(12)	-3189(12)	8686(10)	55(7)
C(3B)	-407(13)	-1814(11)	7019(10)	51(7)
C(4B)	-1350(14)	536(11)	6106(11)	58(8)
C(5B)	-3585(16)	1435(12)	6254(12)	79(8)
C(6B)	2235(16)	1008(13)	7566(11)	86(10)
C(7B)	3620(12)	234(14)	9214(10)	63(8)
C(8B)	-3606(12)	-2364(12)	9756(10)	53(7)
C(9B)	-5186(14)	-982(12)	8752(9)	52(7)
C(10B)	-3345(11)	-2333(10)	8064(8)	42(6)
C(11B)	-2739(10)	-2164(9)	7193(8)	35(5)
C(12B)	-3269(13)	-4138(11)	8236(12)	66(8)
C(13B)	-3626(21)	-5081(15)	8955(18)	131(16)
C(14B)	-3419(24)	-5984(14)	8579(22)	161(21)
C(15B)	-3623(26)	-6874(26)	9237(30)	277(46)

Table 3 (continued)

Atom	x	y	z	U_{eq}^a
C(16B)	–2129(11)	–987(10)	5317(7)	41(5)
C(17B)	–2308(14)	–22(12)	4475(9)	65(8)
C(18B)	–4358(12)	–741(12)	6135(10)	58(7)
C(19B)	–4649(14)	–1631(14)	5945(13)	82(10)
H(1B)	–3748(66)	–67(59)	7511(49)	10(20)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised $U(i,j)$ tensor.

Probe analysis was done by GLC analysis. In preparative experiments reaction mixtures (in this case ~10-fold amounts of reagents and ~25 ml from the reaction vessel were used) were fractionated, and products were identified by NMR spectroscopy and/or MS analysis.

3.7. X-ray diffraction study of compound 1

Crystals of **1** were grown from a saturated solution of the compound in hexane. The crystals of **1** are triclinic; at 296 K, $a = 12.914(3)$, $b = 13.984(4)$, $c = 16.375(4)$ Å, $\alpha = 66.83(2)^\circ$, $\beta = 77.82(2)^\circ$, $\gamma = 77.97(2)^\circ$, $V = 2631.5(11)$ Å³, $d_{calc} = 2.552$ g cm⁻³, space group $P\bar{1}$, $Z = 4$.

The unit-cell parameters and intensities of 7138 independent reflections were determined using a Siemens P3/PC diffractometer (298 K, $\lambda_{Mo K\alpha}$, graphite monochromator; $\Theta/2\Theta$ scan technique; $2\Theta \leq 55^\circ$). The structure was solved by the direct method and refined by the full-matrix least-squares technique. The absorption correction ($\mu(Mo K\alpha) = 145.6$ cm⁻¹) was applied using the psi-scan technique ($T_{min} = 0.296$, $T_{max} = 0.892$). The bridging hydride atom was located in the difference Fourier synthesis and taken into account in isotropic approximation. H atoms bound to carbons were included in calculated positions and refined in the riding model approximation with the common variable $U_{iso} = 0.12(1)$ Å². Final discrepancy factors are $R = 0.0399$ and $R_w = 0.0425$ for 6636 observed independent reflections with $I > 3\sigma(I)$. All calculations were carried out on an IBM PC using the programs SHELXTL-PLUS [24]. Atomic coordinates and thermal displacement parameters are listed in Table 3.

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