C$_\beta$−H Activation of Aldehydes Promoted by an Osmium Complex

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Evidence for the C$_\beta$−H bond activation of aldehydes is shown. Complex OsH$_3$(SnPh$_2$Cl)-{η^2-CH$_2$=C(CH$_3$)P^{i}Pr$_2$}(P^{i}Pr$_3$) (**1**) reacts with benzaldehyde and *p*- and *m*-substituted benzaldehydes to give OsH$_2$(SnPh$_2$Cl){C$_6$H$_3$RC(O)H}(P^{i}Pr$_3$)$_2$ (R = H (**2**), OCH$_3$ (**3, 5, 6**), CF$_3$ (**4, 7**)), which result from the C−H activation of one *ortho*-C−H bond. Reactions of **1** with 3-furaldehyde and 1-cyclohexene-1-carboxaldehyde lead to OsH$_2$(SnPh$_2$Cl){C$_4$(O)H$_2$C(O)H}-(P^{i}Pr$_3$)$_2$ (**8**) and OsH$_2$(SnPh$_2$Cl){C$_6$H$_8$C(O)H}(P^{i}Pr$_3$)$_2$ (**9**), respectively. ^{1}H NMR spectroscopic studies indicate that the OsH$_2$ unit of **2−9** forms elongated dihydrogen systems with H−H separations ranging between 1.41 and 1.50 Å. Furthermore, the hydrogen atoms undergo thermally activated site exchange processes with $\Delta G^\ddagger$ between 9 and 12 kcal·mol^{-1} and quantum exchange coupling. Complexes **2**, **5**, and **8** have been characterized by X-ray diffraction analysis.

Introduction

Ketones play an important role in the field of organic chemistry, and much is known about the reactivity of these carbonyl compounds. One of the great utilities of transition metal chemistry is the ability to enhance the reactivity of organic compounds. Thus, it has been shown that eight-group polyhydride complexes activate an *ortho*-CH bond of aromatic ketones to give ortho-metalated compounds,[1] which are reminiscent species of the intermediates proposed by Murai for the insertion of olefines into *ortho*-CH bonds of aromatic ketones[2] and for the arylation of this type of substrate with aryl-boronates.[3]

Aromatic aldehydes are aromatic ketone counterparts containing the carbonyl group bonded to a hydrogen atom. The C(O)−H$_\alpha$ bonds are about 23 kcal·mol^{-1} weaker than the C−H bonds of a phenyl group. In accordance with this, generally, the reactions of transition metal complexes with aldehydes have given products resulting from the C(O)−H$_\alpha$ activation,[4−6] and the *ortho*-CH activation of aromatic aldehydes has been rarely observed.[7] The preparation of *ortho*-formylaryl complexes requires transmetalation from Hg.[8] *Ortho*-formylaryl palladium complexes have been also prepared by oxidative addition of 2-bromobenzaldehyde to [Pd$_2$(dba)$_3$][9] or by hydrolysis of a cyclopalladated imine.[10]

Complexes with formally 14-valence electrons are recognized as the active catalytic component of olefin polymerization, with both early and late transition metals.[11] For the iron triad, direct experimental evidence for the existence of this type of compound has been reported by Caulton and co-workers.[12] Furthermore, they have proved that agostic interactions are not inevitable in these unsaturated species, but that a triplet state with half-filling of two orbitals is another way to make the best outcome of an otherwise electron-deficient situation.[13]

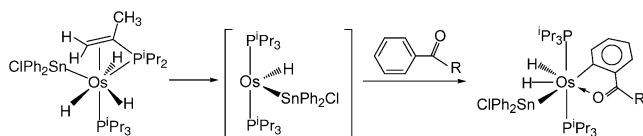We have recently shown that the tetrahydride-osmium(VI) complex OsH$_4$Cl(SnPh$_3$)(P^{i}Pr$_3$)$_2$ reacts with

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Scheme 1

diphenylacetylene to give the trihydride-isopropyldi-
(isopropyl)phosphine-osmium(IV) derivative OsH$_3$(SnPh$_2$-
Cl){η^2-CH$_2$=C(CH$_3$)P^{i}Pr$_2$}(P^{i}Pr$_3$) in a one-pot synthesis
of multiple complex reactions.[14] This complex is a
synthon for the 14-valence-electron monohydride OsH-
(SnClPh$_2$)(P^{i}Pr$_3$)$_2$, which activates an *ortho*-CH bond of
aromatic ketones (Scheme 1).[15]

Figure 1. Molecular diagram of the complex OsH$_2$(SnPh$_2$-
Cl){C$_6$H$_4$C(O)H}(P^{i}Pr$_3$)$_2$ (**2**).

We have now observed that the 14-valence-electron
monohydride also activates an *ortho*-CH bond of benz-
aldehyde and substituted benzaldehydes, as well as
C(sp^2)−H bonds of 3-furaldehyde and 1-cyclohexene-1-
carboxaldehyde. In this paper we report the preparation
of osmium complexes resulting from the direct selective
activation of C$_\beta$(sp^2)−H bonds of aldehydes.

Results and Discussion

**1. *Ortho*-CH Activation of Benzaldehyde and
p-Substituted Benzaldehydes.** Treatment at room
temperature of toluene solutions of OsH$_3$(SnPh$_2$Cl){η^2-
CH$_2$=C(CH$_3$)P^{i}Pr$_2$}(P^{i}Pr$_3$) (**1**) with 1.5 equiv of benzal-
dehyde, *p*-anisaldehyde, and *p*-trifluoromethylbenzal-
dehyde selectively leads to the orthometalated derivatives
OsH$_2$(SnPh$_2$Cl){C$_6$H$_3$RC(O)H}(P^{i}Pr$_3$)$_2$ (R = H (**2**), OCH$_3$
(**3**), CF$_3$ (**4**)), which were isolated as pure red (**2** and **4**)
or orange (**3**) solids in 50−70% yield (eq 1). The
formation of products resulting from the C(O)−H$_\alpha$
activation of the aldehydes was not observed during the
reaction.

(1)

R = H (**2**), OCH$_3$ (**3**), CF$_3$ (**4**)
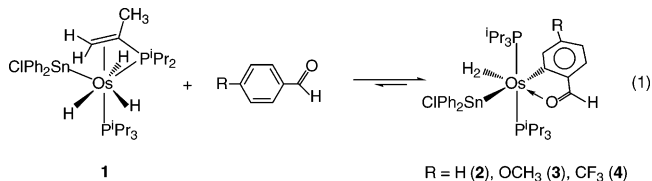
Complexes **2**−**4** are stable for a long time if kept as
solids under argon at temperatures lower than −20 °C.
In toluene-d_8 solution, they slowly lose the aldehyde to
give equilibrium mixtures of **1** and the orthometalated
species. After 48 h at room temperature, the **1**:ortho-
metalated species molar ratios are 1:1.3 (R = H) and
1:5 (R = OCH$_3$, CF$_3$).

A view of the molecular geometry of **2** is shown in
Figure 1. Selected bond distances and angles are listed
in Table 1. The coordination geometry around the
osmium atom can be rationalized as a distorted octa-
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propylphosphine ligands occupying apical positions

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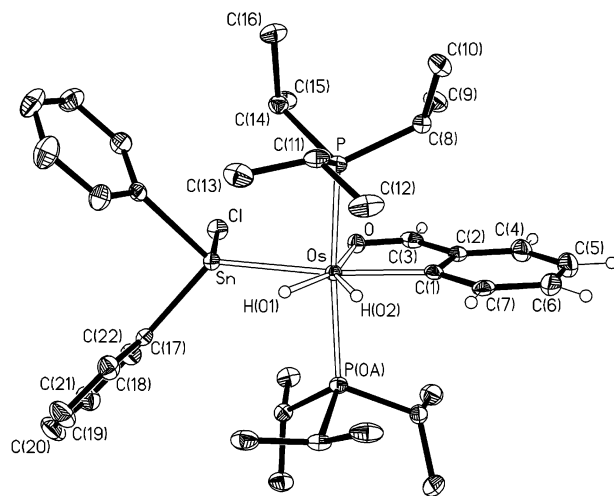E. *Organometallics* **2002**, *21*, 58.
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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex

OsH₂(SnPh₂Cl){C₆H₄C(O)H}(PⁱPr₃)₂ (2)

Os−Sn	2.7114(3)	Sn−Cl	2.4281(10)
Os−P	2.3932(7)	O−C(3)	1.252(4)
Os−O	2.170(2)	C(1)−C(2)	1.418(5)
Os−C(1)	2.072(4)	C(2)−C(3)	1.415(5)
Os−H(01)ᵃ	1.580(10)	H(01)···H(02)	1.46
Os−H(02)ᵃ	1.583(10)		
Sn−Os−P	94.347(17)	O−Os−C(1)	76.48(12)
Sn−Os−O	85.26(7)	O−Os−H(01)	155.6(17)
Sn−Os−C(1)	161.74(10)	O−Os−H(02)	149.9(16)
Os−Sn−C(17)	126.71(7)	C(17)−Sn−C(017)	94.21(13)
Sn−Os−H(01)	70.3(17)	C(1)−Os−H(01)	128.0(17)
Sn−Os−H(02)	124.8(16)	C(1)−Os−H(02)	73.4(16)
P−Os−P*	164.93(3)	H(01)−Os−H(02)	55(2)
P−Os−O	96.485(17)	Os−O−C(3)	115.0(3)
P−Os−C(1)	87.80(2)	Os−C(1)−C(2)	114.6(3)
P−Os−H(01)	85.7(2)	O−C(3)−C(2)	119.5(4)
P−Os−H(02)	82.46(2)	C(1)−C(2)−C(3)	114.5(3)

ᵃ The Os−H lengths were fixed in the refinement. *x, $-y+1.5$, z.

(P−Os−P = 164.93(3)°). The osmium sphere is completed by the orthometalated aldehyde, which acts with a bite angle of 76.48(12)°, the stannyl ligand cisoid disposed to the oxygen atom of the aldehyde (Sn−Os−O = 85.26(7)°) and the hydrogen atoms H(01) and H(02).

The Os−C(1) bond length of 2.072(4) Å is typical for an Os−C(aryl) single bond and agrees well with the values previously found in other orthometalated osmium compounds (between 2.06 and 2.14 Å).[1b,13,14] The Os−O distance of 2.170(2) Å is that expected for a single bond, whereas the O−C(3) bond length (1.252(4) Å) is similar to that found in free benzaldehyde (1.270 Å).[17]

The Os−Sn distance (2.7114(3) Å) agrees well with those reported for other mononuclear osmium-stannyl derivatives (2.6−2.7 Å),[14,15,18] while it is about 0.1 Å shorter than the Os(μ-H)Sn−osmium−tin bond length in the cluster [Os₃SnH₂(CO)₁₀{CH(SiMe₃)₂}₂] (2.855(3) Å).[19] The environment of the tin atom is tetrahedral, with the chlorine atom lying in the equatorial plane of the bipyramid. The angles around the tin atom are between 94.21(13)° (C(17)−Sn−C(017)) and 126.71(7)° (Os−Sn−C(17)).
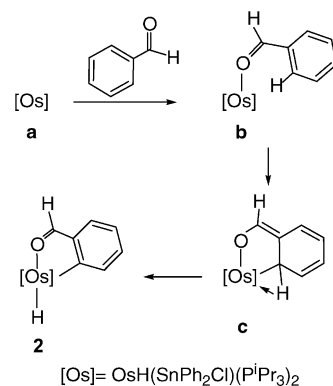
At 100 K, the hydrogen atoms H(01) and H(02) were located in the difference Fourier maps and refined as isotropic atoms together with the remaining non-hydrogen atoms of the structure, the separation between H(01) and H(02) being about 1.46 Å. This value lies

Scheme 2

[Os]= OsH(SnPh₂Cl)(PⁱPr₃)₂

within the range of distances found in the so-called elongated dihydrogen complexes (vide infra).[20]

The IR and ¹H, ¹³C{¹H}, ¹¹⁹Sn{¹H}, and ³¹P{¹H} NMR spectra of **2**−**4** are consistent with the structure show in Figure 1. The IR spectra in Nujol contain ν(Os−H) and ν(C=O) bands between 1946 and 2085 cm⁻¹ and between 1560 and 1587 cm⁻¹, respectively. In the ¹H NMR spectra in toluene-d_8 at room temperature, the most noticeable feature is the presence of a broad resonance between −11.6 and −12.0 ppm, corresponding to the hydrogen atoms bonded to osmium. In the ¹³C{¹H} NMR spectra the carbonyl atom of the aldehydes displays a singlet between 202 and 206 ppm, whereas the metalated carbon atom gives rise to a triplet between 197 and 200 ppm with a C−P coupling constant of about 8 Hz. The ¹¹⁹Sn{¹H} NMR spectra show a triplet between 16 and 21 ppm with a Sn−P coupling constant of about 115 Hz. In agreement with the mutually trans disposition of the phosphine ligands, the ³¹P{¹H} NMR spectra contain a singlet between 7 and 10 ppm.

The formation of **2**−**4** according to eq 1 involves the reduction of the isopropenyl group of the isopropenyldi-(isopropyl)phosphine of **1**[15] and the subsequent addition of the aldehyde to the 14-valence-electron monohydride OsH(SnPh₂Cl)(PⁱPr₃)₂ (**a**). According to a recent density functional study on the *ortho*-CH addition of benzaldehyde to the 14-valence-electron Ru(CO)(PH₃)₂ fragment,[21] the addition of the aldehydes to **a** should involve the elemental steps shown in Scheme 2. Initially the formyl oxygen coordinates to the metallic center. Then the cleavage of the closest *ortho*-CH bond takes place in two steps. First an *ortho*-OsC bond is formed, being driven by the change in π bonds of the conjugated system. Subsequently, in the intermediate **c**, which contains the *ortho*-OsC bond and a CH agostic interaction, the hydrogen of the agostic CH bond is transferred to the osmium atom.
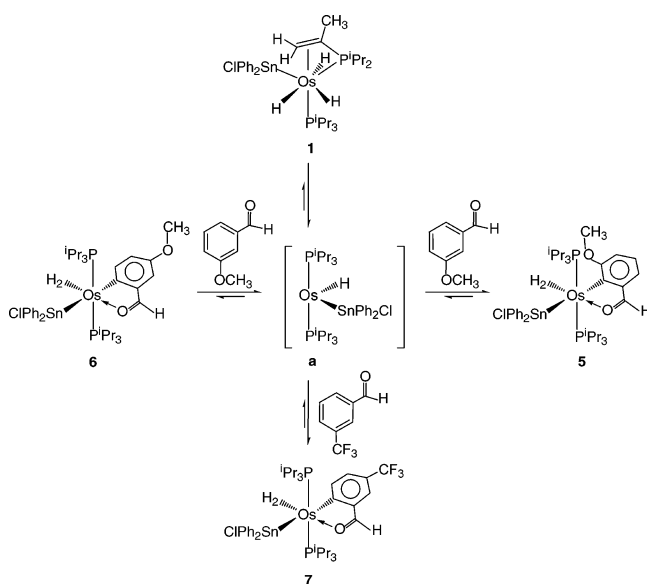
It should be noted that the *ortho*-CH addition of aromatic aldehydes, according to this mechanism, requires two empty valence orbitals in the metallic fragment promoting the activation. The accessible 14-valence-electron systems previously reported are very scarce, and the 16-valence-electron complexes do not comply with this condition. So, it is not surprising that

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Scheme 3

Figure 2. Molecular diagram of the complex $\overline{OsH_2(SnPh_2}$
$\overline{Cl)\{C_6H_3(OCH_3)C(O)H\}}(P^iPr_3)_2$ (**5**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex

$\overline{OsH_2(SnPh_2Cl)\{C_6H_3(OCH_3)C(O)H\}(P^iPr_3)_2}$ (5)			
Os−Sn	2.7070(3)	Sn−Cl	2.4210(9)
Os−P(1)	2.3907(9)	O(1)−C(3)	1.260(4)
Os−P(2)	2.3819(9)	O(2)−C(7)	1.388(4)
Os−O(1)	2.155(2)	O(2)−C(8)	1.422(4)
Os−C(1)	2.084(3)	C(1)−C(2)	1.425(4)
Os−H(01)	1.37(3)	C(2)−C(3)	1.403(5)
Os−H(02)	1.41(3)	H(01)⋯H(02)	1.41
Sn−Os−P(1)	94.70(2)	P(2)−Os−H(01)	80.0(12)
Sn−Os−P(2)	92.37(2)	P(2)−Os−H(02)	85.1(11)
Sn−Os−O(1)	79.39(7)	O(1)−Os−C(1)	76.24(11)
Sn−Os−C(1)	155.49(10)	O(1)−Os−H(01)	150.7(13)
Sn−Os−H(01)	129.9(13)	O(1)−Os−H(02)	149.8(12)
Sn−Os−H(02)	70.8(12)	C(1)−Os−H(01)	74.5(13)
P(1)−Os−P(2)	160.21(3)	C(1)−Os−H(02)	133.7(12)
P(1)−Os−O(1)	98.04(6)	H(01)−Os−H(02)	59.2(15)
P(1)−Os−C(1)	91.25(9)	Os−O(1)−C(3)	115.2(2)
P(1)−Os−H(01)	81.3(12)	Os−C(1)−C(2)	114.7(3)
P(1)−Os−H(02)	80.0(12)	C(1)−C(2)−C(3)	113.6(3)
P(2)−Os−O(1)	101.43(6)	O(1)−C(3)−C(2)	120.2(3)
P(2)−Os−C(1)	89.92(9)	C(7)−O(2)−C(8)	118.0(3)

the *ortho*-CH activation of aromatic aldehydes has been rarely observed.

2. *Ortho*-CH Activation of *m*-Substituted Benzaldehydes. This type of substrate has two different reaction sites at the positions *ortho* to the carbonyl group. We have studied the effect of methoxy and *m*-trifluoromethyl groups on the position of the C−H bond to be cleaved. The results of the study are given in Scheme 3.

A methoxy *meta* disposed to the carbonyl group does not generate any selectivity on the activation, and the cleavage of both *ortho*-CH bonds is equally favored. Thus, the treatment at room temperature of toluene solutions of **1** with 1.5 equiv of *m*-anisaldehyde leads after 24 h to a 1:1 mixture of the isomers **5** and **6**. The mixture was isolated as an orange solid in 50% yield.

In contrast to this result, we note that *m*-methoxyacetophenone reacts with vinyltrimethoxysilane in the presence of RuH$_2$(CO)(PPh$_3$)$_3$ to preferentially give the most congested *ortho*-alkyl product.[22] Similar phenomena have also been reported by several groups in stoichiometric reactions of Mn(alkyl)(CO)$_5$ with *m*-methoxyacetophenone.[23]

Complex **5** was isolated as pure crystals by crystallization of the isomeric mixture from toluene/methanol at −30 °C. In toluene-d_8 solution, it evolves to give an equilibrium mixture of **1**, **5**, and **6**. At room temperature, after 42 h, the **1**:**5**:**6** molar ratio is 2:1:1.

Figure 2 shows a view of the molecular geometry of **5**. Selected bond distances and angles are collected in Table 2. The structure proves the formation of the most congested orthometalated isomer. The coordination polyhedron around the osmium atom is analogous to that of **2** with P(1)−Os−P(2), O(1)−Os−C(1), and Sn−Os−O(1) angles of 160.21(3)°, 76.24(11)°, and 79.39(7)°, respectively. The Os−C(1) (2.084(3) Å),
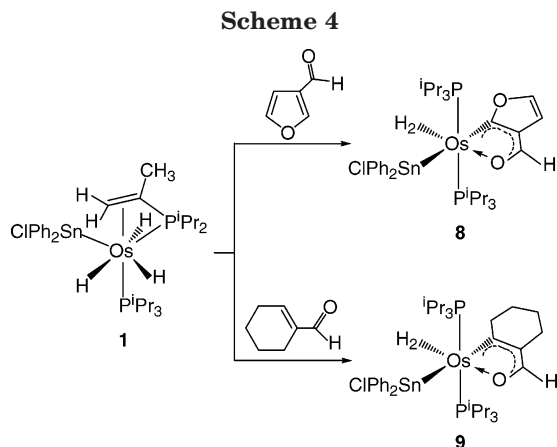
Os−O(1) (2.155(2) Å), and Os−Sn (2.7070(3) Å) are also similar to the related parameters in **2**.

The ^{1}H, ^{13}C{^{1}H}, ^{119}Sn{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **5** and **6** agree well with those of **2**−**4**. In the ^{1}H NMR spectra in toluene-d_8 at room temperature the resonances due to hydrogen atoms bonded to the metallic center are observed at −11.1 (**5**) and −11.9 (**6**) ppm. In the ^{13}C{^{1}H} NMR spectra the carbonyl resonances appear at about 204 ppm, whereas the metalated carbon atoms display triplets ($J_{C−P}$ = 7 Hz) at about 188 ppm. The ^{119}Sn{^{1}H} NMR spectra show triplets at 0.7 (**5**) and 19.3 (**6**) ppm with Sn−P coupling constants of 116 and 110 Hz, respectively. The ^{31}P{^{1}H} NMR spectra contain singlets at 6.2 (**5**) and 8.4 (**6**) ppm.

The behavior of *m*-trifluoromethylbenzaldehyde is significantly different from that of *m*-anisaldehyde. In contrast to methoxy, trifluoromethyl *meta* disposed to the carbonyl group introduces selectivity to the cleavage of the less congested *ortho*-CH bond. Thus, the treatment at room temperature of toluene solutions of **1** with 1.5 equiv of *m*-trifluoromethylbenzaldehyde exclusively

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Scheme 4

Figure 3. Molecular diagram of the complex $\overline{OsH_2(SnPh_2}$ $\overline{Cl)\{C_4(O)H_2C(O)H\}(P^iPr_3)_2}$ (**8**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex

$\overline{OsH_2(SnPh_2Cl)\{C_4(O)H_2C(O)H\}(P^iPr_3)_2}$ (**8**)

Os−Sn	2.7029(3)	Sn−Cl	2.4196(9)
Os−P	2.3860(6)	O(1)−C(5)	1.268(4)
Os−O(1)	2.188(2)	O(2)−C(1)	1.355(4)
Os−C(1)	2.021(4)	O(2)−C(4)	1.402(4)
Os−H(01)^a	1.568(10)	C(1)−C(2)	1.396(5)
Os−H(02)^a	1.568(10)	C(2)−C(5)	1.396(5)
H(01)···H(02)	1.41	C(3)−C(4)	1.318(6)
Sn−Os−P	93.680(16)	C(1)−Os−H(01)	80.3(13)
Sn−Os−O(1)	83.56(6)	C(1)−Os−H(02)	133.7(16)
Sn−Os−C(1)	158.15(12)	H(01)−Os−H(02)	53.4(18)
Sn−Os−H(01)	121.6(13)	Os−O(1)−C(5)	115.2(2)
Sn−Os−H(02)	68.2(16)	Os−C(1)−C(2)	118.7(3)
P−Os−P*	166.10(3)	Os−C(1)−O(2)	134.3(3)
P−Os−O(1)	96.266(16)	O(1)−C(5)−C(2)	118.2(4)
P−Os−C(1)	88.77(2)	O(2)−C(4)−C(3)	112.5(4)
P−Os−H(01)	83.050(16)	C(1)−C(2)−C(5)	113.3(3)
P−Os−H(02)	85.91(16)	C(1)−C(2)−C(3)	108.8(3)
O(1)−Os−C(1)	74.59(13)	C(1)−O(2)−C(4)	107.5(3)
O(1)−Os−H(01)	154.9(13)	C(2)−C(3)−C(4)	104.2(4)
O(1)−Os−H(02)	151.7(16)	C(3)−C(2)−C(5)	137.8(4)

^{a} The Os−H lengths were fixed in the refinement. *x, $-y+0.5$, z.

affords **7** (Scheme 3), which was isolated as a red solid in 55% yield. In toluene-d_8 solution, this complex also loses aldehyde to give an equilibrium mixture of **1** and **7**. At room temperature, after 48 h, the **1**:**7** molar ratio is 1:5.

In agreement with the IR spectra of **2**−**4**, the IR spectrum of **7** shows ν(Os−H) and ν(C=O) bands at 1948 and 1556 cm^{-1}, respectively. In the ^{1}H NMR spectrum in toluene-d_8 at room temperature, the resonance due to the hydrogen atoms bonded to the metallic center appears at −11.7 ppm. In the ^{13}C{^{1}H} NMR spectrum, the carbonyl group of the aldehyde gives rise to a singlet at 205.4 ppm, while the metalated carbon atom displays a triplet at 204.5 ppm with a C−P coupling constant of 7.5 Hz. The ^{119}Sn{^{1}H} NMR spectrum shows a triplet at 12.8 ppm, with a Sn−P coupling constant at 115 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 7.9 ppm.

3. C(sp^2)−H Activation of 3-Furaldehyde and 1-Cyclohexene-1-carboxaldehyde. Murai and co-workers have previously reported that, in the presence of olefins and the ruthenium complex RuH$_2$(CO)(PPh$_3$)$_3$, aldehydes containing a heteroatom at the carbon β to the carbonyl group insert olefins into the C$_\beta$−H bond of the substrate. In the reaction of 1-cyclohexene-1-carboxaldehyde, decarbonylation to cyclohexene appears to be the predominant process.[7c]

To obtain information about the reason for these differences in behavior, we have also studied the reactions of **1** with 3-furaldehyde and 1-cyclohexene-1-carboxaldehyde (Scheme 4).

Treatment at room temperature of toluene solutions of **1** with 1.5 equiv of 3-furaldehyde leads to $\overline{OsH_2(SnPh_2}$ $\overline{Cl)\{C_4(O)H_2C(O)H\}(P^iPr_3)_2}$ (**8**), which was isolated as a yellow solid in 50% yield. It must be pointed out that although the substrate has two carbon atoms β disposed with regard to the carbonyl group, only the C$_\beta$−H bond adjacent to the oxygen atom of the heterocycle is activated.

Figure 3 shows a view of the molecular geometry of **8**. Selected bond distances and angles are listed in Table 3. The coordination polyhedron around the osmium atom is analogous to those of **2** and **5** with P−Os−P(0A), O(1)−Os−C(1), and Sn−Os−O(1) angles of 166.10(3)°, 74.59(13)°, and 83.56(6)°, respectively.

The Os−C(1) distance is 2.021(4) Å, about 0.05 Å and about 0.06 Å shorter than the related parameters in **2**
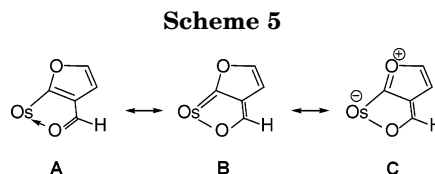
Scheme 5

and **5**, respectively. Both C(1)−C(2) and C(2)−C(5) bond lengths are 1.396(5) Å. This value is between those expected for single and double carbon−carbon bonds and suggests that for an adequate description of the bonding situation in this compound the resonance forms shown in Scheme 5 should be taken into account.

A significant contribution of the alkoxycarbene resonance form **B** to the structure of **8** is also supported by the ^{13}C{^{1}H} spectrum, which shows the resonance due to the metalated carbon atom at 230.6 ppm as a triplet with a C−P coupling constant of 8.7 Hz. This resonance appears shifted 12 ppm to higher field in comparison with the shift observed for the carbene carbon atom of the alkoxycarbene derivative OsH(η^5-C$_5$H$_5$){=C(OMe)-

Ph}(P^iPr_3) (242.6)[24] and more than 30 ppm to lower field with regard to the chemical shift found for the metalated carbon atom of the previous benzaldehyde derivatives. The chemical shift of the resonance of the metalated carbon atom of **8** agrees well with those corresponding to the related resonances of the complexes Os{CHCHC-(O)Ph}Cl(CO)(P^iPr_3)$_2$ (230.13 ppm),[25] OsH{CHCHC(O)-CH$_3$}(CO)(P^iPr_3)$_2$ (250.8),[26] and OsH$_3$\{C$_6$H$_8$C(O)CH$_3$\}-(P^iPr_3)$_2$ (255.9 ppm),[27] where bonding situations intermediate between resonance forms analogous to **A** and **B** have been proposed to exist.

The contribution of the resonance form **C** to the structure of **8** is supported by the difference between the C−O bond lengths within the heterocycle. In agreement with some double bond character between the metalated carbon and the oxygen atom, the C(1)−O(2) distance is 1.335(4) Å, about 0.05 Å shorter than the O(2)−C(4) bond length (1.402(4) Å).

The chemical shift of the carbonyl resonance in the ^{13}C\{^{1}H\} NMR spectrum also reflects the contribution of the resonance forms **B** and **C** to the structure of **8**. Thus, this resonance appears at 188.6 ppm, shifted about 15 ppm to higher field with regard to those of the benzaldehyde derivatives.

The C(5)−O(1) (1.268(4) Å) and Os−O(1) (2.188(2) Å) distances, as well as the Os−Sn (2.7029(3) Å) bond length, do not show notable differences from those found in **2** and **5**.

At 100 K, the hydrogen atoms H(01) and H(02) of **8** were also located in the difference Fourier maps and refined as isotropic atoms together with the remaining non-hydrogen atoms of the structure. The separation between H(01) and H(02) (1.41 Å) agrees well with those found in **2** (1.46 Å) and **5** (1.41 Å). In the ^{1}H NMR spectrum in toluene-d_8 at room temperature these atoms give rise to a broad triplet at −11.48 ppm, with a H−P coupling constant of 11.7 Hz.

The ^{119}Sn\{^{1}H\} NMR spectrum shows a triplet at 19.4 ppm, with a Sn−P coupling of 127 Hz, whereas the ^{31}P\{^{1}H\} NMR spectrum contains a singlet at 13.4 ppm.

1-Cyclohexene-1-carboxaldehyde reacts in a manner similar to that for 3-furaldehyde. Treatment at room temperature of toluene solutions of **1** with 1.5 equiv of this α,β-unsaturated aldehyde leads to OsH$_2$(SnPh$_2$Cl)-{C$_6$H$_8$C(O)H}(P^iPr_3)$_2$ (**9**), which was isolated as an orange solid in 55% yield.

The ^{13}C\{^{1}H\} NMR spectrum of **9** also suggests that for an adequate description of the bonding situation in this compound resonance forms analogous to **A** and **B** should be taken into account. Thus, the resonance corresponding to the metalated carbon atom is observed at 242.9 ppm, shifted about 12 ppm even to lower field than that observed for the metalated carbon atom of **8**. In the ^{1}H NMR spectrum in toluene-d_8, at room tem-

perature, the hydrogen atoms bonded to the osmium give rise to a broad resonance at −11.9 ppm. The ^{119}Sn\{^{1}H\} NMR spectrum contains a broad triplet at −0.1 with a Sn−P coupling constant of 128 Hz, whereas the ^{31}P\{^{1}H\} NMR spectrum shows a singlet a 7.1 ppm.

The differences in behavior observed, in the presence of olefins and the ruthenium complex RuH$_2$(CO)(PPh$_3$)$_3$, between aldehydes containing an heteroatom at the β carbon of the carbonyl group and benzaldehyde or 1-cyclohexene-1-carboxaldehyde have been attributed to the capacity of the heteroatom, in the first ones, to decrease the electrophilicity of the formyl group, by donation of the lone-pair of electrons of the heteroatom.[7c] This diminution should decrease the tendency of the C(O)−H$_\alpha$ bond to undergo activation, which is the first step of the decarbonylation process.

We cannot corroborate this proposal, since benzaldehyde, 3-furaldehyde, and 1-cyclohexene-1-carboxaldehyde react with the 14-valence electron fragment OsH-(SnPh$_2$Cl)(P^iPr_3)$_2$ in the same manner. However, the comparison of the spectroscopic data of the complexes here reported and the structures shown in Figures 1−3 reveals that there are significant differences between the heterometallacycles resulting from the C$_\beta$−H activation.

For an adequate description of the bonding situation in the 3-furaldehyde derivative **8**, the resonance forms **A**, **B**, and **C** shown in Scheme 5 should be taken into account. On the other hand, an adequate description of the structure of the 1-cyclohexene-1-carboxaldehyde derivative **9** requires to take into account only a carbene resonance form, analogous to **B**, in addition to the bonding situation in benzaldehyde. This carbene resonance form does not increase the stability of the heterometallacycle. Similarly to complexes **2**−**7**, in toluene-d_8 solution, complex **9** loses the aldehyde to give an equilibrium mixture of **1** and **9**. As for the substituted benzaldehyde derivatives, after 48 h at room temperature, the **1**:**9** molar ratio is 1:5. In contrast to **9**, complex **8** is stable in toluene-d_8, even at 80 °C. This suggest that, in contrast to **B**, the resonance form **C** certainly has a stabilizing effect on the heterometallacycle of **8**. In addition, it should be noted that the resonance form **C** should not contribute to the stabilization of a heterometallacycle resulting from the activation of the non-oxygen adjacent C$_\beta$−H position of 3-furaldehyde. This can explain why in this type of substrate the C$_\beta$−H bond disposed in the α-position to the heteroatom of the furanyl ring is selectively activated or added to olefins in the Murai's reaction. In addition, it should be noted that the latter is more reactive than that situated at the β-position to the furanyl oxygen atom.

4. Nature of the OsH$_2$ Unit. The ^{1}H NMR spectra of **2**−**9** in the high-field region are temperature-dependent. At room temperature in toluene-d_8 as solvent, they show a broad resonance for two inequivalent hydrogen atoms bonded to the osmium atom. Between 273 and 233 K decoaeslecence occurs, and at temperatures lower than 233 K, ABX$_2$ spin systems are observed. The H−H coupling constants range from 38 to 267 Hz (Table 4). These unusually large values, in particular that of **8**, suggest the operation of quantum exchange coupling between the hydrogen atoms of the OsH$_2$ unit.[28]

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Table 4. Decoalescence Temperature, Chemical Shifts, Enthalpy and Entropy Values of the Thermally Activated Exchange Process, $T_{1(min)}$, and H−H Distance Calculated from the $T_{1(min)}$ Values for the Hydride Resonances of Complexes 2−9

complex	decoalescence temperature (K)	δ (T (K), J_{H-H} (Hz))	$\Delta H^{\ddagger}$ (kcal·mol^{-1})	$\Delta S^{\ddagger}$ (cal·K^{-1}·mol^{-1})	$T_{1(min)}$ (T (K))	d_{H-H} (Å)
2	273	−11.01, −12.93 (233, 42)	11.2(±0.5)	−2.6(±1.1)	78 ± 2 (238)	1.47
3	273	−11.02, −13.15 (233, 48)	11.3(±0.3)	−2.1(±0.6)	74 ± 1 (243)	1.46
4	273	−10.52, −12.86 (233, 42)	11.7(±0.4)	−0.3(±1)	86 ± 2 (233)	1.50
5	253	−10.71, −11.61 (233, 56)	11.7(±0.6)	−0.1(±1.4)	66 ± 3 (233)	1.43
6	273	−11.62, −12.90 (233, 38)	−	−	60 ± 1 (248)	1.41
7	273	−10.65, −12.87 (233, 38)	11.8(±0.4)	−1.4(±1.1)	73 ± 2 (243)	1.45
8	233	−11.46 (203, AB spin system, J_{A-B} = 267, $\Delta\nu$ = 784)	9.1(±0.3)	−3.8(±1)	60 ± 1 (243)	1.41
9	273	−11.30, −13.30 (193, 72)	11.8(±0.2)	− 0.4(±0.7)	69 ± 1 (233)	1.44

The dependence on the temperature of these spectra indicates that the hydrogen atoms also undergo thermally activated site exchange processes. Line-shape analysis of the ^{1}H{^{31}P} NMR spectra (Figure 4 shows
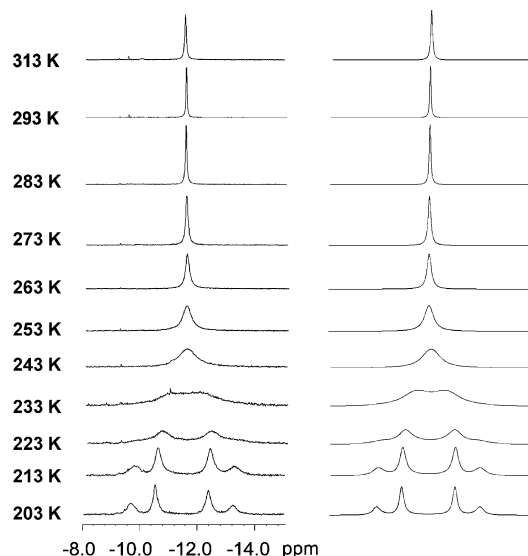
Figure 4. (Left) Variable-temperature ^{1}H{^{31}P} NMR spectra (400 MHz) in C$_7$D$_8$ in the high-field region of OsH$_2$(SnPh$_2$Cl){C$_4$(O)H$_2$C(O)H}(P^{i}Pr$_3$)$_2$ (**8**). (Right) Simulated spectra.

those of **8**) allows the calculation of the rate constants for the processes at each temperature. The activation parameters obtained from the corresponding Eyring analysis are given in Table 4. The values for the entropy of activation, close to zero, are in agreement with an intramolecular process, while the values for the enthalpy of activation, from 9 to 12 kcal·mol^{-1}, are quite similar to those found for blocked rotation processes in elongated dihydrogen complexes.[20,29]

This type of complexes is a class of dihydrogen compounds with the hydrogen−hydrogen separation ranging from 1.0 to 1.6 Å, which have as a distinctive characteristic a very flat energy potential curve for the

H−H stretch.[20,30] The X-ray values obtained for the separation between the H(01) and H(02) atoms of **2**, **5**, and **8**, as well as the enthalpy values collected in Table 4, suggest that the atoms of the OsH$_2$ unit of **2−9** form a elongated dihydrogen ligand. To confirm this, the T_1 values of the OsH$_2$ resonances were determined over the temperature range 273−213 K. The obtained $T_{1(min)}$ are given in Table 4. Assuming slow spinning, these values correspond to hydrogen−hydrogen distances between 1.41 and 1.50 Å,[29] which support the elongated dihydrogen character of **2−9**.

Concluding Remarks

This study reveals that the monohydride OsH(SnPh$_2$-Cl)(P^{i}Pr$_3$)$_2$, generated from $\overline{\text{OsH}_3(\text{SnPh}_2\text{Cl})\{\eta^2\text{-CH}_2=}$ $\overline{\text{C(CH}_3)\text{P}^{i}\text{Pr}_2\}}$(P^{i}Pr$_3$), selectively activates an *ortho*-CH bond of benzaldehyde and *p*- and *m*-substituted benzaldehydes, as well as a C$_\beta$(sp^2)−H bond of 3-furaldehyde and 1-cyclohexene-1-carboxaldehyde. The resulting products are elongated dihydrogen derivatives, containing a metalated aldehyde ligand.

In addition, for substrates with two different reaction sites, some trends are shown:

(i) A substituent at the *meta* position with regard to the carbonyl group has a marked influence on the position of the *ortho*-CH bond to be cleaved in substituted benzaldehydes. While a methoxy group does not generate any selectivity on the activation, and the cleavage of both *ortho*-CH bonds is equally favored, trifluoromethyl introduces selectivity to the cleavage of the less congested *ortho*-CH bond.

(ii) The activation of 3-furaldehyde selectively occurs at the C$_\beta$−H bond adjacent to the oxygen atom of the heterocycle. The origin of the selectivity appears to be thermodynamic, and it is related to a significant contribution of the resonance form **C** (Scheme 5) to the structure of the activation product.

In conclusion, we report C$_\beta$(sp^2)−H activations of aldehydes promoted by an osmium complex and show some reactivity trends for aldehydes containing two different reaction sites.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and

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purified by known procedures and distilled under argon prior to use. The starting material $\overline{OsH_3(SnPh_2Cl)\{\eta^2\text{-}CH_2}$=$C(CH_3)P\text{-}iPr_2\}(PiPr_3)}$ (**1**) was prepared as previously described.[14] Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer as solids (Nujol mull). ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra were recorded on either a Varian Gemini 2000, a Varian UNITY 300, a Bruker AXR 300, or a Bruker Avance 400 instrument. Chemical shifts are referenced to residual solvent peaks (^{1}H and ^{13}C{^{1}H}), external H$_3$PO$_4$ (^{31}P{^{1}H}), or Me$_4$Sn (^{119}Sn{^{1}H}). Coupling constants J and N ($N = J_{P-H} + J_{P'-H}$ for ^{1}H; $N = J_{P-C} + J_{P'-C}$ for ^{13}C{^{1}H}) are given in hertz. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $\overline{OsH_2(SnPh_2Cl)\{C_6H_4C(O)H\}}$**(PiPr$_3$)$_2$ (2).** Benzaldehyde (27.5 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.18 mmol) in toluene (10 mL). After stirring for 2.5 h at room temperature the color of the solution had changed from yellow to red. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a red solid, which was washed with pentane and dried in vacuo. Yield: 82 mg (48.4%). Anal. Calcd for C$_{37}$H$_{59}$ClOOsP$_2$Sn: C, 47.98; H, 6.42. Found: C, 48.87; H, 6.72. IR (Nujol, cm^{-1}): ν(OsH) 2085 (w), ν(CO) 1587 (m). ^{1}H NMR (300 MHz, C$_7$D$_8$, 293 K): δ 9.01 (s, 1H, CHO), 8.30 (d, $J_{H-H} = 7.2$, 4H, SnPh-H_{ortho}), 8.17 (d, $J_{H-H} = 7.4$, 1H, Os-C$_6$H$_4$), 7.41 (dd, $J_{H-H} = 7.4$, $J_{H-H} = 1.1$, 1H, Os-C$_6$H$_4$), 7.30 (t, $J_{H-H} = 7.2$, 4H, SnPh-H_{meta}), 7.16 (t, $J_{H-H} = 7.4$, 2H, SnPh-H_{para}), 6.78 (dt, $J_{H-H} = 7.4$, $J_{H-H} = 1.1$, 1H, Os-C$_6$H$_4$), 6.72 (t, $J_{H-H} = 7.4$ Hz, 1H, Os-C$_6$H$_4$), 2.16 (m, 6H, PCH(CH$_3$)$_2$), 0.96 (dvt, $N = 13$, $J_{H-H} = 6.8$, 18H, PCH(CH_3)$_2$), 0.68 (dvt, $N = 12.7$, $J_{H-H} = 6.5$, 18H, PCH(CH_3)$_2$), −11.88 (br, 2H, OsH). ^{1}H NMR (300 MHz, C$_7$D$_8$, 233 K, hydride region): δ −11.01 (part A of an ABX$_2$ spin system, 1H, $J_{A-X} = 14$, $J_{A-B} = 42$), −12.93 (part B of an ABX$_2$ spin system, 1H, $J_{B-X} = 10$, $J_{A-B} = 42$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 293 K): δ 7.5 (s with tin satellites $J_{P-117Sn} = J_{P-119Sn} = 113$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 183 K): δ 7.4 (AB spin system, $\Delta\nu = 737$ Hz, $J_{A-B} = 210$).[32] ^{13}C{^{1}H} NMR (75.42 MHz, C$_6$D$_6$, 293 K, plus apt): δ 205.4 (s, CHO), 198.2 (t, $J_{P-C} = 7$, OsC), 156.5 (s, C_{ipso}, SnPh$_2$Cl), 143.7 (s, C$_{ipso}$, Ph), 143.1 (s, Ph), 137.7 (s, SnPh$_2$Cl), 133.5 (s, Ph), 132.4 (s, Ph), 127.6 (s, SnPh$_2$Cl), 127.4 (s, SnPh$_2$Cl), 120.8 (s, Ph), 28.5 (vt, $N = 25.5$, PCH(CH$_3$)$_2$), 20.4, 19.7 (both s, PCH(CH_3)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 20.4 (t, $J_{P-119Sn} = 113$). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 238 K): 78 ± 2 (−11.03 ppm, −12.88 ppm).

Preparation of $\overline{OsH_2(SnPh_2Cl)\{C_6H_3(OCH_3)C(O)H\}}$**(PiPr$_3$)$_2$ (3).** p-Anisaldehyde (40 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.18 mmol) in toluene (10 mL). After stirring for 24 h at room temperature the color of the solution had changed from yellow to orange-red. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of an orange solid, which was washed with pentane and dried in vacuo. Yield: 133.8 mg (73%). Anal. Calcd for C$_{38}$H$_{61}$ClO$_2$OsP$_2$Sn: C, 47.73; H, 6.43. Found: C, 47.73; H, 6.30. IR (Nujol, cm^{-1}): ν(OsH) 2134 (w), ν(CO) 1585 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.87 (s, CHO), 8.41 (d, $J_{H-H} = 7.6$, 4H, SnPh-H_{ortho}),

7.73 (d, $J_{H-H} = 2.4$, 1H, Os-C$_6$H$_3$(OCH$_3$)), 7.34 (t, $J_{H-H} = 7.6$, 4H, SnPh-H_{meta}), 7.29 (d, $J_{H-H} = 8.4$, 1H, Os-C$_6$H$_3$(OCH$_3$)), 7.18 (t, $J_{H-H} = 7.6$, 2H, SnPh-H_{para}), 6.44 (dd, $J_{H-H} = 8.4$, $J_{H-H} = 2.4$, 1H, Os-C$_6$H$_3$(OCH$_3$)), 3.34 (s, 3H, OCH_3), 2.24 (m, 6H, PCH(CH$_3$)$_2$), 1.00 (dvt, $N = 13.5$, $J_{H-H} = 6.9$, 18H, PCH(CH_3)$_2$), 0.73 (dvt, $N = 12.8$, $J_{H-H} = 6.8$, 18H, PCH(CH_3)$_2$), −12.01 (br, 2H, OsH). ^{1}H NMR (300 MHz, C$_7$D$_8$, 233 K, hydride region): δ −11.02 (part A of a nonresolved ABX$_2$ spin system, 1H, $J_{A-B} = 48$), −13.15 (part B of a nonresolved ABX$_2$ spin system, 1H, $J_{A-B} = 48$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 7.9 (s with tin satellites $J_{P-119Sn} = J_{P-117Sn} = 113$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 193 K): an unresolved AB spin system centered at 7.4 ppm.[32] ^{13}C{^{1}H} NMR (100.56 MHz, C$_6$D$_6$, 293 K plus apt): δ 202.0 (s, CHO), 200.3 (t, $J_{C-P} = 7$, OsC), 163.9 (s, C_6H$_3$(OCH$_3$)), 156.6 (s, C_{ipso}, SnPh$_2$Cl), 138.6 (s, C_6H$_3$-(OCH$_3$)), 137.7 (s, SnPh$_2$Cl), 133.8 (s, C_6H$_3$(OCH$_3$)), 127.6 (s, SnPh$_2$Cl), 127.3 (s, SnPh$_2$Cl), 125.5 (s, C_6H$_3$(OCH$_3$)), 109.8 (s, C_6H$_3$(OCH$_3$)), 54.7 (s, OCH_3), 28.4 (vt, $N = 25.6$, PCH(CH$_3$)$_2$), 20.4, 19.7 (both s, PCH(CH_3)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 16.0 (t, $J_{P-119Sn} = 113$). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 243 K): 74 ± 1 (−11.11 ppm, −13.12 ppm).

Preparation of $\overline{OsH_2(SnPh_2Cl)\{C_6H_3(CF_3)C(O)H\}}$**(PiPr$_3$)$_2$ (4).** p-Trifluoromethylbenzaldehyde (36 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After stirring for 24 h at room temperature, the color of the solution changed from yellow to deep red. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a red solid, which was washed with pentane and dried in vacuo. Yield: 113 mg (59%). Anal. Calcd for C$_{38}$H$_{58}$ClF$_3$OOsP$_2$Sn: C, 45.9; H, 5.88. Found: C, 45.79; H, 5.61. IR (Nujol, cm^{-1}): ν-(OsH) 1946 (w), ν(CO) 1560 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.98 (s, 1H, CHO), 8.68 (s, 1H, Os-C$_6$H$_3$(CF$_3$)), 8.34 (d, $J_{H-H} = 7.3$, 4H, SnPh-H_{ortho}), 7.33 (t, $J_{H-H} = 7.3$, 4H, SnPh-H_{meta}), 7.25 (d, $J_{H-H} = 7.8$, 1H, Os-C$_6$H$_3$(CF$_3$)), 7.17 (t, $J_{H-H} = 7.3$, 2H, SnPh-H_{para}), 7.00 (d, $J_{H-H} = 7.8$, 1H, Os-C$_6$H$_3$(CF$_3$)), 2.11 (m, 6H, PCH(CH$_3$)$_2$), 0.93 (dvt, $N = 13.5$, $J_{H-H} = 6.9$, 18H, PCH(CH_3)$_2$), 0.61 (dvt, $N = 13.5$, $J_{H-H} = 6.9$, 18H, PCH(CH_3)$_2$), −11.62 (br, 2H, Os-H). ^{1}H NMR (300 MHz, C$_7$D$_8$, 233 K, hydride region): δ −10.52 (part A of an ABX$_2$ spin system, 1H, $J_{A-X} =$ nonresolved, $J_{A-B} = 42$), −12.86 (part B of an ABX$_2$ spin system, 1H, $J_{B-X} = 12.8$, $J_{A-B} = 42$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 9.3 (s with tin satellites $J_{P-119Sn} = J_{P-117Sn} = 117$). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 193 K): AB spin system nonresolved centered at 2.4 ppm.[32] ^{13}C{^{1}H} NMR (100.56 MHz, CD$_2$Cl$_2$, 293 K, plus apt): δ 205.8 (s, CHO), 197.9 (t, $J_{C-P} = 9$, OsC), 155.9 (s, C_{ipso}, SnPh$_2$Cl), 145.3 (s, Os-C_6H$_3$-(CF$_3$)), 139.6 (q, $J_{C-F} = 3.7$, Os-C$_6$H$_3$(CF$_3$)), 137.2 (s, SnPh$_2$Cl), 132.5 (s, Os-C_6H$_3$(CF$_3$)), 127.6 (s, SnPh$_2$Cl), 127.4 (s, SnPh$_2$Cl), 117.4 (q, $J_{C-F} = 3.7$, Os-C_6H$_3$(CF$_3$)), 28.8 (vt, $N = 26.6$, PCH(CH$_3$)$_2$), 20.3, 19.7 (both s, PCH(CH_3)$_2$). ^{19}F NMR (282.33 MHz, C$_6$D$_6$, 293 K): δ −64.4 (s, CF$_3$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 18.2 (t, $J_{P-119Sn} = 117$). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 233 K): 86 ± 2 (−10.54 ppm, −12.82 ppm).

Reacction of $\overline{OsH_3(SnPh_2Cl)\{\eta^2\text{-}CH_2}$=$C(CH_3)PiPr_2\}}$**-(PiPr$_3$) with** *m*-**Anisaldehyde: Preparation of 5 and 6.** m-Anisaldehyde (39.4 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.18 mmol) in toluene (10 mL). After stirring for 24 h at room temperature the color of the solution had changed from yellow to reddish. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of an orange solid, which was washed with pentane and dried in vacuo. Yield: 89 mg (48%). Anal. Calcd for C$_{38}$H$_{61}$ClO$_2$OsP$_2$Sn: C, 47.73; H, 6.43. Found: C, 48.00; H, 6.31. IR (Nujol, cm^{-1}): ν(OsH) 1945 (w), ν(CO) 1555 (m). The ^{1}H and ^{31}P{^{1}H} NMR spectra show the presence of two isomers (**5** and **6**) in a ratio 50:50. Complex **5** could be isolated pure by crystallization of the mixture from toluene/methanol at −30 °C.

(31) (a) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027. (b) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (c) Jessop, P. G.; Morris, R.-H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(32) The presence of an AB spin system is consistent with the existence of a single conformer in which the trans phosphines are inequivalent due to hindered rotation about the Os−P or/and Os−Sn bonds. A similar behavior has been previously observed for some five- and six-coordinate ruthenium and osmium complexes containing bulky phosphine ligands. See for example: (a) Ref 15. (b) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190. (c) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476. (d) Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta* **1995**, *229*, 187.

Spectroscopic data of **5**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 9.14 (s, 1H, C*H*O), 8.44 (d, J_{H-H} = 7.2, 4H, SnPh-*H*$_{ortho}$), 7.34 (t, J_{H-H} = 7.2, 4H, SnPh-*H*$_{meta}$), 7.22 (d, J_{H-H} =7.8, 1H, Os-C$_6$*H*$_3$(OCH$_3$)), 7.18 (t, J_{H-H} = 7.2, 2H, SnPh-*H*$_{para}$), 6.79 (t, J_{H-H} = 7.8, 1H, Os-C$_6$*H*$_3$(OCH$_3$)), 6.21 (d, J_{H-H} = 7.8, 1H, Os-C$_6$*H*$_3$-(OCH$_3$)), 3.28 (s, 3H, (OC*H*$_3$), 2.13 (m, 6H, PC*H*(CH$_3$)$_2$), 0.95 (dvt, N = 13.2, J_{H-H} = 7.2, 18H, PCH(C*H*$_3$)$_2$), 0.66 (dvt, N = 13, J_{H-H} = 6.9, 18H, PCH(C*H*$_3$)$_2$), −11.11 (t, J_{H-P} = 7.2, 2H, Os*H*). ^{1}H NMR (300 MHz, C$_7$D$_8$, 233 K, hydride region): δ −10.71 (part A of an ABX$_2$ spin system, 1H, J_{A-X} = nonresolved, J_{A-B} = 56), −11.61 (part B of an ABX$_2$ spin system, 1H, J_{B-X} = nonresolved, J_{A-B} =56). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 6.2 (s with tin satellites $J_{P-117Sn}$ = $J_{P-119Sn}$ = 116). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 183 K): δ 5.5 (s). ^{13}C{^{1}H} NMR (100.56 MHz, C$_6$D$_6$, 253 K, plus apt): δ 204.5 (s, *C*HO), 188.2 (t, J_{P-C} = 7, Os*C*), 162.6 (s, *C*$_6$H$_3$(OCH$_3$)), 156.5 (s, C$_{ipso}$, SnPh$_2$Cl), 145.2 (s, *C*$_6$H$_3$(OCH$_3$)), 137.8 (s, SnPh$_2$Cl), 129.3 (s, *C*$_6$H$_3$(OCH$_3$)), 127.4 (s, SnPh$_2$Cl), 127.2 (s, SnPh$_2$Cl), 122.3 (s, *C*$_6$H$_3$(OCH$_3$)), 111.3 (s, *C*$_6$H$_3$(OCH$_3$)), 54.2 (s, OCH$_3$), 29.6 (m, PC*H*(CH$_3$)$_2$), 20.7, 19.6 (both s, PCH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 0.7 (t, $J_{P-119Sn}$ = 116). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 233 K): 66 $\pm$ 3 (−10.87, −11.60 ppm).

Spectroscopic data of **6**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 9.02 (s, 1H, C*H*O), 8.41 (d, J_{H-H} = 7.5, 4H, SnPh-*H*$_{ortho}$), 8.05 (d, J_{H-H} = 8.4, 1H, Os-C$_6$*H*$_3$(OCH$_3$)), 7.35 (t, J_{H-H} = 7.5, 4H, SnPh-*H*$_{meta}$), 7.18 (t, J_{H-H} = 7.5, 2H, SnPh-*H*$_{para}$), 7.01 (d, J_{H-H} = 3, 1H, Os-C$_6$*H*$_3$(OCH$_3$)), 6.77 (dd, J_{H-H} = 8.4, J_{H-H} = 3, 2H, Os-C$_6$*H*$_3$(OCH$_3$)), 3.29 (s, 3H, OC*H*$_3$), 2.14−2.10 (m, 6H, PC*H*(CH$_3$)$_2$), 1.01−0.83 (m, 18H, PCH(C*H*$_3$)$_2$), 0.70−0.60 (m, 18H, PCH(C*H*$_3$)$_2$), −11.93 (br, 2H, Os*H*). ^{1}H NMR (300 MHz, C$_7$D$_8$, 233 K, hydride region): δ −11.62 (part A of an ABX$_2$ spin system, 1H, J_{A-X} = 11.6, J_{A-B} = 38), −12.90 (part B of an ABX$_2$ spin system, 1H, J_{B-X} = 12.4, J_{A-B} = 38). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 8.4 (s with tin satellites $J_{P-117Sn}$ = $J_{P-119Sn}$ = 110). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 183 K): an unresolved AB spin system centered at 10.6 ppm. ^{13}C{^{1}H} NMR (100.56 MHz, C$_6$D$_6$, 293 K, plus apt): δ 204.4 (t, J_{C-P} = 2.8, *C*HO), 188.8 (t, J_{P-C} = 7, Os*C*), 156.5 (s, C$_{ipso}$, SnPh$_2$Cl), 155.3 (s, *C*$_6$H$_3$(OCH$_3$)), 143.5 (s, *C*$_6$H$_3$(OCH$_3$)), 137.8 (s, SnPh$_2$Cl), 127.5 (s, SnPh$_2$Cl), 127.3 (s, SnPh$_2$Cl), 125.1 (s, *C*$_6$H$_3$(OCH$_3$)), 123.9 (s, *C*$_6$H$_3$(OCH$_3$)), 112.8 (s, *C*$_6$H$_3$(OCH$_3$)), 54.8 (s, O*C*H$_3$), 29.7 (vt, N = 25.7, PC*H*(CH$_3$)$_2$), 20.6, 19.8 (both s, PCH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 19.3 (t, $J_{P-119Sn}$ = 110). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 248 K): 60 $\pm$ 1 (−12.96 ppm).

Preparation of OsH$_2$(SnPh$_2$Cl){C$_6$H$_3$(CF$_3$)C(O)H}(P^{i}Pr$_3$)$_2$ (7). *m*-Trifluoromethylbenzaldehyde (36.1 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After stirring for 6.5 h at room temperature, the color of the solution changed from yellow to reddish orange. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a red solid, which was washed with pentane and dried in vacuo. Yield: 70 mg (55%). Anal. Calcd for C$_{38}$H$_{58}$-ClF$_3$OOsP$_2$Sn: C, 45.90; H, 5.88. Found: C, 45.81; H, 5.61. IR (Nujol, cm^{-1}): ν(OsH) 1948 (w), ν(CO) 1556 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.89 (s, 1H, C*H*O), 8.33 (d, J_{H-H} = 6.9, 4H, SnPh-*H*$_{ortho}$), 8.16 (d, J_{H-H} = 8.2, 1H, Os-C$_6$*H*$_3$(CF$_3$)), 7.73 (s, 1H, Os-C$_6$*H*$_3$(CF$_3$)), 7.32 (t, J_{H-H} = 6.9, 4H, SnPh-*H*$_{meta}$), 7.17 (t, J_{H-H} = 6.9, 2H, SnPh-*H*$_{para}$), 6.95 (d, J_{H-H} = 8.2, 1H, Os-C$_6$*H*$_3$(CF$_3$)), 2.09 (m, 6H, PC*H*(CH$_3$)$_2$), 0.88 (dvt, N = 13.2, J_{H-H} = 6.6, 18H, PCH(C*H*$_3$)$_2$), 0.59 (dvt, N = 12.6, J_{H-H} = 6.3, 18H, PCH(C*H*$_3$)$_2$), −11.72 (br, 2H, Os-*H*). ^{1}H NMR (300 MHz, C$_7$D$_8$, 233 K, hydride region): δ −10.65 (part A of an ABX$_2$ spin system, 1H, J_{A-X} = 10.5, J_{A-B} = 38), −12.87 (part B of an ABX$_2$ spin system, 1H, J_{B-X} = 12.4, J_{A-B} = 38). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 7.9 (s with tin satellites $J_{P-119Sn}$ = $J_{P-117Sn}$ = 115). ^{31}P{^{1}H} NMR (121.42 MHz, C$_7$D$_8$, 183 K): δ 6.6 (AB spin system, $\Delta\nu$ = 754 Hz, J_{A-B} = 181).[32]

^{13}C{^{1}H} NMR (100.56 MHz, CD$_2$Cl$_2$, 293 K, plus apt): δ 205.4 (s, *C*HO), 204.5 (t, J_{C-P} = 7.5, Os*C*), 155.6 (s, C$_{ipso}$, SnPh$_2$Cl), 143.8 (s, Os-*C*$_6$H$_3$(CF$_3$)), 137.1 (s, SnPh$_2$Cl), 129.4 (s, Os-*C*$_6$H$_3$-(CF$_3$)), 127.7 (s, SnPh$_2$Cl), 127.4 (s, SnPh$_2$Cl), 125.6 (s, Os-*C*$_6$H$_3$(CF$_3$)), 123.3 (q, J_{C-F} = 31.6, Os-*C*$_6$H$_3$(CF$_3$)), 28.9 (vt, N = 25.7, PC*H*(CH$_3$)$_2$), 20.3, 19.8 (both s, PCH(*C*H$_3$)$_2$). ^{19}F NMR (282.33 MHz, C$_6$D$_6$, 293 K): δ −63.5 (s, CF$_3$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 12.8 (t, $J_{P-119Sn}$ = 115). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 243 K): 73 $\pm$ 2 (−10.73 ppm, −12.84 ppm).

Preparation of $\overline{\textbf{OsH}_2\textbf{(SnPh}_2\textbf{Cl)\{C}_4\textbf{(O)H}_2\textbf{C(O)H\}}}$**(P^{i}Pr$_3$)$_2$ (8).** 3-Furaldehyde (24.1 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.19 mmol) in toluene (10 mL). After stirring for 8 h at room temperature the color of the solution had changed from yellow to orange. The resulting solution was filtered through Celite and was taken to dryness. Subsequent addition of pentane caused the precipitation of a yellow solid, which was washed with pentane and dried in vacuo. Yield: 88 mg (50%). Anal. Calcd for C$_{35}$H$_{57}$ClO$_2$OsP$_2$Sn: C, 45.88; H, 6.27. Found: C, 45.58; H, 6.07. IR (Nujol, cm^{-1}): ν(OsH) 1946 (m), ν(CO) 1548 (m). ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.51 (s, 1H, C*H*O), 8.42 (d, J_{H-H} = 7.5, 4H, SnPh-*H*$_{ortho}$), 7.33 (t, J_{H-H} = 7.5, 4H, SnPh-*H*$_{meta}$), 7.17 (t, J_{H-H} = 7.5, 2H, SnPh-*H*$_{para}$), 7.01 (d, J_{H-H} = 2, 1H, Os-C$_4$*H*$_2$O), 6.11 (d, J_{H-H} = 2, 1H, Os-C$_4$*H*$_2$O), 2.05 (m, 6H, PC*H*(CH$_3$)$_2$), 0.99 (dvt, J_{H-H} = 6.9, N = 13.5, 18H, PCH(C*H*$_3$)$_2$), 0.85 (dvt, J_{H-H} = 6.9, N = 13.2, 18H, PCH(C*H*$_3$)$_2$), −11.48 (br tr, J_{H-H} = 11.7, 2H, Os*H*). ^{1}H NMR (300 MHz, C$_7$D$_8$, 203 K, hydride region): δ −11.46 (AB spin system, $\Delta\nu$ = 784 Hz, J_{A-B} = 267). ^{31}P{^{1}H} NMR (121.42 MHz, C$_6$D$_6$, 293 K): δ 13.4 (s with tin satellites $J_{P-119Sn}$ = $J_{P-117Sn}$ = 127). ^{13}C{^{1}H} NMR (100.56 MHz, C$_6$D$_6$, 293 K, plus apt): δ 230.6 (t, J_{C-P} = 8.7, Os*C*), 188.6 (s, *C*HO) 155.8 (s, C$_{ipso}$, SnPh$_2$Cl), 146.9 (s, Os-*C*$_4$H$_2$O), 137.8 (s, SnPh$_2$Cl), 135.0 (s, Os-*C*$_4$H$_2$O), 127.7 (s, SnPh$_2$Cl), 127.5 (s, SnPh$_2$Cl), 106.4 (s, Os-*C*$_4$H$_2$O), 28.9 (vt, N = 26, PC*H*(CH$_3$)$_2$), 20.1, 19.9 (both s, PCH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ 19.4 (t, $J_{P-119Sn}$ = 127). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 243 K): 60 $\pm$ 1 (−11.59 ppm).

Preparation of $\overline{\textbf{OsH}_2\textbf{(SnPh}_2\textbf{Cl)\{C}_6\textbf{H}_8\textbf{C(O)H\}}}$**(P^{i}Pr$_3$)$_2$ (9).** 1-Cyclohexene-1-carboxaldehyde (31.7 μL, 0.27 mmol) was added to a solution of **1** (150 mg, 0.18 mmol) in toluene (10 mL). After stirring for 27 h at room temperature, the color of the solution changed from yellow to orange. The resulting solution was filtered through Celite, and the solution was taken to dryness. Subsequent addition of pentane caused the precipitation of an orange solid, which was washed with pentane and dried in vacuo. Yield: 99 mg (55%). Anal. Calcd for C$_{37}$H$_{63}$ClOOsP$_2$Sn: C, 47.80; H, 6.83. Found: C, 47.48; H, 6.45. IR (Nujol, cm^{-1}): ν(OsH) 1946 (w), ν(CO) 1542 (m). ^{1}H NMR (400 MHz, C$_7$D$_8$, 293 K): δ 8.54 (s, 1H, C*H*O), 8.29 (d, J_{H-H} = 7, 4H, SnPh-*H*$_{ortho}$), 7.28 (t, J_{H-H} = 7, 4H, SnPh-*H*$_{meta}$), 7.15 (t, J_{H-H} = 7, 2H, SnPh-*H*$_{para}$), 3.53 (t, J_{H-H} = 5.8, 2H, Os-C$_6$*H*$_8$), 2.38 (t, J_{H-H} = 5.8, 2H, Os-C$_6$*H*$_8$), 2.21 (m, 6H, PC*H*(CH$_3$)$_2$), 1.52 (m, 2H, Os-C$_6$*H*$_8$), 1.45 (m, 2H, Os-C$_6$*H*$_8$), 1.01 (dvt, J_{H-H} = 6.9, N = 13.5, 18H, PCH(C*H*$_3$)$_2$), 0.83 (dvt, J_{H-H} = 6.6, N = 12.8, 18H, PCH(C*H*$_3$)$_2$), −11.92 (br, 2H, Os*H*). ^{1}H NMR (400 MHz, C$_7$D$_8$, 193 K, hydride region): δ −11.30 (part A of an ABX$_2$ spin system, 1H, J_{A-X} = nonresolved, J_{A-B} = 72), −13.30 (part B of an ABX$_2$ spin system, 1H, J_{B-X} = 14.6, J_{A-B} = 72). ^{31}P{^{1}H} NMR (161.9 MHz, C$_7$D$_8$, 293 K): δ 7.1 (s with tin satellites $J_{P-119Sn}$ = $J_{P-117Sn}$ = 128). ^{13}C{^{1}H} NMR (100.56 MHz, C$_6$D$_6$, 293 K, plus apt): δ 242.9 (t, J_{C-P} = 6.5, Os*C*), 197.7 (s, *C*HO) 157.3 (s, C$_{ipso}$, SnPh$_2$Cl), 137.9 (s, SnPh$_2$Cl), 136.5 (s, Os-*C*$_6$H$_8$), 127.4 (s, SnPh$_2$Cl), 127.2 (s, SnPh$_2$Cl), 48.2 (s, Os-*C*$_6$H$_8$), 29.5 (vt, N = 24.8, PC*H*(CH$_3$)$_2$), 25.9 (s, Os-*C*$_6$H$_8$), 24.5 (s, Os-*C*$_6$H$_8$), 23.1 (s, Os-*C*$_6$H$_8$), 20.9, 20.1 (both s, PCH(*C*H$_3$)$_2$). ^{119}Sn{^{1}H} NMR (111.83 MHz, C$_6$D$_6$, 293 K): δ −0.1 (br t, $J_{P-119Sn}$ = 128). $T_{1(min)}$ (ms, OsH$_2$, 300 MHz, C$_7$D$_8$, 233 K): 69 $\pm$ 1 (−11.24 ppm, −13.30 ppm).

Table 5. Crystal Data and Data Collection and Refinement for 2, 5, and 8

	2	5	8
		Crystal Data	
formula	$C_{37}H_{59}ClOOsP_2Sn$	$C_{38}H_{57}ClO_2OsP_2Sn$ $\cdot 0.5C_7H_8 \cdot 0.5(C_4H_{10}O)$	$C_{35}H_{57}ClO_2OsP_2Sn$
molecular wt	926.12	1002.22	916.09
color and habit	red	red	yellow
	irregular prism	irregular block	irregular prism
symmetry, space group	orthorhombic, *Pnma*	monoclinic, *P*2₁/*n*	orthorhombic, *Pnma*
a, Å	15.1979(7)	18.1388(11)	14.7802(6)
b, Å	21.2309(9)	11.9563(7)	21.1176(9)
c, Å	11.7399(5)	20.2587(12)	11.6165(5)
β, deg		109.4170(10)	
V, Å³	3788.1(3)	4143.7(4)	3625.8(3)
Z	4	4	4
D_{calc}, g cm⁻³	1.624	1.607	1.678
		Data Collection and Refinement	
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm⁻¹	4.192	3.841	4.381
2θ, range deg	3, 57	3, 57	3, 57
temp, K	100	100	100
no. of data collected	40 989	50 784	67 277
no. of unique data	4902 (R_{int} = 0.0477)	10 246 (R_{int} = 0.0517)	4703 (R_{int} = 0.0433)
no. of params/restraints	225/2	448/0	223/2
R_1^a [$F^2 > 2\sigma(F^2)$]	0.0219	0.0295	0.0233
wR_2^b [all data]	0.0387	0.0469	0.0401
S^c [all data]	0.857	0.846	0.923

^{a} $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. ^{c} Goof $= S = \{\Sigma[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

Structural Analysis of Complexes 2, 5, and 8. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time were 10 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS[33] program. The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[34] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. For **5** the asymmetric unit shows a solvent molecule of toluene over a center of symmetry. The hydrogen atoms for nondisordered groups were observed or calculated and refined using a restricted riding model or freely. Hydride ligands were located, but not all of them refined appropriately, and some restraints were used in **2** and **8** (Os−H bonds). All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense. Crystal data and details of the data collection and refinement are given in Table 5.

Supporting Information Available: Tables of positional and displacement parameters, crystallographic data, and bond lengths and angles of complexes **2**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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