Reactions of a Hexahydride-Osmium Complex with Aldehydes: Double C−H$_\alpha$ Activation−Decarbonylation and Single C−H$_\alpha$ Activation−Hydroxylation Tandem Processes and Catalytic Tishchenko Reactions

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The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) activates the C−H$_\alpha$ bond of aldehydes. In toluene under reflux, the reactions with benzaldehyde, cyclohexanecarboxaldehyde, and isobutyraldehyde lead to products resulting from two C−H$_\alpha$ activation−decarbonylation tandem processes. The reaction with benzaldehyde gives the hydride-phenyl-*cis*-dicarbonyl derivative $OsHPh(CO)_2(P^iPr_3)_2$ (**2**) and benzene, while cyclohexanecarboxaldehyde and isobutyraldehyde yield the *cis*-dihydride-*cis*-dicarbonyl compound $OsH_2(CO)_2(P^iPr_3)_2$ (**3**) and the corresponding alkane. In the presence of water **1** reacts with benzaldehyde to give **2**. However, cyclohexanecarboxaldehyde and isobutyraldehyde afford the carboxylate complexes $OsH_3(\kappa^2\text{-}O_2CR)(P^iPr_3)_2$ (R = Cy (**4**), $(CH_3)_2CH$ (**5**)), which can also be obtained by reaction of **1** and the corresponding carboxylic acid. Similarly, the treatment of **1** with benzoic acid gives $OsH_3(\kappa^2\text{-}O_2CPh)(P^iPr_3)_2$ (**6**). The structure of **5** in the solid state has been determined by X-ray diffraction analysis. The coordination geometry around the osmium atom can be described as a distorted pentagonal bipyramid with the phosphorus atoms of the phosphines occupying axial positions. In solution, the central hydride ligand of **4**−**6** exchanges its position with that of the hydrides disposed *cisoid* to the oxygen atoms. The activation parameters for the exchange process are $\Delta H^\ddagger = 10.2 \pm 0.4$ kcal·mol^{-1} and $\Delta S^\ddagger = -4.3 \pm 1.0$ cal·mol^{-1}·K^{-1} for **4**, $\Delta H^\ddagger = 10.6 \pm 0.3$ kcal·mol^{-1} and $\Delta S^\ddagger = 1.1 \pm 0.9$ cal·mol^{-1}·K^{-1} for **5**, and $\Delta H^\ddagger = 10.4 \pm 0.4$ kcal·mol^{-1} and $\Delta S^\ddagger = -1.3 \pm 1.2$ cal·mol^{-1}·K^{-1} for **6**. Complexes **1**, **3**, and **4** are active catalyst precursors for classical Tishchenko dimerization of cyclohexanecarboxaldehyde. Complexes **1** and **3** are also active catalyst precursors for the classical Tishchenko dimerization of benzaldehyde and for the homo aldo-Tishchenko trimerization of isobutyraldehyde to (3-hydroxy-2,2,4-trimethylpentyl)-2-methylpropionate.

Introduction

We have recently shown that the saturated d^2 hexahydride $OsH_6(P^iPr_3)_2$ can be thermally activated to generate the unsaturated short-lived dihydride-dihydrogen $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$.[1] This species activates *ortho*-CH bonds of aromatic ketones and imines[2] and *ortho*-CF bonds of partially fluorinated aromatic ketones.[1] The reactions give complexes that are reminiscent of the intermediates proposed by Murai for the insertion of olefins into *ortho*-CH bonds of ketones and imines[3] and for the arylation of aromatic ketones with arylboronates.[4] For partially fluorinated aromatic ketones, the *ortho*-CH activation is preferred over the *ortho*-CF activation in ketones containing only one aromatic ring. However, the *ortho*-CF activation is preferred over the *ortho*-CH activation in 2,3,4,5,6-pentafluoroacetophenone.[1]

In addition to the activation of aromatic ketones, intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ is capable of producing the triple C−H activation of the cyclohexylmethyl ketone to afford the cyclohexenyl-keto derivative $OsH_3\{C_6H_8C(O)CH_3\}(P^iPr_3)_2$.[5] The formation of this complex suggests that cycloalkyl ketones should be able to afford alkylcycloalkenyl ketones by the Murai method.

The activation of the C−H$_\alpha$ bond of aldehydes is a reaction of great interest due to its connection with the catalytic decarbonylation of these substrates[6] and by its importance in organometallic[7] and organic[8] synthesis. Our interest in the activation processes of carbonyl compounds promoted by the species $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$

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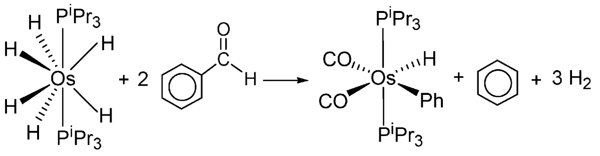
prompted us to study the activation of the C$-$H$_\alpha$ bond of aldehydes, in particular those containing aryl and cyclohexyl groups.

This paper reveals that the intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ promotes two different stoichiometric tandem processes: carbon hydrogen activation$-$decarbonylation and carbon hydrogen activation$-$hydroxylation. Furthermore, it shows that the hexahydride $OsH_6(P^iPr_3)_2$ and related compounds are active catalyst precursors for the Tishchenko reaction.

Results and Discussion

1. C$-$H$_\alpha$ Activation$-$Decarbonylation. The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with benzaldehyde, cyclohexanecarboxaldehyde, and isobutyraldehyde in toluene under reflux to give organometallic and organic (identified by gas chromatography-MS) products, which are the result of C$-$H$_\alpha$ activation$-$decarbonylation tandem processes between 2 equiv of aldehyde and 1 equiv of hexahydride.

The reaction of **1** with benzaldehyde leads to benzene and the hydride-phenyl-dicarbonyl derivative $OsHPh(CO)_2(P^iPr_3)_2$ (**2**), according to eq 1.

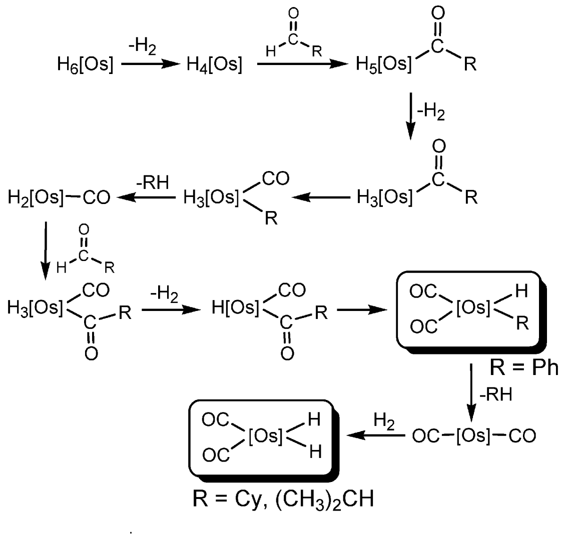


(**1**)

1 **2**

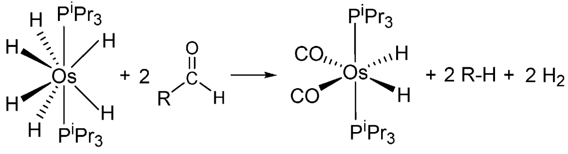
Complex **2** was isolated as a white solid in 82% yield. In the IR spectrum in KBr the most noticeable features are the presence of a ν(Os$-$H) absorption at 2016 cm^{-1} and two ν(CO) bands at 1959 and 1887 cm^{-1}. The mutual *cis* disposition of the carbonyl groups is strongly supported by the intensity ratio (1.02) of the ν(CO) bands, which suggests an angle between these ligands of 90.6°.[9] In agreement with this, the $^{13}C\{^1H\}$ NMR spectrum contains resonances corresponding to inequivalent carbonyl groups at 191.4 and 185.6 ppm. These resonances are observed as triplets with C$-$P coupling constants of 5.8 and 8.5 Hz, respectively. In addition, the spectrum shows six resonances due to the aryl carbon atoms, at 150.4, 147.0, 145.7, 127.1, 126,9, and 121.9 ppm. The resonance at 147.0 appears as a triplet with a C$-$P coupling constant of 10.6 Hz and was assigned to the Os$-$C carbon atom. In the ^1H NMR spectrum, the protons of the aryl group display resonances at 8.26 and 8.11 (*o*-H), 7.1$-$6.9 (*m*-H), and 7.00 (*p*-H) ppm, whereas the hydride ligand gives rise to a triplet at -6.59 ppm with a H$-$P coupling constant of 22.1 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 22.0 ppm.

Scheme 1



The reactions of **1** with cyclohexanecarboxaldehyde and isobutyraldehyde lead to the previously reported *cis*-dihydride, *cis*-dicarbonyl derivative $OsH_2(CO)_2(P^iPr_3)_2$[10] (**3**) and the corresponding alkane, according to eq 2.

Scheme 1 shows a sequence of steps that rationalizes the products of these reactions.



(**2**)

1 **3** R = Cy, (CH$_3$)$_2$CH

The dissociation of a hydrogen molecule from the hexahydride starting complex affords the short-lived intermediate $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ (H_4[Os] in Scheme 1), which is capable of selectively activating the C$-$H$_\alpha$ bond of aldehydes, in the presence of aromatic or aliphatic C$-$H bonds, to give saturated H_5-acyl intermediates. In this context, it should be noted that the C$-$H$_\alpha$ bond of an aldehyde is about 23 kcal·mol^{-1} weaker than the C$-$H bonds of a phenyl group and about 14 kcal·mol^{-1} weaker than the C$-$H bonds of an alkyl group.

The loss of a second hydrogen molecule from the saturated H_5-acyl intermediates should lead to unsaturated species, which could evolve by deinsertion of R and subsequent reductive elimination of R$-$H, into the unsaturated dihydride-carbonyl-osmium(II) intermediate $OsH_2(CO)(P^iPr_3)_2$ (H_2[Os]-CO in Scheme 1). This short-lived derivative has been previously proposed as the key species for the formation of the hydride-alkynyl complexes $OsH(C_2R)(CO)(P^iPr_3)_2$ (R = Ph, SiMe$_3$),[11] by

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[7] See for example: (a) Gómez, M.; Kisenyi, J. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *296*, 197. (b) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 5269. (c) Alaimo, P. J.; Arndtsen, B. A.; Bergman, R. G. *Organometallics* **2000**, *19*, 2130. (d) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569.

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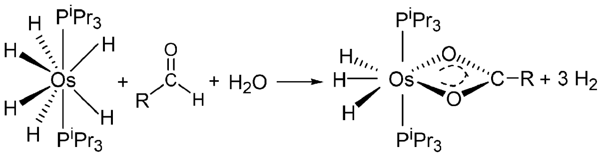
reaction of the dihydride-dihydrogen $OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ [12] with the corresponding alkyne.

The oxidative addition of a second molecule of aldehyde to $OsH_2(CO)(P^iPr_3)_2$ should lead to saturated H_3-carbonyl-acyl species. The dissociation of a new hydrogen molecule from these intermediates, followed by the deinsertion of R, should give **2** (R = Ph) or hydride-alkyl intermediates. In contrast to **2**, these hydride-alkyl intermediates are unstable under the reaction conditions and evolve by reductive elimination of alkane into an unsaturated osmium(0) species. The oxidative addition of molecular hydrogen to the latter should yield **3**.

We note that the dimeric ruthenium complex $[RuHCl(P^iPr_3)_2]_2$ also reacts with aldehydes to give C−H_α activation−decarbonylation products. However, in contrast to **1**, this ruthenium derivative is capable of producing only one tandem process.[7d] The reactions with alkyl aldehydes lead to the well-known compound $RuHCl(CO)(P^iPr_3)_2$ [13] and alkane, while in the presence of benzalehyde, the phenyl derivative $RuPhCl(CO)(P^iPr_3)_2$ is formed. Although complex $RuHCl(CO)(P^iPr_3)_2$ is formally an unsaturated compound, at first glance as the short-lived intermediate $OsH_2(CO)(P^iPr_3)_2$, the mutually *trans* disposition of the Cl and CO ligands increases the π-donor capacity of chloro by means of the "push−pull" effect, making this molecule not a truly 16-valence-electron species[14] and therefore less reactive than $OsH_2(CO)(P^iPr_3)_2$.

The higher stability of **2** in comparison with the related hydride-alkyl species should be attributed to an osmium−carbon bond much stronger for aryl than for alkyl. In this context, it should be mentioned that although the arene C−H bond is between 14 and 8 kcal·mol^{-1} stronger than the alkane C−H bond, in general, the arene C−H activation is thermodynamically favored with regard to the alkane C−H activation.[15]

2. C−H$_\alpha$ Activation−Hydroxylation. In the presence of 30 equiv of water the reaction of **1** with benzaldehyde leads to **2** and benzene. However the reactions of **1** with cyclohexanecarboxaldehyde and isobutyraldehyde give the trihydride-carboxylate compounds $OsH_3(\kappa^2\text{-}O_2CR)(P^iPr_3)_2$ (R = Cy (**4**), $(CH_3)_2CH$ (**5**)), according to eq 3. In this case the formation of alkane is not observed.



(3)

1

R = Cy (**4**), $(CH_3)_2CH$ (**5**)

Complexes **4** and **5** were isolated as yellow solids in high yield and characterized by MS, elemental analysis, and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies. Complex **5** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of this compound is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

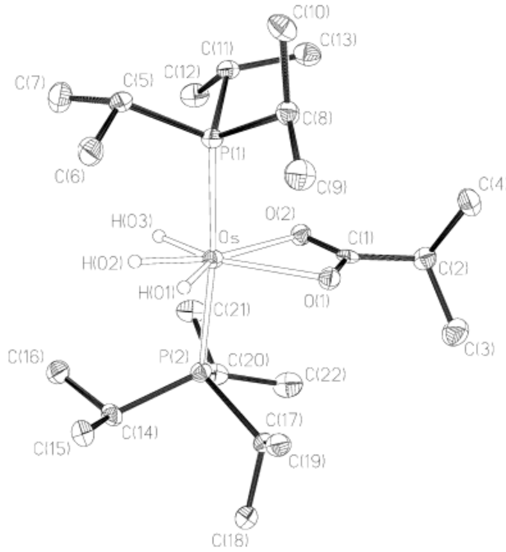


Figure 1. Molecular diagram of the complex $OsH_3(\kappa^2\text{-}O_2CCH(CH_3)_2)(P^iPr_3)_2$ (**5**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsH_3[\kappa^2\text{-}O_2CCH(CH_3)_2](P^iPr_3)_2$ (5)

Os−P(1)	2.3227(9)	Os−H(02)	1.44(3)
Os−P(2)	2.3198(9)	Os−H(03)	1.45(3)
Os−O(1)	2.208(2)	O(1)−C(1)	1.262(4)
Os−O(2)	2.2509(19)	O(2)−C(1)	1.266(3)
Os−H(01)	1.42(3)	C(1)−C(2)	1.514(4)
P(1)−Os−P(2)	174.14(3)	O(1)−Os−H(02)	154.9(12)
P(1)−Os−O(1)	93.37(6)	O(1)−Os−H(03)	151.8(11)
P(1)−Os−O(2)	92.67(6)	O(2)−Os−H(01)	152.1(11)
P(1)−Os−H(01)	90.2(10)	O(2)−Os−H(02)	146.6(12)
P(1)−Os−H(02)	88.5(10)	O(2)−Os−H(03)	93.5(11)
P(1)−Os−H(03)	87.7(11)	H(01)−Os−H(02)	61.2(13)
P(2)−Os−O(1)	92.19(6)	H(01)−Os−H(03)	114.4(15)
P(2)−Os−O(2)	91.82(6)	H(02)−Os−H(03)	53.2(13)
P(2)−Os−H(01)	87.6(10)	Os−O(1)−C(1)	92.5(2)
P(2)−Os−H(02)	85.6(10)	Os−O(2)−C(1)	90.47(19)
P(2)−Os−H(03)	88.3(11)	O(1)−C(1)−O(2)	118.6(3)
O(1)−Os−O(2)	58.35(8)	O(1)−C(1)−C(2)	119.5(3)
O(1)−Os−H(01)	93.8(11)	O(2)−C(1)−C(2)	121.9(3)

The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the two phosphorus atoms of the triisopropylphosphine ligands occupying axial positions (P(2)−Os−P(1) = 174.14(3)°). The osmium sphere is completed by the hydride ligands and the carboxylate group, which acts with a bite angle of 58.35(8)°.

The IR spectra of these compounds in KBr exhibit two ν(OsH) bands at 2156 and 2142 (**4**) and 2159 and 2144 (**5**) cm^{-1} as well as the ν_{asym}(OCO) (1524 (**4**) and 1534 (**5**) cm^{-1}) and ν_{sym}(OCO) (1447 (**4**) and 1484 (**5**) cm^{-1}) absorptions corresponding to the carboxylate groups, which are separated by 77 (**4**) and 50 (**5**) cm^{-1}, in agreement with the chelate coordination mode of these ligands.[16] In the $^{13}C\{^1H\}$ NMR spectra, the resonances due to the C(sp^2) carbon atom of the carboxylate groups appear at 185.7 (**4**) and 186.3 (**5**) ppm, as triplets with C−P coupling constants of 1.4 and 1.2 Hz, respectively.

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The $^{31}P\{^{1}H\}$ NMR spectra show singlets at 40.7 (**4**) and 40.5 (**5**) ppm, in accordance with the mutually *trans* position of the phosphine ligands.

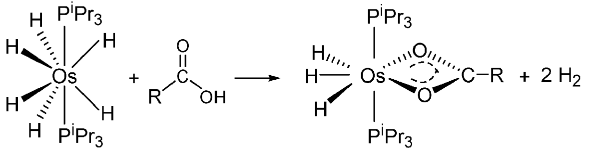
The $^{31}P\{^{1}H\}$ NMR spectra are temperature invariant between 293 and 203 K. However, the ^{1}H NMR spectra are temperature dependent and consistent with the operation of a thermally activated exchange process between the central hydride and those disposed *cisoid* to the oxygen atoms of the carboxylate. At 293 K, for both compounds, the exchange process proceeds at a rate sufficient to lead to single hydride resonances, which appear at −14.51 (**4**) and −14.97 (**5**) ppm as triplets with H−P coupling constants of 11.8 and 11.7 Hz, respectively. Lowering the sample temperature leads to broadening of the resonances. At 213 K decoalescence occurs and AB_2X_2 (X = ^{31}P) spin systems are observed, which become well resolved at 203 K. The $^{1}H\{^{31}P\}$ NMR spectra are simplified to the expected AB_2 spin systems. They are defined by $\delta_A = -14.33$, $\delta_B = -14.52$, and $J_{A-B} = 18.03$ Hz (**4**) and $\delta_A = -14.76$, $\delta_B = -15.27$, and $J_{A-B} = 20.7$ Hz (**5**).

Line-shape analysis of the $^{1}H\{^{31}P\}$ NMR spectra allows the calculation of the rate constants for the thermal exchange processes at different temperatures. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 10.2 \pm 0.4$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -4.3 \pm 1.0$ cal·mol^{-1}·K^{-1} for **4** and $\Delta H^{\ddagger} = 10.6 \pm 0.3$ kcal·mol^{-1} and $\Delta S^{\ddagger} = 1.1 \pm 0.9$ cal·mol^{-1}·K^{-1} for **5**. The values for the entropy of activation, close to zero, are in agreement with an intramolecular process, whereas the values for the enthalpy of activation lie in the range reported for thermal exchange processes in related osmium-trihydride complexes.[1−3,17]

The T_1 values of the hydrogen nuclei of the OsH_3 unit of **4** and **5** were determined over the temperature range 293−183 K. $T_{1(min)}$ values of 74 ± 2 (**4**) and 82 ± 1 (**5**) ms were obtained at 220 K. They support the trihydride character of both compounds.[18]

The reactions shown in eq 3 describe C−H$_\alpha$ activation−hydroxylation tandem processes for cyclohexanecarboxaldehyde and isobutyraldehyde, which can be rationalized according Scheme 2. The nucleophilic addition of water to the H_5-acyl intermediates of Scheme 1 leads to the corresponding carboxylic acid, regenerating **1**. The subsequent reactions of **1** with the acids afford **4** and **5**. The fact that benzaldehyde does not react in the same manner as cyclohexanecarboxaldehyde and isobutyraldehyde suggests that the deinsertion of R is faster for phenyl than alkyl, which could be related to the higher stability of the M−Ph bonds in comparison with the M−alkyl bonds.

In agreement with Scheme 2, we have observed that **1** reacts with cyclohexanecarboxylic acid and isobutyric acid to give **4** and **5**, respectively. Similarly, the reaction of **1** with benzoic acid affords $OsH_3(\kappa^2\text{-}O_2CPh)(P^iPr_3)_2$ (**6**), as a yellow solid in 78% yield (eq 4).

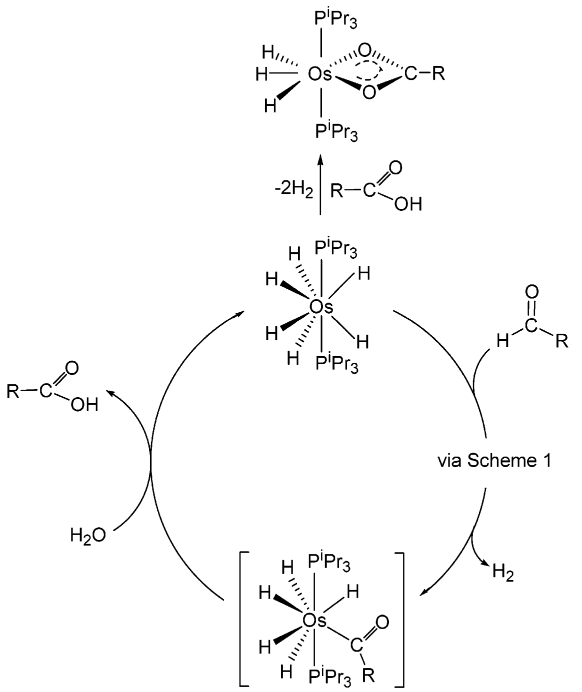


(4)

1

R = Cy (**4**), $(CH_3)_2CH$ (**5**), Ph (**6**)

Scheme 2



The spectroscopic data of **6** agree well with those of **4** and **5**. The IR spectrum contains two ν(OsH) bands at 2160 and 2140 cm^{-1} along with the ν_{asym}(OCO) and ν_{sym}(OCO) absorptions at 1525 and 1465 cm^{-1}, respectively. In the $^{13}C\{^{1}H\}$ NMR spectrum, the resonance due to the CO_2-carbon atom of the carboxylate appears as a singlet at 176.2 ppm. The $^{31}P\{^{1}H\}$ shows a singlet at 40.2 ppm.

As for **4** and **5**, the ^{1}H NMR spectra of **6** are consistent with the operation of a thermally activated exchange process between the central hydride and those disposed *cisoid* to the oxygen atoms of the carboxylate. Thus, at room temperature, the spectrum shows only one hydride resonance at −14.38 ppm, which appears as a triplet with a H−P coupling constant of 11.6 Hz, while at 193 K the characteristic AB_2X_2 (X = ^{31}P) spin system for a structure as that shown in Figure 1 is observed. In the $^{1}H\{^{31}P\}$ NMR spectrum, the simplified AB_2 spin system is defined by $\delta_A = -14.03$, $\delta_B = -14.37$, and $J_{A-B} = 22.04$ Hz. The activation parameters for the exchange are $\Delta H^{\ddagger} = 10.4 \pm 0.4$ kcal·mol^{-1} and $\Delta S^{\ddagger} = -1.3 \pm 1.2$ cal·mol^{-1}·K^{-1}. These values are very similar as those obtained for **4** and **5** and suggest that the substituent R of the carboxylate has no significant contribution to the properties of the OsH_3 unit of these compounds.

The T_1 values of the hydrogen nuclei of the OsH_3 unit of **6** were determined over the temperature range 293−193 K. $T_{1(min)}$ values of 68 ± 3 (δ_A) and 78 ± 2 (δ_B) ms were obtained at 218 K, after the decoalescence. They are consistent with a separation H_A-H_B of between 1.5 and 1.6 Å.[18]

3. Catalytic Tishchenko Reactions. The classical Tishchenko reaction, by which an aldehyde can be

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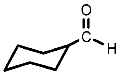
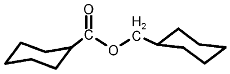
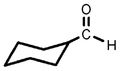
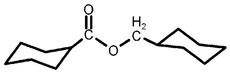
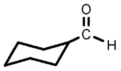
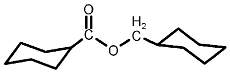
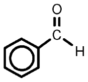
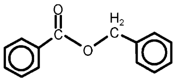
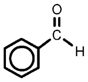
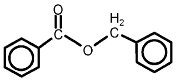
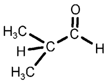
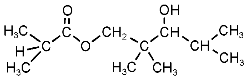
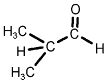
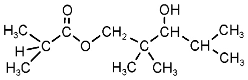
[17] (a) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E.; Tolosa, J. I. *Inorg. Chem.* **1996**, *35*, 7811. (b) Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *J. Am. Chem. Soc.* **1997**, *119*, 9691. (c) Castillo, A.; Barea, G.; Esteruelas, M. A.; Lahoz, F. J.; Lledós, A.; Maseras, F.; Modrego, J.; Oñate, E.; Oro, L. A.; Ruiz, N.; Sola, E. *Inorg. Chem.* **1999**, *38*, 1814.

[18] Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

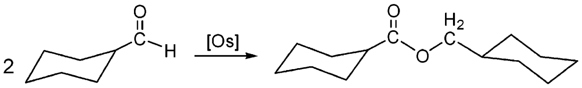
Table 2. Catalytic Tishchenko Reaction Results

Substrate	Catalyst	Product	Yield (%)	Time (h)
	$OsH_6(P^iPr_3)_2$		90 98	1/6 1/2
	$OsH_2(CO)_2(P^iPr_3)_2$		92	22
	$OsH_3(\kappa^2\text{-}O_2CCy)(P^iPr_3)_2$		76	22
	$OsH_6(P^iPr_3)_2$		20	75
	$OsH_2(CO)_2(P^iPr_3)_2$		92	141
	$OsH_6(P^iPr_3)_2$		86	140
	$OsH_2(CO)_2(P^iPr_3)_2$		100	126

converted into a simple monofunctional ester, has important industrial applications. Thus, for example, the Tishchenko ester of 3-cyclohexenecarbaldehyde is the precursor for the formation of epoxy resine, and benzylbenzoate is used as a dye carrier. Traditionally aluminum[19] or transition metal[20] alkoxides, lithium tungsten dioxide,[21] SmI_2,[22] or boric acid,[23] have been employed as catalysts. More recently transition metal complexes, including phosphine-rhodium-[24] and cyclopentadienyl-nickel-enolates,[25] lanthanide amides,[26] $Cp^*{}_2La[CH(SiMe_3)_2]$,[27] Cp_2ZrH_2,[28] $RuH_2(PPh_3)_4$,[29] or $K_2[Fe(CO)_4]$,[30] are used. To our knowledge osmium catalysts have not been reported.

This absence prompted us to explore the catalytic activity of complexes **1**−**6** for the Tishchenko dimerizations of cyclohexanecarboxaldehyde, benzaldehyde, and isobutyraldehyde. The reactions were carried out under reflux in the aldehyde (cyclohexanecarboxaldehyde and benzaldehyde) or toluene (isobutyraldehyde) as solvent, using a 1:100 catalyst:aldehyde molar ratio. The formed products and the yields of the reactions are given in Table 2.

Complex **1** is a very active catalyst precursor for the Tishchenko dimerization of cyclohexanecarboxaldehyde (eq 5). Thus, after 10 min, the ester is formed in 90% yield. All the aldehyde is converted to ester (98%) and cyclohexane (2%) after 30 min. In agreement with the formation of the alkane, the ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue resulting from the evaporation of the ester under reduced pressure show the characteristic resonances of the dihydride-dicarbonyl derivative **3**. However, complex **3** is not the responsible species for the fast formation of the ester. In fact, complex **3** is also an active catalyst precursor for the reaction shown in eq 5, but its activity (92% yield after 22 h) is much lower than that of **1**. Furthermore, in the presence of **3** the formation of methylcyclohexanol, in about 5% yield, was also observed. The formation of **3** seems to be the result of the stoichiometric reaction of **1** with cyclohexanecarboxaldehyde at the end of the catalysis. The acetate complex **4** is also active for the Tishchenko dimerization of cyclohexanecarboxaldehyde. Its activity (76% yield after 22 h) is even lower than that of **3**.



(**5**)

The Tishchenko dimerization of cyclohexanecarboxaldehyde in the presence of **1** can be rationalized according to Scheme 3. The insertion of an aldehyde molecule into one of the Os−H bonds of the H_3-acyl intermediate shown in Scheme 1 should afford an acylalkoxy species, which could evolve by reductive elimina-

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[20] (a) Bernard, K. A.; Atwood, J. D. *Organometallics* **1988**, *7*, 235. (b) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795. (c) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063. (d) Mascarenhas, C. M.; Miller, S. P.; White, P. S.; Morken, J. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 601.

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[27] Onozawa, S.; Sakakura, T.; Tanaka, M.; Shiro, M. *Tetrahedron* **1996**, *52*, 4291.

[28] (a) Morita, K.-I.; Nishiyama, Y.; Ishii, Y. *Organometallics* **1993**, *12*, 3748. (b) Umekawa, Y.; Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1997**, *62*, 3409.

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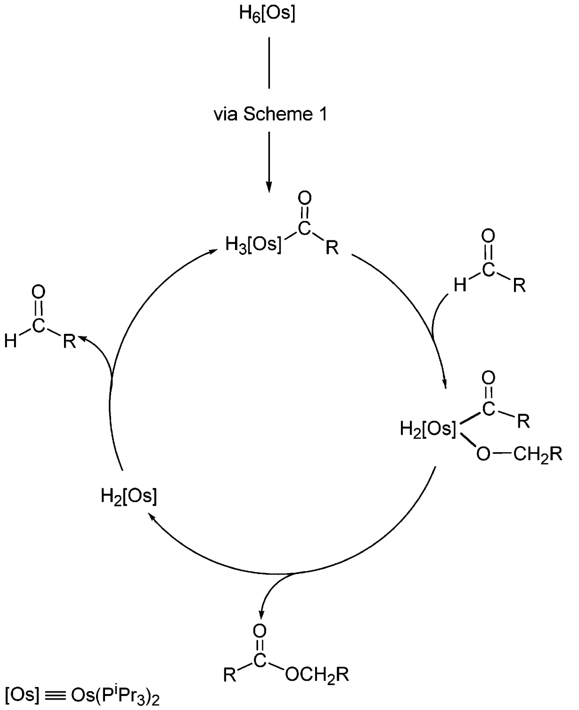
[30] Yamashita, M.; Ohishi, T. *Appl. Organomet. Chem.* **1993**, *7*, 357.

[31] Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*: VCH Publisher: New York, 1997; Chapter 3.

Scheme 3



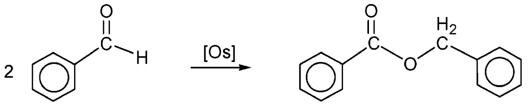
tion of ester to give a 14-electron $OsH_2(P^iPr_3)_2$ intermediate. The oxidative addition of the C−H$_\alpha$ bond of another molecule of aldehyde to this species should regenerate the key H_3-acyl intermediate.

Since complex **3** is a saturated species, and therefore initially inactive, it seems reasonable to think that its activation involves the dissociation of a carbonyl or/and phosphine group. Thus an unsaturated dihydride could catalyze the formation of the ester via osmium(II) and osmium(IV) intermediates (cycle A in Scheme 4). The lower activity of **3** in comparison with **1** can be related to the low tendency shown by the saturated osmium(II) complexes toward the dissociation of any ligand.[31]

According to cycle A, the dimerization of the aldehyde should also involve an acyl-alkoxy intermediate, similar to that shown in Scheme 3. However, the formation of traces of cyclohexanemethanol during the reaction carried out in the presence of **3** suggests that, in this case, the first molecule of aldehyde reacts to afford an alkoxy intermediate. In a subsequent step, this species could activate the C−H$_\alpha$ bond of a second molecule of aldehyde to give the acyl-alkoxy intermediate.

The reductive elimination of alcohol from the intermediate $(L_{n-1})OsH(OCH_2R)$ could afford an unsaturated $(L_{n-1})Os$ species, which should also catalyze the dimerization of the aldehyde by an alternative pathway involving osmium(0) and osmium(II) intermediates instead of osmium(II) and osmium(IV) species (cycle B in Scheme 4).

Complex **1** is also an active catalyst precursor for the dimerization of benzaldehyde (eq 6). However its stability under the reaction conditions is very low, and it rapidly undergoes deactivation. After 2, 24, and 75 h, the yields of the reaction are 8%, 18%, and 20%, respectively. The resulting species from the deactivation process is the hydride-phenyl derivative **2**. This is supported by the ^1H and $^{31}P\{^1H\}$ NMR spectra of the residue obtained from removing the volatiles of the catalytic mixture, after 24 h of reaction, which show the characteristic resonances of **2**, and by the fact that **2** is inactive for the Tishchenko dimerization of benzaldehyde. The transformation of **1** into **2** during the catalysis suggests that the deinsertion of the phenyl of the acyl group occurs at a rate comparable with the rate of insertion of benzaldehyde into an Os−H bond, and it agrees well with the null tendency shown by this aldehyde to be hydroxylated according to eq 3.

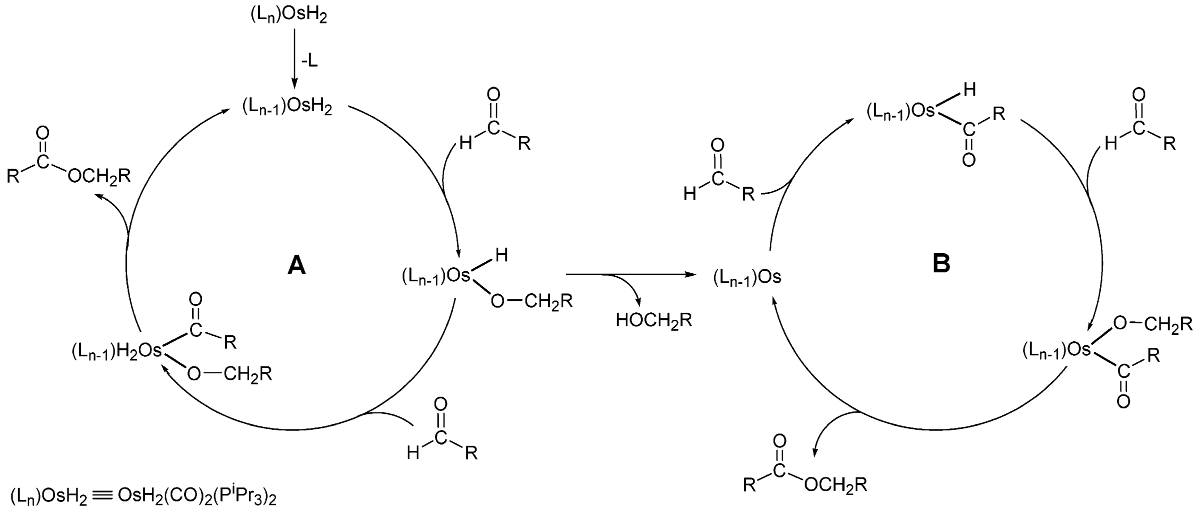


(**6**)

For the Tishchenko dimerization of benzaldehyde, the dihydride-dicarbonyl complex **3** is also a catalyst precursor less active than **1**. Thus after 50 h of reaction in the presence of **3**, the yield of the dimerization is only 10%. However, it is much more stable than **1** and does not undergo deactivation. The reaction shows a uniform rate for the formation of the ester, which becomes 92% after 141 h.

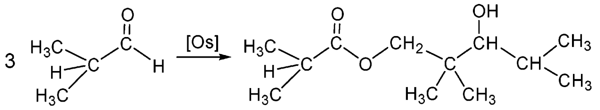
It should be noted that the dimerization of cyclohexanecarboxaldehyde is faster than the dimerization of

Scheme 4



benzaldehyde. This can be due to the fact that the insertion of cyclohexanecarboxaldehyde into an Os−H bond is favored with regard to the insertion of benzaldehyde. In this context, it should be mentioned that the formation of alcohol is not observed during the dimerization of benzaldehyde and that, in general, the catalytic reduction of cycloalkyl ketones is faster than the catalytic reduction of aromatic ketones.[32]

Complex **1** and **3** are also active catalyst precursors for the homo aldo-Tishchenko trimerization of isobutyraldehyde. The reactions lead selectively to (3-hydroxy-2,2,4-trimethylpentyl)-2-methylpropionate (eq 7).



(7)

In the presence of **3**, the reaction is slow, but the rate is uniform until the end. After 126 h the product is obtained in 100% yield, and the catalyst precursor can be recovered in high yield from the resulting solution, by removing the trimer under reduced pressure and subsequent addition of methanol.

In the presence of **1**, the reaction shows some significant differences. Initially an induction period of about 1 day is observed. Subsequently, the rate is uniform but lower than that with **3**. Thus, after 140 h, only 86% of product is formed. Attempts to identify the catalyst of the reaction were unsuccessful. From the catalytic solution, a complex mixture of metallic compounds was isolated. However, it does not contain either **1** or **3**.

The acetate complexes **5** and **6** are not active for the catalytic reactions shown in eqs 7 and 6, respectively.

Concluding Remarks

This study reveals that the short-lived dihydride-dihydrogen species $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$, generated by thermal activation of the hexahydride $OsH_6(P^iPr_3)_2$, activates the $C-H_\alpha$ bond of aromatic and alkyl aldehydes to afford short-lived acyl derivatives. These species are highly unstable and rapidly evolve to give different types of isolated compounds, depending upon the reaction conditions.

In the absence of water, the acyl intermediates undergo deinsertion of the R substituent (alkyl or phenyl) and subsequent reductive elimination of R−H. The resulting species are capable of promoting the activation−deinsertion tandem process of a second aldehyde molecule to give $OsH_2(CO)_2(P^iPr_3)_2$ (cyclohexanecarboxaldehyde and isobutyraldehyde) or $OsHPh(CO)_2(P^iPr_3)_2$ (benzaldehyde).

The deinsertion of R is faster for phenyl than for alkyl. Thus, while in the presence of water and the aldehyde, the acyl group of the short-lived Os-C(O)Ph species evolves into $OsHPh(CO)_2(P^iPr_3)_2$, and the acyl group of the Os-C(O)alkyl intermediates undergoes nucleophilic addition of water before the deinsertion. As a result, the corresponding carboxylic acid and the starting hexahydride are formed. The subsequent reaction between both leads finally to the trithydride-acetate derivatives $OsH_3(\kappa^2\text{-}O_2CR)(P^iPr_3)_2$ (R = Cy, $(CH_3)_2CH$).

The capacity shown by $OsH_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ to activate the $C-H_\alpha$ bond of aldehydes together with the presence of hydride ligands in the resulting addition product, which have the property of inserting a second aldehyde molecule, makes the hexahydride an active catalyst precursor for the classical Tishchenko dimerization of aldehydes. The stability of the catalyst precursor during the reaction is a function of the tendency of the R substituent of the acyl group of the Os-C(O)R intermediate to undergo deinsertion. Thus, while cyclohexanecarboxaldehyde can be rapidly converted into the ester dimer (90% yield after 10 min), and the transformation of the catalyst precursor into $OsH_2(CO)_2(P^iPr_3)_2$ occurs only at the end of the catalysis, benzaldehyde deactivates the catalyst precursor to give $OsHPh(CO)_2(P^iPr_3)_2$ during the first cycles of the catalysis.

In conclusion, the reactions of transition metal polyhydrides with aldehydes should merit more attention than that given until now. They afford short-lived hydride-acyl species, which are the key to prepare several types of complexes and to generate catalytic processes.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $OsH_6(P^iPr_3)_2$[32b] and $OsH_2(CO)_2(P^iPr_3)_2$[33] were prepared by published methods. Commercial aldehydes were freshly distilled over 4 Å molecular sieves.

^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300, a Varian Gemini 2000, or a Bruker AXR 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants, J and N ($N = J_{P-H} + J_{P'-H}$ for ^1H and $N = J_{P-C} + J_{P'-C}$ for $^{13}C\{^1H\}$) are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer as solids (KBr pellet). C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. For the organometallic compounds, mass spectral analyses were performed with a VG Austospec instrument. In FAB^+ mode, ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix. For the organic products of the catalytic reactions, GC−MS analyses were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min, 35 to 280 °C at 25 °C/min, 280 °C for 4 min. The carrier gas was helium at a flow rate of 1 mL/min.

Kinetic Analysis. Complete line-shape analysis of the $^1H\{^{31}P\}$ NMR spectra of complexes **4**, **5**, and **6** was achieved using the program gNMR (Cherwell Scientific Publishing Limited). The rate constants for various temperatures were obtained by fitting calculated to experimental spectra by full line-shape iterations. The transverse relaxation time, T_2, was estimated at the lowest interval of temperatures using the resonances corresponding to the hydride ligands. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated by least-squares fit of $\ln(k_1/T)$ versus $1/T$ (Eyring equation). Error analysis assumed a

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10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.[34]

Reaction of $OsH_6(P^iPr_3)_2$ with Benzaldehyde. A colorless solution of **1** (212.6 mg, 0.411 mmol) in 15 mL of toluene was treated with 2.0 equiv of benzaldehyde (84 μL, 0.826 mmol) and heated under reflux for 5 h. An analysis of the resulting solution by chromatography revealed the presence of benzene. The pale yellow solution obtained was filtered through Celite and dried in vacuo. Methanol was added to afford the complex $OsHPh(CO)_2(P^iPr_3)_2$ as a white solid, which was washed with further portions of methanol and dried in vacuo. Data for $OsHPh(CO)_2(P^iPr_3)_2$ (**2**): Yield: 218.4 mg (82%). Anal. Calcd for $C_{26}H_{48}O_2OsP_2$: C 48.43, H 7.50. Found: C 47.97, H 7.31. IR (KBr, cm^{-1}): ν(OsH) 2016 (s), ν(CO) 1959 (s), 1887 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.26 and 8.11 (both m, 1H, *o*-Ph), 7.1−6.9 (both m, 1H, *m*-Ph), 7.00 (m, 1H, *p*-Ph), 1.97 (m, 6H, PC*H*), 1.11 and 1.09 (both dvt, N = 14.1 Hz, J_{H-H} = 7.3 Hz, 18H, PCHCH_3), −6.59 (t, J_{H-P} = 22.1 Hz. 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 22.0 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 191.4 (t, J_{P-C} = 5.8 Hz, CO), 185.6 (t, J_{P-C} = 8.5 Hz, CO), 150.4 (s, Ph), 147.0 (t, J_{P-C} = 10.6 Hz, $C_{ipso(Ph)}$), 145.7, 127.1, 126.9, and 121.9 (all s, Ph), 26.3 (vt, N = 13.9 Hz, P*C*H), 19.5 and 19.2 (both s, PCH*C*H_3). MS (FAB$^+$): *m*/*z* 645 (M^+ − H).

Reaction of $OsH_6(P^iPr_3)_2$ with Cyclohexanecarboxaldehyde. A colorless solution of **1** (150.0 mg, 0.290 mmol) in 15 mL of toluene was treated with 2.0 equiv of cyclohexanecarboxaldehyde (70 μL, 0.578 mmol) and heated under reflux for 5 h. An analysis of the resulting solution by chromatography revealed the presence of cyclohexane. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol at 243 K was added to afford the complex $OsH_2(CO)_2(P^iPr_3)_2$ (**3**) as a white solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 125.3 mg (76%). Data for *cis*,*cis*,*trans*-$OsH_2(CO)_2(P^iPr_3)_2$ (**3**) (in agreement with the previously reported data):[10] ^1H NMR (300 MHz, C_6D_6, 293 K): δ 1.99 (m, 6H, PC*H*), 1.14 (dvt, N = 13.7 Hz, J_{H-H} = 7.1 Hz, 18H, PCHCH_3), −9.59 (t, J_{H-P} = 22.1 Hz, 2H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 41.9 (s).

Reaction of $OsH_6(P^iPr_3)_2$ with Isobutyraldehyde. A colorless solution of **1** (150.0 mg, 0.290 mmol) in 15 mL of toluene was treated with 2.0 equiv of isobutyraldehyde (53 μL, 0.583 mmol) and heated under reflux for 5 h. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol at 243 K was added to afford the complex $OsH_2(CO)_2(P^iPr_3)_2$ (**3**) as a white solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 102.3 mg (62%).

Reaction of $OsH_6(P^iPr_3)_2$ with Cyclohexanecarboxaldehyde in the Presence of Water. A colorless solution of **1** (185.5 mg, 0.359 mmol) in 15 mL of toluene was treated with cyclohexanecarboxaldehyde (56 μL, 0.462 mmol) and water (0.25 mL, 0.014 mol) and heated under reflux for 5 h. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol at 243 K was added to afford the complex $OsH_3(\kappa^2\text{-}O_2CCy)(P^iPr_3)_2$ (**4**) as a yellow solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 147.3 mg (64%). Data for $OsH_3(\kappa^2\text{-}O_2CCy)(P^iPr_3)_2$ (**4**): Anal. Calcd for $C_{25}H_{56}O_2OsP_2$: C 46.85, H 8.81. Found: C 47.01, H 8.73. IR (KBr, cm^{-1}): ν(OsH) 2156 (s), 2142 (s); ν_{asym}(OCO) 1524 (s), ν_{sym}(OCO) 1447 (s). ^1H NMR (300 MHz, C_7D_8, 293 K): δ 2.3−1.0 (all s, 11H, Cy), 1.99 (m, 6H, PC*H*), 1.24 (dvt, N = 12.7 Hz, J_{H-H} = 6.5 Hz, 36H, PCHCH_3), −14.51 (t, J_{H-P} = 11.8 Hz 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, C_7D_8, 203 K, high-field region (OsH_3 unit)): AB_2 spin system, δ_A −14.33, δ_B −14.52, J_{A-B} = 18.03 Hz. $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 40.7 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 185.7 (t, J_{P-C} = 1.4 Hz, OCO), 47.1 (s, CH_{Cy}), 28.9 (s, $CH_{2(Cy)}$), 26.7 (vt, N = 23.9 Hz, P*C*H), 26.2 (s, *p*-$CH_{2(Cy)}$), 25.9 (s, $CH_{2(Cy)}$), 20.3 (s, PCH*C*H_3). MS (FAB$^+$): *m*/*z* 640 (M^+ − 2H). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 220 K): 74 ± 2 (−14.51 ppm, 3H).

Reaction of $OsH_6(P^iPr_3)_2$ with Isobutyraldehyde in the Presence of Water. A colorless solution of **1** (157.0 mg, 0.304 mmol) in 15 mL of toluene was treated with isobutyraldehyde (33 μL, 0.363 mmol) and water (0.25 mL, 0.014 mol) and heated under reflux for 5 h. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol at 243 K was added to afford the complex $OsH_3(\kappa^2\text{-}O_2CCH(CH_3)_2)(P^iPr_3)_2$ (**5**) as a yellow solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 113.1 mg (62%). Data for $OsH_3(\kappa^2\text{-}O_2CCH(CH_3)_2)(P^iPr_3)_2$ (**5**): Anal. Calcd for $C_{22}H_{52}O_2OsP_2$: C 43.98, H 8.72. Found: C 43.65, H 9.07. IR (KBr, cm^{-1}): ν(OsH) 2159 (s), 2144 (s); ν_{asym}(OCO) 1534 (s), ν_{sym}(OCO) 1484 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 2.24 (sept, J_{H-H} = 6.9 Hz, 1H, CH), 2.02 (m, 6H, PC*H*), 1.17 (dvt, N = 12.9 Hz, J_{H-H} = 6.9 Hz, 36H, PCHCH_3), 1.08 (d, J_{H-H} = 6.9 Hz, 6H, C(CH_3)$_2$), −14.97 (t, J_{H-P} = 11.7 Hz. 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 203 K, high-field region (OsH_3 unit)): AB_2 spin system, δ_A = −14.76, δ_B = −15.27, J_{A-B} = 20.7 Hz. $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 40.5 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 186.3 (t, J_{C-P} = 1.2 Hz, OCO), 37.7 (s, CH), 26.9 (vt, N = 23.5 Hz, P*C*H), 20.4 (s, PCH*C*H_3), 18.6 (s, C(*C*H_3)$_2$). MS (FAB$^+$): *m*/*z* 598 (M^+ − 4H). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 220 K): 82 ± 1 (−14.76 ppm, 3H).

Reaction of $OsH_6(P^iPr_3)_2$ with Cyclohexanecarboxylic Acid. A colorless solution of **1** (185.5 mg, 0.359 mmol) in 15 mL of toluene was treated with 1.0 equiv of cyclohexanecarboxylic acid (45 μL, 0.363 mmol) and heated under reflux for 5 h. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol at 243 K was added to afford the complex $OsH_3(\kappa^2\text{-}O_2CCy)(P^iPr_3)_2$ (**4**) as a yellow solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 176.0 mg (77%).

Reaction of $OsH_6(P^iPr_3)_2$ with Isobutyric Acid. A colorless solution of **1** (157.0 mg, 0.304 mmol) in 15 mL of toluene was treated with isobutyric acid (34 μL, 0.367 mmol) and heated under reflux for 5 h. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol at 243 K was added to afford the complex $OsH_3(\kappa^2\text{-}O_2CCH(CH_3)_2)(P^iPr_3)_2$ (**5**) as a yellow solid, which was washed with further portions of cold methanol and dried in vacuo. Yield: 155.1 mg (85%).

Reaction of $OsH_6(P^iPr_3)_2$ with Benzoic Acid. A colorless solution of **1** (304.2 mg, 0.589 mmol) in 15 mL of toluene was treated with benzoic acid (75.4 mg, 0.617 mmol) and heated under reflux for 5 h. The yellow solution obtained was filtered through Celite and dried in vacuo. Methanol was added to afford the complex $OsH_3(\kappa^2\text{-}O_2CPh)(P^iPr_3)_2$ as a yellow solid, which was washed with further portions of methanol and dried in vacuo. Yield: 292.3 mg (78%). Data for $OsH_3(\kappa^2\text{-}O_2CPh)(P^iPr_3)_2$ (**6**): Anal. Calcd for $C_{25}H_{50}O_2OsP_2$: C 47.30, H 7.94. Found: C 47.24, H 8.02. IR (KBr, cm^{-1}): ν(OsH) 2160 (s), 2140 (s); ν_{asym}(OCO) 1525 (s), ν_{sym}(OCO) 1465 (s). ^1H NMR (300 MHz, C_7D_8, 293 K): δ 8.24 (m, 2H, *o*-Ph), 7.11 (m, 1H, *p*-Ph), 7.09 (m, 2H, *m*-Ph), 1.95 (m, 6H, PC*H*), 1.21 (dvt, N = 12.6 Hz, J_{H-H} = 6.9 Hz, 36H, PCHCH_3), −14.38 (t, J_{H-P} = 11.6 Hz. 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, C_7D_8, 193 K, high-field region (OsH_3 unit)): AB_2 spin system, δ_A = −14.03, δ_B = −14.37, J_{A-B} = 22.04 H. $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 40.2 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 176.2 (s, OCO), 135.4 (s, $C_{ipso(Ph)}$), 131.5, 128.3, and 128.2 (all s, Ph), 26.9 (vt, N = 24.1 Hz, P*C*H), 20.4 (s, PCH*C*H_3). MS (FAB$^+$): *m*/*z* 634 (M^+ − 2H). $T_{1(min)}$ (ms, OsH_3, 300 MHz, C_7D_8, 218 K): 68 ± 3 (−14.17 ppm, 1H), 78 ± 2 (−14.46 ppm, 2H).

General Procedure for the Tishchenko Reaction. The freshly distilled aldehyde was added at room temperature into the Schlenk tube containing catalyst (100:1 catalyst:aldehyde molar ratio). The reactions were carried out under reflux either

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[34] Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

in the aldehyde (cyclohexanecarboxaldehyde and benzaldehyde) or in toluene (isobutyraldehyde). The reactions were monitored by GS–MS. The products were identified by comparison of their mass spectra with those of the G1045B Spectral Library (Willey 7N, Agilent Technologies, 2000). In addition (3-hydroxy-2,2,4-trimethylpentyl)-2-methylpropionate was characterized by mass spectrum ($m/z = 217$ (M^+)) and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. ^1H NMR (300 MHz, $CDCl_3$, 293 K): AB spin system, δ 3.88 ($\Delta\nu = 97.8$ Hz, $J_{A-B} = 11.1$ Hz, 2H, CH_2), 3.19 (dd, $J_{H-H} = 6.3$ Hz, $J_{H-H} = 2.1$ Hz, 1H, C*H*OH), 2.52 (sept, $J_{H-H} = 6.9$ Hz, 1H, C(O)C*H*($CH_3)_2$), 2.18 (d, $J_{H-H} = 6.3$ Hz, 1H, OH), 1.85 (double sept, $J_{H-H} = 6.9$ Hz, $J_{H-H} = 2.1$ Hz, 1H, CH(OH)C*H*), 1.12 (d, $J_{H-H} = 6.9$ Hz, 6H, C(O)CH($CH_3)_2$), 0.96 (s, 3H, $CH_2C(CH_3)_2$), 0.92 (d, $J_{H-H} = 6.9$ Hz, 3H, CH(OH)CH($CH_3)_2$), 0.90 (s, 3H, $CH_2C(CH_3)_2$), 0.87 (d, $J_{H-H} = 6.9$ Hz, 3H, CH(OH)CH($CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K): δ 177.2 (C═O), 79.0 (CH(OH)), 71.1 (CH_2), 39.0, 33.8, and 28.3 (all s, *C*($CH_3)_2$), 23.2, 21.8, 19.3, 18.9, 18.7, 16.4 (CH_3).

When the reactions were stopped, the resulting solutions were concentrated in vacuo and the residues were analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The observed organometallic complexes are indicated below.

Cyclohexanecarboxaldehyde. When $OsH_6(P^iPr_3)_2$ or $OsH_2(CO)_2(P^iPr_3)_2$ was used as catalyst, only $OsH_2(CO)_2(P^iPr_3)_2$ was observed.

Benzaldehyde. When $OsH_6(P^iPr_3)_2$ was used as catalyst, $OsHPh(CO)_2(P^iPr_3)_2$ was formed.

Isobutyraldehyde. When $OsH_6(P^iPr_3)_2$ was used as catalyst, a complex mixture of unidentified metallic compounds was obtained. When $OsH_2(CO)_2(P^iPr_3)_2$ was used as catalyst, this complex was observed as the unique organometallic compound at the end of the reaction, and it could be recovered by precipitation with methanol.

X-ray Analysis of 5. An irregular crystal of size 0.16 × 0.14 × 0.02 mm (**5**) was mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K 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 was 10 s covering 0.3° in ω. The cell parameters were determined and refined by least-squares fit of 941 collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS[35] program. Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL[36] program package minimizing $w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were anisotropically refined. The hydrogen atoms were observed or calculated and refined riding on the bonded carbon atoms. The hydride ligands were observed in the difference Fourier maps and refined freely with a common thermal parameter. Weighted R factors (R_w) and goodness of fit (S) are based on F^2; conventional R factors are based on F. Crystal data and details of the data collection and refinement are given in Table 3.

Table 3. Crystal Data and Data Collection and Refinement for $OsH_3[\kappa^2\text{-}O_2CCH(CH_3)_2](P^iPr_3)_2$ (5)

Crystal Data	
formula	$C_{22}H_{52}O_2OsP_2$
molecular wt	600.78
color and habit	light yellow, plate
symmetry, space group	monoclinic, $P2_1/n$
a, Å	16.107(3)
b, Å	8.9282(15)
c, Å	20.093(3)
β, deg	112.585(2)
V, Å^3	2667.8(8)
Z	4
D_{calc}, g cm^{-3}	1.496
Data Collection and Refinement	
diffractometer	Bruker Smart APEX
λ(Mo Kα), Å	0.71073
monochromator	graphite oriented
scan type	ω scans
μ, mm^{-1}	4.913
2θ, range deg	3, 56
temp, K	100
no. of data collect	26 977
no. of unique data	6350 (R_{int}= 0.0486)
no. of params/restraints	268/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0246
wR_2[b] [all data]	0.0389
S[c] [all data]	0.735

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

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

OM034389L

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