# Reactions of a Dihydride−Osmium(IV) Complex with Aldehydes: Influence of the Substituent at the Carbonyl Group

Miguel A. Esteruelas,* Yohar A. Hernández, Ana M. López,* Montserrat Oliván, and Lucía Rubio

*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza−CSIC, 50009 Zaragoza, Spain*

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*Summary: The reactivity of the dihydride−acetone complex [OsH$_2$($\eta^5$-C$_5$H$_5$)($\kappa^1$-OCMe$_2$)(P$^i$Pr$_3$)]BF$_4$ (**1**) toward cinnamaldehyde, isovaleraldehyde, and benzaldehyde has been investigated. In addition to the reduction of the aldehydes, three different reaction patterns have been observed, which depend on the alkenyl, alkyl, and aryl nature of the substituent at the carbonyl group. As a result, the complexes [Os($\eta^5$-C$_5$H$_5$)(CO)($\eta^2$-PhCH=CH$_2$)(P$^i$Pr$_3$)]BF$_4$ (**2**), [Os($\eta^5$-C$_5$H$_5$)(CO)$_2$(P$^i$Pr$_3$)]BF$_4$ (**3**), and [OsH($\eta^5$-C$_5$H$_5$){C$_6$H$_4$C(O)H}(P$^i$Pr$_3$)]BF$_4$ (**6**) have been isolated and characterized, including the X-ray structure of **2**.*

The characteristic chemical reactions of an organic compound are determined by an specific moiety within the molecule. Those parts of the compound attached to this core have influence in the reactivity of the compound but play a secondary role. Transition-metal elements have the remarkable ability to enhance the reactivity of some parts of the organic molecules and to inhibit the reactions of others. A crucial consequence of this ability is the dramatic increase of the influence of the substituents in the reactions of the organic compounds with the transition-metal complexes. An attractive illustration may be found in the reactions of the dihydride−solvento complex [OsH$_2$($\eta^5$-C$_5$H$_5$)($\kappa^1$-OCMe$_2$)(P$^i$Pr$_3$)]BF$_4$ (**1**) with alkynes.[1]

The reactions of **1** with 1-phenyl-1-propyne and 2-butyne give rise to $\gamma$-($\eta^3$-allyl)-$\alpha$-alkenylphosphine [OsH($\eta^5$-C$_5$H$_5$){$\kappa^4$*P*,*C*,*C*,*C*-CH$_2$C[CH$_2$C(=CH$_2$)P$^i$Pr$_2$]CHR}]BF$_4$ (R = Ph, CH$_3$) derivatives.[1a] On the other hand, phenylacetylene leads to the allenylcarbene [Os($\eta^5$-C$_5$H$_5$){=CPh($\eta^2$-CH=C=CHPh)}(P$^i$Pr$_3$)]BF$_4$.[1b] Although both processes take place through the same type of key intermediate, $\pi$-alkyne species [Os($\eta^5$-C$_5$H$_5$)($\eta^2$-R′C≡CR″)(P$^i$Pr$_3$)]BF$_4$,[2] the trend of phenylacetylene to generate vinylidene complexes[3] determinates the difference in behavior between the terminal and internal alkynes. While 1-phenyl-1-propyne and 2-butyne promote the dehydrogenation of an isopropyl group of the phosphine to afford an isopropenyl substituent,[4] which leads to the $\gamma$-($\eta^3$-allyl)-$\alpha$-alkenylphosphine via an ene-type reaction with a new alkyne molecule,[1a] the vinylidene resulting from the tautomerization of phenylacetylene undergoes a [2 + 2] cycloaddition with the new alkyne molecule to give the allenylcarbene ligand.[1b]

Complex **1** also reduces $\alpha,\beta$-unsaturated and aromatic ketones.[5] The reactions afford [Os($\eta^5$-C$_5$H$_5$)(P$^i$Pr$_3$)]BF$_4$. Although this metal fragment activates a C$_\beta$(sp$^2$)−H bond of both types of molecules, the exclusive activation of the olefinic bond is observed in substrates containing both olefinic and aromatic substituents at the carbonyl group.

Aldehydes are ketone counterparts with the carbonyl group bonded to a hydrogen atom. The activation of this OC−H bond is a reaction of great interest, due to its connection with the decarbonylation of these substrates[6] and by its importance in organometallic[7] and organic synthesis.[8] Our interest in understanding the influence of the substituents in the reactions of the organic molecules with transition-metal complexes, in particular hydride derivatives,[9] prompted us to investigate the reactions of **1** with cinnamaldehyde, isovaleraldehyde, and benzaldehyde (Scheme 1).

Treatment of **1** with 3.0 equiv of cinnamaldehyde in dichloromethane at 50 °C for 24 h gives rise to the reduction of the C−C double bond of 1 equiv of aldehyde and the formation of

* To whom correspondence should be addressed. E-mail: maester@unizar.es (M.A.E.); amlopez@unizar.es (A.M.L.).

(1) (a) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 2193. (b) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oñate, E. *Organometallics* **2007**, *26*, 6009.

(2) Carbó, J. J.; Crochet, P.; Esteruelas, M. A.; Jean, Y.; Lledós, A.; López, A. M.; Oñate, E. *Organometallics* **2002**, *21*, 305.

(3) (a) Esteruelas, M. A.; López, A. M. *Organometallics* **2005**, *24*, 3584. (b) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev.* **2007**, *251*, 795.

(4) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1416.

(5) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989.

(6) See for example: (a) Beck, C. M.; Rathmill, S. E.; Park, Y. J.; Chen, J.; Crabtree, R. H.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5311. (b) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248. (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. (e) Cordaro, J. G.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 3432. (f) Graham, P. M.; Mocella, C. J.; Sabat, M.; Harman, W. D. *Organometallics* **2005**, *24*, 911. (g) Kreis, M.; Palmelund, A.; Bunch, L.; Madsen, R. *Adv. Synth. Catal.* **2006**, *348*, 2148. (h) Lee, J. P; Pittard, K. A.; DeYonker, N. J.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2006**, *25*, 1500.

(7) See for example: (a) Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R. *Organometallics* **2003**, *22*, 3600. (b) Corkey, B. K.; Taw, F. L.; Bergman, R. G.; Brookhart, M. *Polyhedron* **2004**, *23*, 2943. (c) Garralda, M. A.; Hernández, R.; Ibarlucea, L.; Pinilla, E.; Torres, M. R.; Zarandona, M. *Organometallics* **2007**, *26*, 1031. (d) Song, X.; Chan, K. S. *Organometallics* **2007**, *26*, 965. (e) Chan, K. S.; Lau, C. M.; Yeung, S. K.; Lai, T. H. *Organometallics* **2007**, *26*, 1981.

(8) See for example: (a) Jun, C.-H.; Jo, E.-A.; Park, J.-W. *Eur. J. Org. Chem.* **2007**, 1869. (b) Lantos, D.; Contel, M.; Sanz, S.; Bodor, A.; Horváth, I. T. *J. Organomet. Chem.* **2007**, *692*, 1799. (c) Wile, B. M.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2007**, *26*, 1069. (d) Roy, A. H.; Lenges, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 2082.

(9) See for example: (a) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Tomàs, J. *Organometallics* **2001**, *20*, 442. (b) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2635. (c) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 2491. (d) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2003**, *22*, 2472. (e) Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E.; Tajada, M. A.; Ujaque, G. *Organometallics* **2003**, *22*, 3753. (f) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627. (g) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428.

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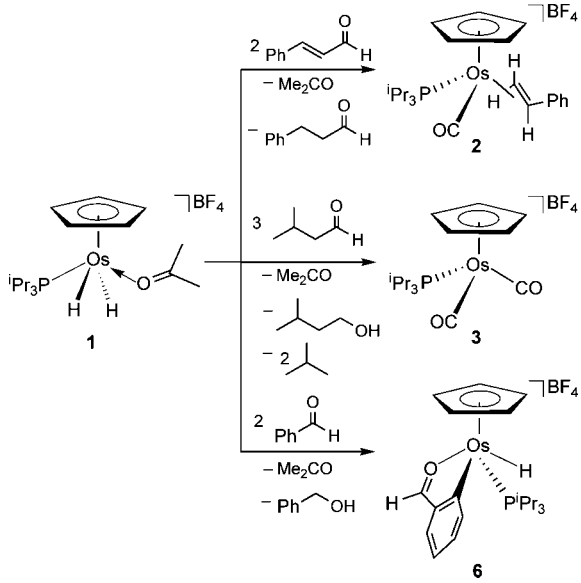
**Scheme 1**




the carbonyl-$\pi$-styrene derivative $[Os(\eta^5\text{-}C_5H_5)(CO)(\eta^2\text{-}Ph\text{-}CH{=}CH_2)(P^iPr_3)]BF_4$ (**2**), which is isolated as a beige solid in 84% yield.

As a consequence of the chirality of the osmium atom and the prochirality of the olefin, four pairs of diastereoisomers could be formed: *C*Ph carbon atom cisoid to the phosphine with the phenyl group toward or away from the osmium atom and *C*Ph carbon atom cisoid to the carbonyl ligand with the phenyl group toward or away from the osmium atom. However, only the pair with the lowest steric hindrance is obtained, suggesting a thermodynamic control of the reaction. Figure 1 shows a view of the structure of one of the enantiomers of the obtained pair. The geometry around the metal center is close to octahedral, with the cyclopentadienyl group occupying three sites of a face and the *C*Ph carbon atom C(2) cisoid to the carbonyl ligand with the phenyl ring away from the metal center. The Os−styrene coordination exhibits Os−C(1) and Os−C(2) bond lengths of 2.167(8) and 2.214(7) Å, respectively, which agree well with those found in other osmium−olefin complexes (between 2.13 and 2.28 Å).[10]Similarly, the olefin bond distance C(1)−C(2) of 1.404(10) Å is within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).[11]

In agreement with the presence of a carbonyl ligand in **2**, its IR in Nujol contains a $\nu$(CO) band at 1973 $cm^{-1}$. In the $^1H$

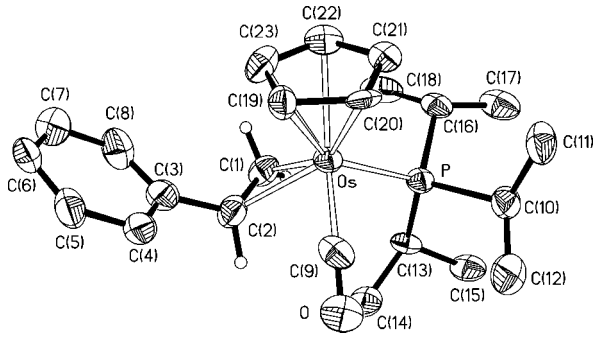
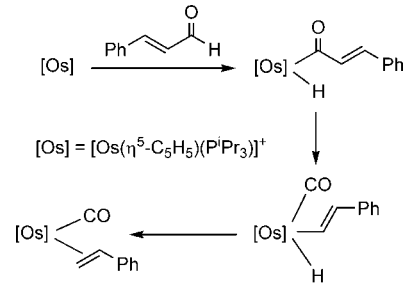



**Figure 1.** Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−P = 2.374(2), Os−C(1) = 2.167(8), Os−C(2) = 2.214(7), Os−C(9) = 1.822(9), C(1)−C(2) = 1.404(10), C(9)−O = 1.199(9); C(1)−Os−P = 87.2(2), C(1)−Os−C(9) = 104.0(3), C(2)−O−P = 111.8(2), C(2)−Os−C(9) = 76.5(3), C(1)−Os−C(2) = 37.4(3), C(9)−Os−P = 89.5(2).

**Scheme 2**




NMR spectrum in dichloromethane-$d_2$ at room temperature the resonances corresponding to the vinylic protons are observed at 4.90, 3.91, and 2.85 ppm, whereas in the $^{13}C\{^1H\}$ NMR spectrum the resonances due to the coordinated carbon atoms of the olefin appear at 56.4 (CHPh) and 19.9 ($CH_2$) ppm.

The formation of **2** can be rationalized as an OC−H bond activation−decarbonylation *tandem* process (Scheme 2). The reduction of the C−C double bond of an aldehyde molecule should afford the 14-valence-electron species $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$, which could selectively activate the OC−H bond of a second aldehyde in the presence of the olefinic group. In this context, it should be noted that the OC−H bond of an aldehyde is about 19 kcal $mol^{-1}$ weaker than the C−H bond of an alkenyl group. The resulting hydride−acyl species could evolve into **2** by deinsertion of the styryl substituent of the acyl ligand and subsequent reductive elimination of styrene.

The substituent at the OC−H unit has a marked influence on the nature of the resulting products of the reactions of **1** with aldehydes. In contrast to cinnamaldehyde, isovaleraldehyde gives the dicarbonyl complex $[Os(\eta^5\text{-}C_5H_5)(CO)_2(P^iPr_3)]BF_4$ (**3**) in addition to 3-methyl-1-butanol and isobutane (Scheme 1). Its formation can be rationalized as a double OC−H bond activation−decarbonylation *tandem* process (Scheme 3), which takes place via two acyl intermediates through elemental steps similar to those shown in Scheme 2. The stronger coordination power of styrene with regard to isobutane explains the observed differences between the reactions of cinnamaldehyde and isovaleraldehyde.

Complex **3** is isolated as a beige solid in 73% yield. The most noticeable spectroscopic feature of this compound is the presence of two $\nu$(CO) bands at 2033 and 1968 $cm^{-1}$ in the IR spectrum.

1,3-Hydrogen shifts from the metal center to the oxygen atom in hydride−acyl complexes afford hydroxycarbene tautomers.[12] The equilibrium between both species has been studied in some cases.[13] The substituent at the carbonyl group of the aldehyde also appears to have a marked influence on the stability of the hydroxycarbene form in this case. Thus, while only **1** and **2** are observed by NMR spectroscopy during the reaction with cinnamaldehyde, the alkoxycarbene derivatives $[OsH_2(\eta^5\text{-}$

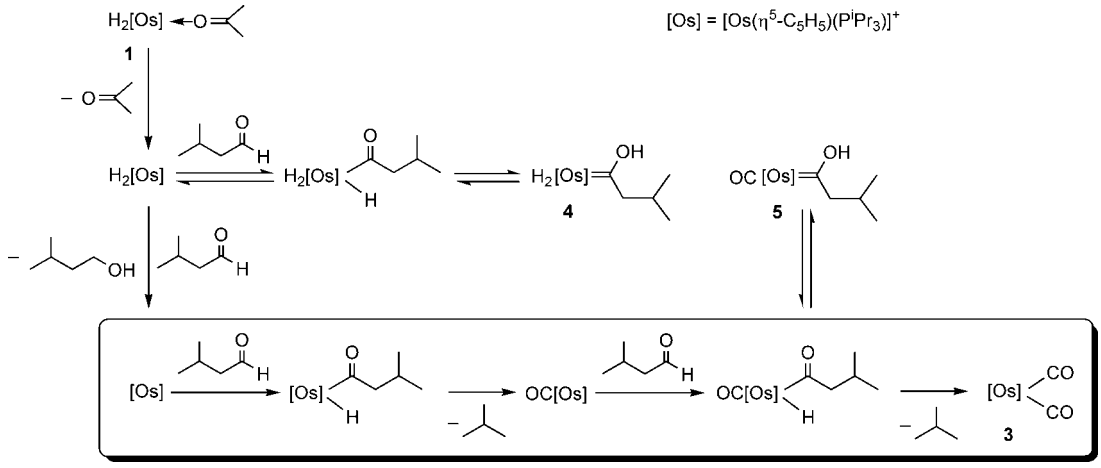
(10) (a) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2002**, *21*, 5681. (b) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2003**, *22*, 414. (c) Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oliván, M.; Oñate, E.; Tajada, M. A.; Tomàs, J. *Organometallics* **2003**, *22*, 2087. (d) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 2030. (e) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596. (f) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Inorg. Chem.* **2006**, *45*, 10162.

(11) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

(12) Kunz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3405.

(13) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971.

**Scheme 3**




$C_5H_5)\{=C(OH)CH_2CH(CH_3)_2\}(P^iPr_3)]BF_4$ (**4**) and $[Os(\eta^5$-$C_5H_5)\{=C(OH)CH_2CH(CH_3)_2\}(CO)(P^iPr_3)]BF_4$ (**5**) were detected and spectroscopically characterized for the reaction with isovaleraldehyde. Complex **4** (Scheme 3) is the result of the oxidative addition of the OC−H bond of the aldehyde to the unsaturated species $[OsH_2(\eta^5$-$C_5H_5)(P^iPr_3)]^+$, generated by dissociation of acetone from **1**, and the subsequent migration of a hydride ligand from the metal center to the oxygen atom of the acyl group. Complex **5** is produced by a similar pathway starting from the 16-valence-electron monocarbonyl intermediate $[Os(\eta^5$-$C_5H_5)(CO)(P^iPr_3)]^+$, which is generated from the reduction of an aldehyde molecule and the decarbonylation of another. Both **4** and **5** are products of kinetic control, which do not play any significant role in the decarbonylation process. In this context, it should be mentioned that hydroxycarbene species have been detected as reactive intermediates in the reactions of $C_\alpha-C_\beta$ bonds of allenylidene[14] and alkynyl[15] groups with water to give carbonyl ligands and alkene and alkane, respectively. However, the key steps for the $C_\alpha-C_\beta$ bond cleavage are the hydroxycarbene−hydride acyl tautomerization and the deinsertion of the substituent at the carbonyl group of the acyl ligand.[14,15]

In the $^1H$ NMR spectrum of **4** the most noticeable resonance of the hydroxycarbene ligand is that corresponding to the OH proton, which is observed at 13.48 ppm as a broad singlet. In the high-field region of the spectrum, the hydride ligands give rise to a doublet ($J_{HP}$ = 32.7 Hz) at −10.16 ppm. The presence of two hydrogen atoms bonded to the metal is supported not only by the $^1H$ NMR spectrum but also by the $^{31}P\{^1H\}$ NMR spectrum, which shows a singlet at 40.6 ppm that under off-resonance conditions is split into a triplet. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the $C_\alpha$ atom of the hydroxycarbene ligand appears at 280.5 ppm. Characteristic resonances of the hydroxycarbene ligand of **5** are a broad singlet at 12.80 ppm due to the OH proton in the $^1H$ NMR spectrum and a doublet ($J_{CP}$ = 7 Hz) at 278.8 ppm, corresponding to the $C_\alpha$ atom in the $^{13}C\{^1H\}$ NMR spectrum. The carbonyl ligand gives rise to a doublet ($J_{CP}$ = 10 Hz) at 182.5 ppm in the latter spectrum.

In contrast to the reactions with cinnamaldehyde and isovaleraldehyde, the treatment of dichloromethane solutions of **1** with 3.0 equiv of benzaldehyde leads to benzyl alcohol and the orthometalated derivative $[Os(\eta^5$-$C_5H_5)(CO)\{C_6H_4C(O)H\}(P^iPr_3)]BF_4$ (**6**), which is isolated as a yellow solid in 74% yield.

The $^1H$ NMR spectrum of **6** is consistent with a four-legged piano-stool structure with the hydride cisoid to the triisopropylphosphine ligand. Thus, it shows at −13.74 ppm a doublet with a H−P coupling constant of 32.1 Hz, which is a typical value for this arrangement.[16] The OC−H resonance is observed at 9.40 ppm as a singlet. The $^{13}C\{^1H\}$ NMR spectrum supports the formation of the heterometallacycle and the transoid disposition of the metalated carbon atom and the phosphine ligand.[5,16] In agreement with the coordination of the oxygen atom of the aldehyde to the metal, the resonance due to the OC carbon appears as a doublet ($J_{CP}$ = 2 Hz) at 211.6 ppm. The signal corresponding to the metalated atom of the phenyl group is observed at 184.2 ppm also as a doublet ($J_{CP}$ = 3 Hz). The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 28.0 ppm, which is split into a doublet under off-resonance conditions.

Complex **6** is a result of the reduction of 1 equiv of aldehyde and the subsequent *o*-CH addition of the phenyl substituent of a second aldehyde molecule to the resulting 14-valence-electron fragment $[Os(\eta^5$-$C_5H_5)(P^iPr_3)]^+$. The behavior of **1** agrees well with that observed for the trihydride $OsH_3(SnPh_2Cl)\{\kappa^3P,C,C$-$[CH_2{=}C(CH_3)]P^iPr_2\}(P^iPr_3)$, which also reacts with aromatic aldehydes to form ortho-metalated species.[17] However, it is in contrast with that reported for the hexahydride $OsH_6(P^iPr_3)_2$, which upon treatment with benzaldehyde affords the hydride−phenyl−dicarbonyl complex $OsHPh(CO)_2(P^iPr_3)_2$.[18]

The OC−H bonds are about 23 kcal mol$^{-1}$ weaker than the C−H bonds of a phenyl group. This could be one of the reasons why the *o*-CH bond activation of aromatic aldehydes has been rarely observed.[19] According to a recent density functional study on the *o*-CH addition of benzaldehyde to the 14-valence-electron

(14) See for example: Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (b) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2005**, *347*, 393. (c) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2007**, *349*, 933.

(15) Buil, M. L.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **1997**, *16*, 3169.

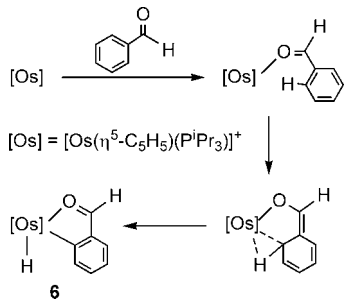
(16) See for example: Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275. (b) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*, 2585. (c) Baya, M.; Crochet, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 240. (d) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (e) Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2004**, *23*, 4858.

(17) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2004**, *23*, 6015.

(18) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1340.

(19) (a) Robinson, N. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *349*, 209. (b) Cambie, R. C.; Metzler, M. R.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1990**, *398*, C22. (c) Kakiuchi, F.; Sato, T.; Igi, K.; Chatani, N.; Murai, S. *Chem. Lett.* **2001**, 386.

**Scheme 4**




fragment $Ru(CO)(PH_3)_2$,[20] the C−H bond activation process should involve the elemental steps shown in Scheme 4. Initially the formyl oxygen coordinates to the metal center. Then the cleavage of the closest *o*-CH bond takes place in two steps. First an *o*-OsC bond is formed, being driven by the change in the $\pi$ bonds of the conjugated system. Subsequently, in this intermediate, containing the *o*-OsC bond and a CH-agostic interaction, the hydrogen of the agostic CH bond is transferred to the osmium atom.[21]

In conclusion, the nature of the products of the reactions of the dihydride−solvento complex $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ with aldehydes is a function of the reactivity of the substituent at the carbonyl group of the aldehyde toward the unsaturated metal fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$, which is generated as a consequence of the hydride transfer from the metal center of the starting complex to a first aldehyde molecule. Thus, three different reaction patterns are observed: monodecarbonylation, double decarbonylation, and aromatic *o*-CH bond activation, depending on the alkenyl, alkyl, and aryl nature, respectively, of the substituent.

## Experimental Section

Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material **1** was prepared as previously described.[1a] Commercial aldehydes were distilled and stored over 4 Å molecular sieves. NMR spectra were recorded in $CD_2Cl_2$ at 293 K, chemical shifts (expressed in ppm) are referenced to residual solvent peaks ($^1H$, $^{13}C\{^1H\}$) or external $H_3PO_4$ ($^{31}P\{^1H\}$), and coupling constants, *J*, are given in hertz.

**Preparation of $[Os(\eta^5\text{-}C_5H_5)(CO)(\eta^2\text{-}PhCH{=}CH_2)(P^iPr_3)]BF_4$ (2).** A solution of **1** (151 mg, 0.27 mmol) in 2.5 mL of dichloromethane was treated with cinnamaldehyde (100 $\mu$L, 0.80 mmol) at 50 °C for 24 h. The resulting solution was concentrated to ca. 1 mL. The addition of diethyl ether caused the formation of a beige solid. Yield: 124 mg (84%). GC-MS analysis of the mother liquor showed the presence of cinnamaldehyde and 3-phenylpropanal. Anal. Calcd for $C_{23}H_{34}BF_4OOsP$: C, 43.54; H, 5.40. Found: C, 43.55; H, 5.15. IR (Nujol, $cm^{-1}$): $\nu$(CO) 1973 (s). $^1H$ NMR (400 MHz): 7.35 (m, 5H, Ph), 5.32 (s, 5H, $C_5H_5$), 4.90 (dd, $J_{HH}$ = 12.6 and 8.4, 1H, =CHPh), 3.91 (d, $J_{HH}$ = 12.6, 1H, =C$H_{trans}$), 2.85 (dd, $J_{HH}$ = 8.4, $J_{HP}$ = 8.4, 1H, =C$H_{cis}$), 2.54 (m, 3H, PCH), 1.28 (dd, $J_{HP}$ = 15.6, $J_{HH}$ = 7.2, 9H, PCHC$H_3$), 1.24 (dd, $J_{HP}$ = 16.8, $J_{HH}$ = 7.2, 9H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz): 17.8 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz): 184.9 (d, $J_{CP}$ = 13, CO), 141.6, 129.6, 129.2, and 127.3 (all s, Ph), 89.7 (s, $C_5H_5$), 56.4 (s, =CH), 29.2 (d, $J_{CP}$ = 30, PCH), 20.3 (s, PCH*C*$H_3$), 20.1 (d, $J_{CP}$ = 2, PCH*C*$H_3$), 19.9 (s, =$CH_2$). MS (MALDI-TOF): *m*/*z* 444.8 ($M^+$ − styrene).

**Preparation of $[Os(\eta^5\text{-}C_5H_5)(CO)_2(P^iPr_3)]BF_4$ (3).** This complex was prepared as described for **2** by starting from **1** (154 mg, 0.27 mmol) and isovaleraldehyde (105 $\mu$L, 0.96 mmol). Beige solid. Yield: 112 mg (73%). GC-MS analysis of the mother liquor showed the presence of isovaleraldehyde and 3-methyl-1-butanol. Anal. Calcd for $C_{16}H_{26}BF_4O_2OsP$: C, 34.42; H, 4.69. Found: C, 34.57; H, 4.52. IR (ATR, $cm^{-1}$): $\nu$(CO) 2033 (s), 1968 (s). $^1H$ NMR (300 MHz): 5.92 (s, 5H, $C_5H_5$), 2.48 (m, 3H, PCH), 1.29 (dd, $J_{HP}$ = 15.8, $J_{HH}$ = 7.1, 18H, PCHC$H_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz): 32.1 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz): 176.0 (d, $J_{CP}$ = 9, CO), 87.3 (s, $C_5H_5$), 29.5 (d, $J_{CP}$ = 31, PCH), 20.3 (d, $J_{CP}$ = 2, PCH*C*$H_3$). MS (MALDI-TOF): *m*/*z* 473.1 ($M^+$).

**Reaction of $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ with Isovaleraldehyde: Formation of $[OsH_2(\eta^5\text{-}C_5H_5)\{{=}C(OH)CH_2\text{-}CH(CH_3)_2\}(P^iPr_3)]BF_4$ (4) and $[Os(\eta^5\text{-}C_5H_5)\{{=}C(OH)CH_2\text{-}CH(CH_3)_2\}(CO)(P^iPr_3)]BF_4$ (5).** An NMR tube containing **1** (51 mg, 0.09 mmol) in 0.5 mL of dichloromethane-$d_2$ was treated with isovaleraldehyde (35 $\mu$L, 0.32 mmol) at room temperature for 12 h. After that, the NMR spectra showed the presence of **4** and **5** in the molar ratio 1:1.5. Spectroscopic data for **4** are as follows. $^1H$ NMR (300 MHz): 13.48 (br s, 1H, OH), 5.44 (s, 5H, $C_5H_5$), 2.90 (d, $J_{HH}$ = 6.9, 2H, $CH_2$), 2.50−2.05 (m, 4H, PCH and C$H$($CH_3$)$_2$), 1.34−1.18 (m, 18H, PCHC$H_3$), 1.09 (d, $J_{HH}$ = 6.9, 6H, CH(C$H_3$)$_2$), −10.16 (d, $J_{HP}$ = 32.7, 2H, Os−H). $^{31}P\{^1H\}$ NMR (121.49 MHz): 40.6 (s, t in off-resonance). $^{13}C\{^1H\}$ NMR (75.48 MHz): 280.5 (s, Os=C), 82.9 (s, $C_5H_5$), 76.5 (s, $CH_2$), 29.5 (d, $J_{CP}$ = 32, PCH), 27.6 (s, *C*H($CH_3$)$_2$), 22.3 (s, CH(*C*$H_3$)$_2$), 19.4 (s, PCH*C*$H_3$), 19.2 (d, $J_{CP}$ = 2, PCH*C*$H_3$). Spectroscopic data for **5** are as follows. $^1H$ NMR (300 MHz): 12.80 (br s, 1H, OH), 5.69 (s, 5H, $C_5H_5$), 3.20 (dd, $J_{HH}$ = 11.5 and 6.0, 1H, $CH_2$), 2.78 (dd, $J_{HH}$ = 11.5 and 8.3, 1H, $CH_2$), 2.50−2.05 (m, 4H, PCH and C$H$($CH_3$)$_2$), 1.34−1.18 (18H, PCHC$H_3$), 0.98 (d, $J_{HH}$ = 6.6, 3H, CH(C$H_3$)$_2$), 0.91 (d, $J_{HH}$ = 6.6, 3H, CH(C$H_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz): 27.0 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz): 278.8 (d, $J_{CP}$ = 7, Os=C), 182.5 (d, $J_{CP}$ = 10, CO), 86.8 (s, $C_5H_5$), 71.5 (s, $CH_2$), 30.1 (d, $J_{CP}$ = 30, PCH), 29.1 (s, *C*H($CH_3$)$_2$), 22.5 and 22.0 (s, CH(*C*$H_3$)$_2$), 19.4 (s, PCH*C*$H_3$), 19.3 (d, $J_{CP}$ = 2, PCH*C*$H_3$).

**Preparation of $[OsH(\eta^5\text{-}C_5H_5)\{C_6H_4C(O)H\}(P^iPr_3)]BF_4$ (6).** This complex was prepared as described for **2** starting from **1** (139 mg, 0.25 mmol) and benzaldehyde (100 $\mu$L, 0.74 mmol). Yellow solid. Yield: 111 mg (74%). GC-MS analysis of the mother liquor showed the presence of benzaldehyde and benzyl alcohol. Anal. Calcd for $C_{21}H_{32}BF_4OOsP$: C, 41.45; H, 5.30. Found: C, 41.01; H, 5.02. IR (Nujol, $cm^{-1}$): $\nu$(OsH) 2120 (m), $\nu$(CO) 1590 (s). $^1H$ NMR (300 MHz): 9.40 (s, 1H, CHO), 8.27, 8.24 (both d, $J_{HH}$ = 7.5, each 1H, Ph), 7.30, 7.16 (both dd, $J_{HH}$ = 7.5, each 1H, Ph), 5.68 (s, 5H, $C_5H_5$), 2.36 (m, 3H, PCH), 1.22 (dd, $J_{HP}$ = 15.1, $J_{HH}$ = 7.0, 9H, PCHC$H_3$), 0.97 (dd, $J_{HP}$ = 14.2, $J_{HH}$ = 7.0, 9H, PCHC$H_3$), −13.74 (d, $J_{HP}$ = 32.1, 1H, Os-H). $^{31}P\{^1H\}$ NMR (121.49 MHz): 28.0 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz): 211.6 (d, $J_{CP}$ = 2, CHO), 184.2 (d, $J_{CP}$ = 3, Os-C), 148.1, 145.0, 135.3, 134.7, and 124.8 (all s, Ph), 86.9 (s, $C_5H_5$), 27.9 (d, $J_{CP}$ = 30, PCH), 20.3 (s, PCH*C*$H_3$), 19.0 (d, $J_{CP}$ = 2, PCH*C*$H_3$). MS (MALDI-TOF): *m*/*z* 522.9 ($M^+$).

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**Supporting Information Available:** Text giving additional details on the preparation of the $BF_4$ salt of **2** and crystal structure determination and a CIF file giving crystal data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Matsubara, T.; Koga, N.; Musaev, D. G.; Morokuma, K. *Organometallics* **2000**, *19*, 2318.

(21) It should be noted that the *o*-CH addition of aromatic aldehydes, according to this mechanism, requires two empty valence orbitals in the metallic fragment promoting the activation. Thus, the 14-valence-electron character of the metal fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$ appears to be determinant for the addition in this case.