C-H Bond Activation Reactions in Ketones and Aldehydes Promoted by POP-Pincer Osmium and Ruthenium Complexes

Joaquín Alós, Miguel A. Esteruelas,* Montserrat Oliván, Enrique Oñate, and Pim Puylaert

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza – CSIC, 50009 Zaragoza, Spain

Supporting Information Placeholder

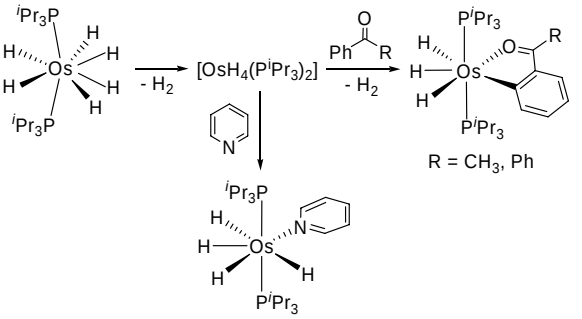
ABSTRACT: The tetrahydride complex $OsH_4\{xant(P^iPr_2)_2\}$ (**1**, $xant(P^iPr_2)_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) activates an *ortho*-C-H bond of benzophenone and acetophenone to give the osmaisobenzofuran derivatives $OsH\{\kappa^2\text{-C,O-}[C_6H_4C(R)O]\}\{xant(P^iPr_2)_2\}$ (R = Ph (**2**), CH_3 (**3**)). The reaction of **1** with perdeuterated benzophenone leads to **2** partially protiated. The deuterium distribution in the latter suggests that the carbonyl group of the ketone traps the *ortho*-C-H addition product, which is the most disfavored from a kinetic point of view. The ruthenium counterpart $RuH_2(\eta^2\text{-}H_2)\{xant(P^iPr_2)_2\}$, generated *in situ* from the tetrahydrideborate $RuH(\eta^2\text{-}H_2BH_2)\{xant(P^iPr_2)_2\}$ (**4**) and 2-propanol, also activates benzophenone and acetophenone to afford the ruthenaisobenzofurans $RuH\{\kappa^2\text{-C,O-}[C_6H_4C(R)O]\}\{xant(P^iPr_2)_2\}$ (R = Ph (**5**), CH_3 (**6**)). Both precursors favor the C-H bond activation over the C-F bond cleavage in fluorinated aromatic ketones. Thus, the fluorinated metalaisobenzofuran derivatives $OsH\{\kappa^2\text{-C,O-}[C_6H_3FC(Me)O]\}\{xant(P^iPr_2)_2\}$ (**7**), $OsH\{\kappa^2\text{-C,O-}[C_6H_4C(C_6H_3F_2)O]\}\{xant(P^iPr_2)_2\}$ (**8**), and $RuH\{\kappa^2\text{-C,O-}[C_6H_3FC(Me)O]\}\{xant(P^iPr_2)_2\}$ (**9**) have been obtained from the *ortho*-C-H bond activation of the corresponding substrates. Complex **1** also promotes the C_β-H bond activation of benzylidenacetone and methyl vinyl ketone to afford the osmafurans $OsH\{\kappa^2\text{-C,O-}[C(R)CHC(Me)O]\}\{xant(P^iPr_2)_2\}$ (R = Ph (**10**), H (**11**)). The ruthenafuran counterparts $RuH\{\kappa^2\text{-C,O-}[C(R)CHC(Me)O]\}\{xant(P^iPr_2)_2\}$ (R = Ph (**12**), H (**13**)) were similarly generated by using **4** in the presence of 2-propanol. The analogous reactions with benzylidenacetophenone yield mixtures of $OsH\{\kappa^2\text{-C,O-}[C_6H_4C(CH{=}CHPh)O]\}\{xant(P^iPr_2)_2\}$ (**14**) and $OsH\{\kappa^2\text{-C,O-}[C(Ph)CHC(Ph)O]\}\{xant(P^iPr_2)_2\}$ (**15**), and $RuH\{\kappa^2\text{-C,O-}[C_6H_4C(CH{=}CHPh)O]\}\{xant(P^iPr_2)_2\}$ (**16**) and $RuH\{\kappa^2\text{-C,O-}[C(Ph)CHC(Ph)O]\}\{xant(P^iPr_2)_2\}$ (**17**). While the formation of the osmaisobenzofuran **14** is slightly favored with regard to that of **15**, no preference is observed for ruthenium. In contrast, both precursors favor OC-H activation over the cleavage of an *ortho*-C-H bond in aromatic aldehydes. Thus, their reactions with benzaldehyde yield $MH(Ph)(CO)\{xant(P^iPr_2)_2\}$ (M = Os (**18**), Ru (**19**)). The decarbonylation of the substrate is also observed with *α,β*-unsaturated aldehydes. Thus, the reaction of **1** with 1-cyclohexene-1-carboxaldehyde gives $OsH(C_6H_9)(CO)\{xant(P^iPr_2)_2\}$ (**20**). Decarbonylation and dehydrogenation of the aldehyde to form the *trans*-dihydride $OsH_2(CO)\{xant(P^iPr_2)_2\}$ (**21**) take place with cyclohexane carboxaldehyde.

INTRODUCTION

The C-H bond activation reactions promoted by transition metal complexes, which are omnipresent in organometallics,[1] have a broad value in the current chemistry due to their connection with the functionalization of inert C-H bonds[2] and as ~~an~~ intermediate steps in the preparation of new materials.[3] A major goal is to control the selectivity of the process when C-H bonds of similar dissociation energies are present in the same substrate. One strategy is using a pre-existing functional group, which being well positioned in the molecule, facilitates the desired C-H bond cleavage.[4] From a catalytic point of view, carbonyl groups have advantages over pyridines, oxazolines, sulphides, or phosphines, among others.[5] The weakly coordinating power of the carbonyl group reduces the stability of the resulting cyclometalated products, decreasing the activation energy of subsequent reactions. Thus, for instance, reactions involving ketones such as the additions of *ortho*-C-H bonds to olefins, alkynes, CO/olefins[6] and the *ortho*-arylations with arylbromides and arylboronates have received great attention.[7]

Also, we have been actively interested in the C-H bond activation of ketones and aldehydes for a long time. Thus, as a part of our work in C-H bond activation chemistry,[8] we have reported on C-H bond activation of cycloalkyl, aromatic, and *α,β*-unsaturated ketones,[9] and aldehydes[10] promoted by osmium-polyhydride complexes containing the monodentate triisopropylphosphine ligand, including the saturated d^2 hexahydride $OsH_6(P^iPr_3)_2$ (Scheme 1). The thermal activation of the latter involves the release of molecular hydrogen. The resulting $OsH_4(P^iPr_3)_2$ species has been trapped with pyridines and characterized as the corresponding tetrahydride compounds $OsH_4(pyridine\text{-}R)(P^iPr_3)_2$.[11] The C-H bond cleavage has in general high activation energy and therefore requires high temperatures and long times. In the search for more robust metal precursors, and at the same time more rigid, than those based on *trans*-$M(P^iPr_3)_2$ metal fragments, five years ago, we initiated a research program centered on pincer moieties-M(POP) (M = Ru, Os, Rh, Ir; POP = 4,6-

bis(diisopropylphosphino)dibenzofuran (dbf(P^iPr_2)$_2$), 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant(P^iPr_2)$_2$)).[12] Recently, we have described the preparation of the tetrahydride derivative OsH_4{xant(P^iPr_2)$_2$}, [12d] as a part of the results of this program, which is a rigid counterpart of the previous species OsH_4(pyridine-R)(P^iPr_3)$_2$. In spite of its saturated character, the hemilabile properties of the central oxygen atom of the diphosphine[13] prompted us to study the ability of OsH_4{xant(P^iPr_2)$_2$} for promoting C-H bond activation of aromatic, fluorinated aromatic, and α,β-unsaturated ketones, and aldehydes. Because there are marked differences between the chemistries of osmium and ruthenium,[14] including those of the M(POP) fragments,[12f] the ability of the counterpart pincer ruthenium compound $RuH_2(\eta^2\text{-}H_2)${xant(P^iPr_2)$_2$} is also studied in parallel, for comparative purposes.

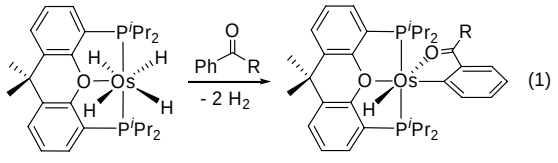


Scheme 1

The chemistry of the pincer osmium complexes has received scarce attention[15] in comparison with that of the rest of platinum group metals. As a consequence, only a few systems have proved to promote the C-H cleavage,[16] although interesting stoichiometric and catalytic transformations involving the activation of C-H bonds have been performed with other pincer transition metal compounds.[17] In this paper, we report the first study on the C-H bond activation of ketones and aldehydes promoted by a pincer osmium complex and the systematic comparison of each reaction with that performed using the ruthenium counterpart.

RESULTS AND DISCUSSION

1. Aromatic Ketones. Treatment of toluene solutions of the tetrahydride-osmium(IV) complex OsH_4{xant(P^iPr_2)$_2$} (**1**) with 1.0 equiv of benzophenone and acetophenone, under reflux, for 12 h leads to the osmium(II) derivatives $OsH\{\kappa^2\text{-}C,O\text{-}[C_6H_4C(R)O]\}${xant($P^iPr_2$)$_2$} (R = Ph (**2**), CH_3 (**3**)), as a result of the release of two hydrogen molecules and the selective *ortho*-C-H bond activation of the ketones. These compounds were isolated as purple (**2**) and dark red (**3**) solids in 73% and 69% yield, respectively, according to eq 1.



Complex **2** was characterized by X-ray diffraction analysis. The structure (Figure 1) proves the cleavage of the *ortho*-C-H bond of the substrate. As expected for the *mer*-coordination of the pincer, the Os{xant(P^iPr_2)$_2$} skeleton is T-shaped with the osmium atom situated in the common vertex and P(1)-Os-P(2), P(1)-Os-O(2), and P(2)-Os-O(2) angles of 153.28(5)º, 79.84(9)º and 80.24(9)º, respectively. Thus, the coordination geometry around the metal center can be described as a distorted octahedron with the orthometalated ketone, which acts with a bite angle of 77.33(19)º, placed in the perpendicular plane to the P-Os-P direction along with the hydride ligand *trans* to the carbonyl oxygen atom (O(1)-Os-H(01) = 167.8(19)º) and the oxygen atom of the diphosphine *trans* to the metalated carbon atom (O(2)-Os-C(1) = 173.69(18)º). The Os-O(1) and Os-C(1) bond lengths of 2.190(4) and 1.975(5) Å, respectively, compare well with the distances found in other five-membered osmacycles resulting from related C-H bond activations.[9]

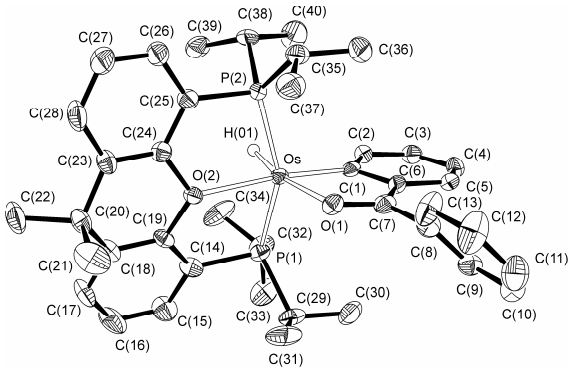


Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths (Å) and angles (º): Os-P(1) = 2.2745(14), Os-P(2) = 2.2821(14), Os-O(1) = 2.190(4), Os-O(2) = 2.328(4), Os-C(1) = 1.975(5), Os-H(01) = 1.584(10), O(1)-C(7) = 1.275(6), C(1)-C(6) = 1.429(8), C(6)-C(7) = 1.435(8); P(1)-Os-P(2) = 153.28(5), P(1)-Os-O(2) = 79.84(9), P(2)-Os-O(2) = 80.24(9), O(1)-Os-C(1) = 77.33(19), O(2)-Os-C(1) = 173.69(18), O(1)-Os-H(01) = 167.8(19).

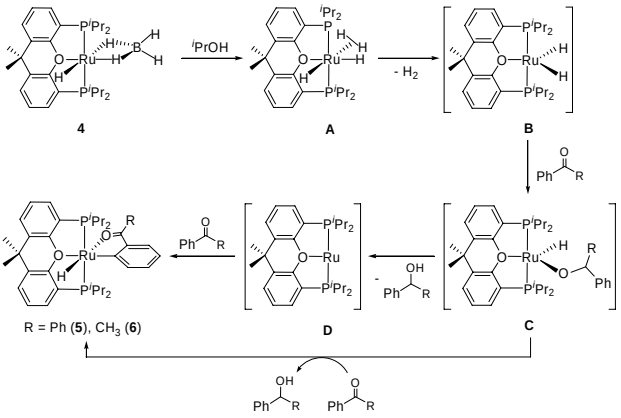
The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **2** and **3**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 1. In agreement with the presence of a hydride ligand in the compounds, their ^1H NMR spectra contain a triplet, with a H-P coupling constant of about 23 Hz, at -17.03 ppm for **2** and at -18.01 ppm for **3**. In the $^{13}C\{^1H\}$ NMR spectra, the most noticeable feature is the resonance corresponding to the metalated carbon atom, which is observed at 187.4 ppm for **2** and at 184.3 ppm for **3** as a triplet with a C-P coupling constant of about 4 Hz. The $^{31}P\{^1H\}$ NMR spectra show a singlet at 47.0 ppm for **2** and at 46.3 ppm for **3**, as expected for equivalent P^iPr_2 groups.

Matsubara and Morokuma have proposed on the basis of DFT calculations using PH_3 and benzaldehyde as models of phosphine and substrate, respectively, that the *ortho*-C-H bond activation of aromatic ketones promoted by Murai's catalyst involves the initial formyl coordination to the metal center followed by the cleavage of the closest *ortho*-C-H bond.[18] In contrast to this proposal, Goldman has demonstrated that the coordinating group does not direct the C-H bond addition to Ir(PCP) skeletons. To the contrary, the functional group is found to actually prevent the C-H addition from a kinetic point of view. However, after the C-H bond cleavage, the coordinating group acts to trap the *ortho*-C-H addition product afford-

ing orthometalated compounds.[17a] To gain insight into the origin of the selectivity of the *ortho*-C-H bond activation in our case, we carried out the reaction of **1** with perdeuterated benzophenone. Under the same conditions at those employed with the protiated substrate, the reaction led to the compound with the orthometalated ketone almost completely protiated in positions distal to the carbonyl group, whereas it keeps about 0.4 deuterium atoms at each one of the *ortho* positions to the carbonyl group and about 0.2 deuterium atoms at the *ortho* position to the metal center. This result reveals that the C-H bond activation of the reaction solvent, toluene, is kinetically favored with regard to that of the ketone, fully agrees with Goldman's observations, and demonstrates that the selectivity of the *ortho*-C-H bond activation of aromatic ketones is thermodynamic in origin while the activations of the C-H bonds in *meta* and *para* positions are kinetically preferred.

Complex **1** is relatively stable under the reaction conditions in the absence of substrate. Thus, it is recovered after 24 h under reflux whereas under hydrogen atmosphere it is in equilibrium with the previously described hexahydride $OsH_6\{xant(P^iPr_2)_2\}$, containing a bidentate κ^2-PP diphosphine.[12d] This is consistent with the behavior of complexes OsH_4(pyridine-R)$(P^iPr_3)_2$, which in the presence of added pyridine exchange the coordinated heterocycle by the free one.[11] These experimental observations suggest that the C-H bond activation takes place through Os(IV) species, including OsH_5-intermediates, related to those formed in the $OsH_6(P^iPr_3)_2$-mediated C-H bond activation of imidazolium salts.[19] These (POP)OsH_5 intermediates are transformed into POP-counterparts of complexes $OsH_3\{\kappa^2$-C,O-$[C_6H_4C(R)O]\}(P^iPr_3)_2$ shown in Scheme 1.

Osmium is more reducing than ruthenium. As a consequence, the $Ru\{xant(P^iPr_2)_2\}$ metal fragment avoids the oxidation state four. Thus, osmium d^4-polyhydrides are d^6-dihydrogen species in the ruthenium chemistry, which require different synthetic procedures from those of osmium for their preparation.[12f] The ruthenium counterpart of **1** is the d^6-dihydride-dihydrogen derivative $RuH_2(\eta^2$-$H_2)\{xant(P^iPr_2)_2\}$ (**A**, in Scheme 2), which rapidly loses the coordinated hydrogen molecule under an argon atmosphere to afford the dihydride $RuH_2\{xant(P^iPr_2)_2\}$ (**B**). Both **A** and **B** are not handy compounds from an experimental point of view. However, they can be generated *in situ* by treatment of the hydride-tetrahydrideborate complex $RuH(\eta^2$-$H_2BH_2)\{xant(P^iPr_2)_2\}$ (**4**) with 2-propanol. So, in order to compare the $Os\{xant(P^iPr_2)_2\}$ and $Ru\{xant(P^iPr_2)_2\}$ metal fragments, we performed reactions analogous to those shown in eq 1 starting from **4** and 2-propanol. Because the dihydride **B** reduces ketones, 2 equiv of substrate were used. Thus, treatment of toluene solutions of **4** with 2 equiv of benzophenone and acetophenone, in the presence of 1.0 equiv of 2-propanol, at 80 ºC, for 6 h gives rise to 1.0 equiv of the corresponding alcohol and to the complexes $RuH\{\kappa^2$-C,O-$[C_6H_4C(R)O]\}\{xant(P^iPr_2)_2\}$ (R = Ph (**5**), CH_3 (**6**)), which were isolated as purple (**5**) and dark red (**6**) solids in 61% and 52% yield, respectively.



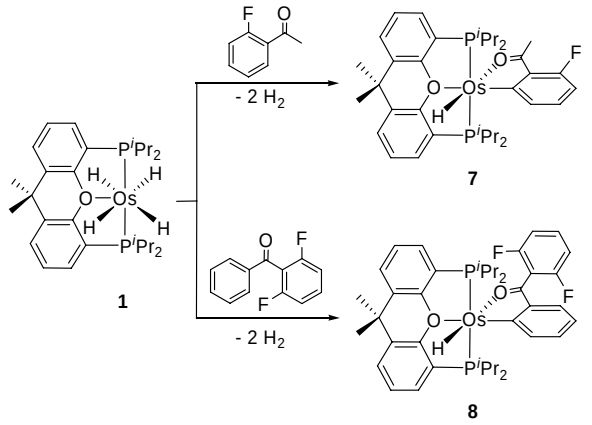
Scheme 2

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **5** and **6**, in benzene-d_6, at room temperature agree well with those of **2** and **3** and strongly support the structures shown in Scheme 2. In the ^1H NMR spectra, the hydride resonance appears at -15.42 ppm for **5** and at -16.36 ppm for **6**, as a triplet with a H-P coupling constant between 26 and 27 Hz. In the $^{13}C\{^1H\}$ NMR spectra, the metalated carbon atom displays a triplet, with a C-P coupling constant of about 8 Hz, at 212.4 ppm for **5** and at 209.0 ppm for **6**. It should be pointed out that these resonances are shifted about 25 ppm to lower field with regard to those of the osmium counterparts, suggesting that the metalaisobenzofuran character of the fused rings is higher for ruthenium than for osmium. A singlet at about 62 ppm in the $^{31}P\{^1H\}$ NMR spectra is also a characteristic feature of these compounds.

The reduction of the ketone during the reaction could occur via intermediate **C**, resulting from the insertion of the C=O double bond into one of Ru-H bonds of **B** (Scheme 2). Thus, the elimination of alcohol should afford the 14 electrons valence ruthenium(0) intermediate $Ru\{xant(P^iPr_2)_2\}$ (**D**), which could undergo the *ortho*-C-H bond oxidative addition of a second molecule of ketone to yield **5** and **6**. An alternative pathway would involve the direct heterolytic C-H bond activation of the second ketone molecule promoted by **C**, which uses the alkoxide ligand as a base. The participation of both mechanisms is consistent with the presence of about 0.5 deuterium atoms at the hydride position of the product resulting from the reaction of **4** with perdeuterated benzophenone. Furthermore, although the metalated ketone is mainly deuterated, it contains 0.6 hydrogen atoms at the *ortho*-position with regard to the metal center (*meta* with regard to the carbonyl group) and about 0.2 hydrogen atoms at each *ortho*-position with regard to the carbonyl group. This indicates that the activation of the *meta*-C-H bond of the ketone is kinetically favored over the *ortho*-C-H bond, and suggests that the *ortho*-CH bond cleavage is not chelated assisted.

2. Fluorinated Aromatic Ketones. The activations of C-H and C-F bonds are competitive processes, when both bonds coexist in the same molecule. In general, the C-H bond activation is a stronger competitor in a kinetic sense,[20] whereas the C-F cleavage is thermodynamically more favored, in particular when HF is formed.[21] We have previously observed that the hexahydride complex $OsH_6(P^iPr_3)_2$ activates not only *ortho*-C-H bonds of aromatic ketones but also C-F bonds.[9a] The *ortho*-C-H bond activation is preferred over the *ortho*-C-F bond activation in ketones containing only one aromatic ring. How-

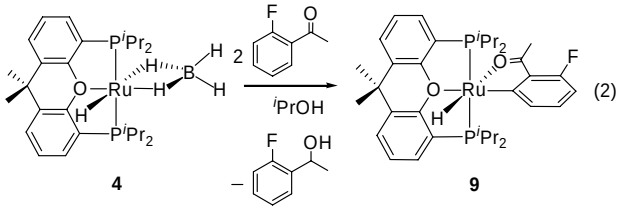
ever, the *ortho*-C-F bond activation is preferred over the *ortho*-C-H bond activation for ketones with both di*ortho*-fluorinated and di*ortho*-protiated aromatic groups. In contrast to $Os(P^iPr_3)_2$, the $Os\{xant(P^iPr_2)_2\}$-mediated C-H bond activation is preferred in both cases (Scheme 3). Treatment of toluene solutions of **1** with 1.0 equiv of 2-fluoroacetophenone and 2,6-difluorobenzophenone, under reflux, for 14 h selectively leads to the corresponding C-H bond activation products $OsH\{\kappa^2\text{-}C,O\text{-}[C_6H_3FC(Me)O]\}\{xant(P^iPr_2)_2\}$ (**7**) and $OsH\{\kappa^2\text{-}C,O\text{-}[C_6H_4C(C_6H_3F_2)O]\}\{xant(P^iPr_2)_2\}$ (**8**), which were isolated as dark red and purple solids in 30% and 72% yield, respectively. Although the M-C bond energies increase with the *ortho*-fluorine substitution,[22] products resulting from the cleavage of a C-H bond *ortho* to the fluorine substituents were also not observed. The behavior of **1** is as that of the trihydride-stannyl osmium(IV) complex $OsH_3(SnPh_2Cl)\{\kappa^3\text{-}P,C,C\text{-}[^iPr_2PC(Me)=CH_2]\}(P^iPr_3)$, which reacts with 2-fluoroacetophenone and 2,3,4,5,6-pentafluorobenzophenone to afford the respective *ortho*-C-H bond activation products.[9c]



Scheme 3

The C-H bond activation of the substrates is strongly supported by the ^1H, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the obtained solids, in benzene-d_6, at room temperature. In agreement with the presence of a hydride ligand in the reaction products, the ^1H NMR spectra show at -17.83 ppm for **7** and at -17.33 ppm for **8** a triplet with a H-P coupling constant between 22 and 24 Hz, whereas the $^{19}F\{^1H\}$ NMR spectra contain a singlet at -113.4 ppm for **7** and at -109.2 ppm for **8**. In the $^{13}C\{^1H\}$ NMR spectrum of **7**, the metalated carbon atom displays at 188.5 ppm a double triplet with C-F and C-P coupling constants of about 4 Hz, whereas the related resonance of **8** is observed at 188.1 ppm as a triplet with a C-P coupling constant of 3.7 Hz. The $^{31}P\{^1H\}$ NMR spectra show a singlet at 46.2 ppm for **7** and at 48.5 ppm for **8**.

The $Ru\{xant(P^iPr_2)_2\}$ fragment also favors the C-H bond activation over the C-F bond cleavage. Treatment of toluene solutions of **4** with 2.0 equiv of 2-fluoroacetophenone, in the presence of 1.0 equiv of 2-propanol, at 80 ºC, for 6 h leads to the C-H bond activation product $RuH\{\kappa^2\text{-}C,O\text{-}[C_6H_3FC(Me)O]\}\{xant(P^iPr_2)_2\}$ (**9**), which was isolated as a red solid in 38% yield, according to eq 2.

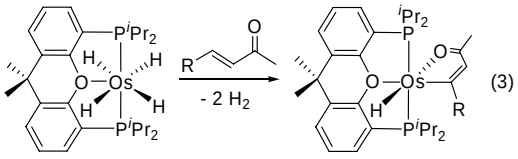


The ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **9**, in benzene-d_6, at room temperature agree well with those of the osmium counterpart **7**. In the ^1H NMR spectrum, the hydride resonance appears at -16.11 ppm, as a triplet with a H-P coupling constant of 25.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the metalated carbon atom displays a double triplet with C-F and C-P coupling constants of 6.0 and 8.3 Hz, respectively, at 213.7 ppm, i.e., shifted about 25 ppm to lower field with regard to the metalated resonance of **7**, in agreement with **5** and **6**. Singlets at -109.1 ppm and 62.1 ppm in the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, respectively, are also characteristic features of this compound.

The behavior of **1** and **4** in these competitive reactions is in contrast to that observed by Zhang and Li for the iron complex $Fe(PMe_3)_4$ which reacts with 2,6-difluorobenzophenone to give an iron(II) derivative resulting from the C-F bond activation of two substrate molecules.[23] Similarly, the cobalt precursor $CoMe(PMe_3)_4$ promotes the cleavage of a C-F bond of the same substrate.[24]

3. *α,β*-Unsaturated Ketones. The insertion of alkenes into metal-hydride bonds to afford alkyl derivatives is one of the most typical reactions of transition-metal-hydride complexes and constitutes the key step for the catalytic hydrogenation of olefins. This reaction frequently competes with the addition of vinylic C-H bonds to the metal center when the hydride complex is an unsaturated species. *α,β*-Unsaturated ketones are organic molecules that could undergo both processes.[25] Thus, in order to investigate the competition between them, for the reactions mediated by $Os\{xant(P^iPr_2)_2\}$ and $Ru\{xant(P^iPr_2)_2\}$ systems, we have extended the study on carbonyl derivatives to these substrates.

Treatment of toluene solutions of **1** with 1.0 equiv of benzylidenacetone and methyl vinyl ketone, under reflux, overnight leads to the hydride-osmafuran derivatives $OsH\{\kappa^2\text{-}C,O\text{-}[C(R)CHC(Me)O]\}\{xant(P^iPr_2)_2\}$ (R = Ph (**10**), H (**11**)), as a result of the C-H bond activation of the substrates. Insertion products of the C-C double bond into a Os-H bond were not detected during the reactions. Complexes **10** and **11** were isolated as dark green solids in 90% (**10**) and 64% (**11**) yield, according to eq 3.



Complex **10** was characterized by X-ray diffraction analysis. The structure, which proves the activation of the C_β-H bond of the substrate, has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 2 shows a drawing of one of them. In agreement with **2**, the $Os\{xant(P^iPr_2)_2\}$ skeleton displays a *mer* coordination with

P(1)-Os(1)-P(2), P(1)-Os(1)-O(2), and P(2)-Os(1)-O(2) angles of 154.58(9)º and 156.38(9)º, 80.58(15)º and 80.14(16)º, and 80.24(15)º and 80.12(16)º, respectively. Thus, the coordination polyhedron around the osmium atom can be rationalized as a distorted octahedron with the oxygen atom of the diphosphine *trans* to the metalated carbon atom of the activated ketone (O(2)-Os(1)-C(1) = 171.3(3)º and 168.6(3)º) and the hydride ligand *trans* to the oxygen atom (O(1)-Os(1)-H(01) = 175(3)º and 177(3)º). The activated substrate certainly forms with the metal center an osmafuran ring. The Os(1)-C(1) bond lengths of 1.970(9) and 1.953(9) Å agree well with those expected for a derivative of this type where the resonance forms shown in Chart 1 should be taken into account to describe the bonding situation in the heterometalacycle.[9d-f,25b,26] In accordance with this, the C(1)-C(8) and C(8)-C(9) distances of 1.419(14) and 1.444(14) Å, and 1.377(14) and 1.380(14) Å, respectively, are between those expected for single and double carbon-carbon bonds and indicate a very important contribution of the resonance form **b**. The Os(1)-O(1) and O(1)-C(9) bond lengths of 2.164(7) and 2.152(7) Å, and 1.282(11) and 1.281(12) Å, respectively, also support the metalafuran character.[27]

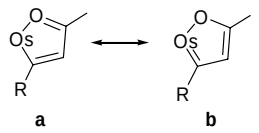


Chart 1

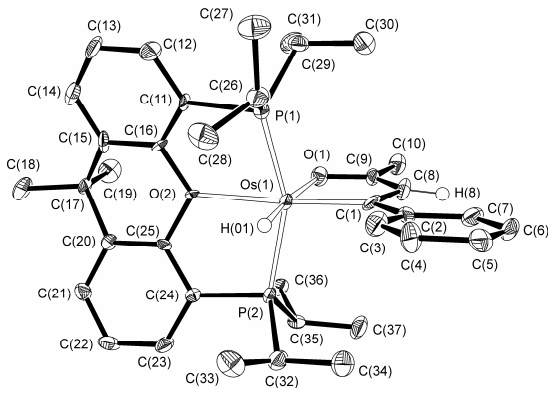
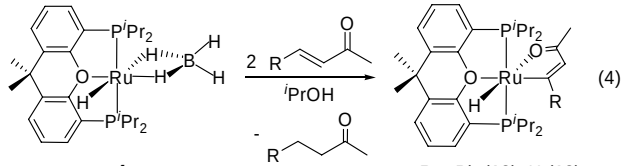


Figure 2. ORTEP diagram of complex **10** (50% probability ellipsoids). Hydrogen atoms (except the hydride and H(8)) are omitted for clarity. Selected bond lengths (Å) and angles (º): Os(1)-P(1) = 2.286(2), 2.276(3), Os(1)-P(2) = 2.287(2), 2.303(2), Os(1)-O(1) = 2.164(7), 2.152(7), Os(1)-O(2) = 2.336(6), 2.312(6), Os(1)-C(1) = 1.970(9), 1.953(9), Os(1)-H(01) = 1.583(10), 1.594(10), C(1)-C(8) = 1.419(14), 1.444(14), C(8)-C(9) = 1.377(14), 1.380(14), O(1)-C(9) = 1.282(11), 1.281(12); P(1)-Os(1)-P(2) = 154.58(9), 156.38(9), P(1)-Os(1)-O(2) = 80.58(15), 80.14(16), P(2)-Os(1)-O(2) = 80.24(15), 80.12(16), O(1)-Os(1)-H(01) = 175(3), 177(3), O(2)-Os(1)-C(1) = 171.3(3), 168.6(3), O(1)-Os(1)-C(1) = 79.3(3), 79.9(3).

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **10** and **11**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 2. As expected for the presence of a hydride ligand in the compounds, the ^{1}H NMR spectra show a high field resonance at -17.11 ppm for **10** and at -17.81 ppm for **11**, which appears as a triplet with a H-P coupling constant of about 23 Hz. The ^{13}C{^{1}H} NMR spectra also reveal a main contribution of the resonance form **b**. Thus, in agreement with other compounds of this type,[9d-f,25b,26,27] they contain a low field resonance at 224.7 ppm for **10** and at 213.8 ppm for **11**, which is observed as a triplet with a C-P coupling constant of about 3 Hz. According to equivalent P^{i}Pr$_2$ groups, the ^{31}P{^{1}H} NMR spectra show a singlet at 46.8 ppm for **10** and at 57.7 ppm for **11**.

The ruthenium dihydride **B** also reduces the C-C double bond of *α,β*-unsaturated ketones. The resulting ruthenium(0) species **D** adds a vinylic C$_\beta$-H bond of a second molecule of substrate to yield the corresponding hydride-ruthenafuran derivatives. Thus, treatment of toluene solutions of **4** with 2.0 equiv of benzylidenacetone and methyl vinyl ketone, in the presence of 1.0 equiv of 2-propanol, under reflux, for 6 h leads to RuH{κ^2-C,O-[C(R)CHC(Me)O]}{xant(P^{i}Pr$_2$)$_2$} (R = Ph (**12**), H (**13**)), the ruthenium counterparts of **10** and **11**, which were isolated as dark green (**12**) and dark yellow (**13**) solids in 75% and 52% yield, respectively, according to eq 4.



(4)

4 R = Ph (**12**), H (**13**)

Complex **13** was characterized by X-ray diffraction analysis. Its structure, as that of **10**, has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 3 shows a drawing of one of them. As expected, the Ru{xant(P^{i}Pr$_2$)$_2$} skeleton is *mer*-coordinated, in this case with angles P(1)-Ru(1)-P(2), P(1)-Ru(1)-O(2), and P(2)-Ru(1)-O(2) of 153.25(9)º and 153.50(9)º, 80.77(15)º and 81.23(15)º, and 80.45(15)º and 80.69(16)º, respectively, in a distorted octahedral geometry. The bond lengths in the sequence Ru(1)-C(4)-C(3)-C(1)-O(1)-Ru(1) of 1.946(11) and 1.933(10) Å, 1.386(16) and 1.373(15) Å, 1.369(15) and 1.414(14) Å, 1.287(12) and 1.257(12) Å, and 2.196(6) and 2.187(6) Å, respectively, agree well with the related parameters of **10** and support the ruthenafuran formulation.

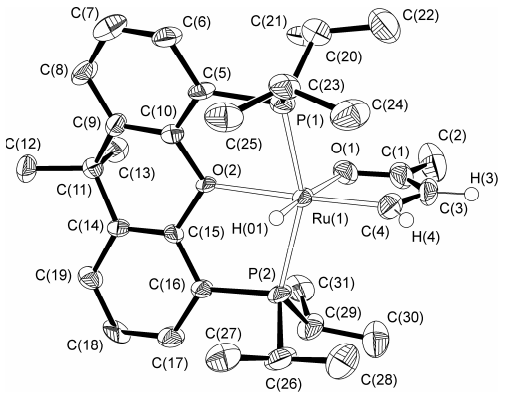
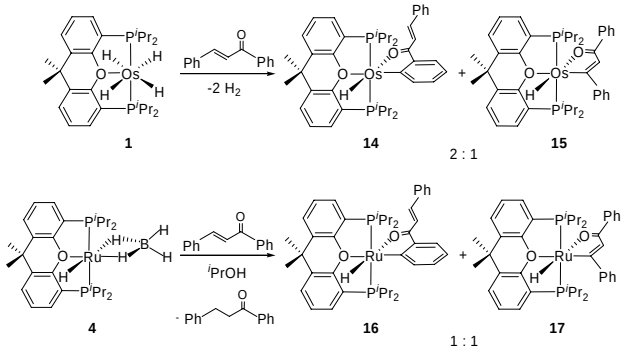


Figure 3. ORTEP diagram of complex **13** (50% probability ellipsoids). Hydrogen atoms (except hydride, H(3) and H(4)) are omitted for clarity. Selected bond lengths (Å) and angles (º): Ru(1)-P(1) = 2.267(3), 2.265(2), Ru(1)-P(2) = 2.264(2), 2.274(2), Ru(1)-O(1) = 2.196(6), 2.187(6), Ru(1)-O(2) = 2.318(6), 2.317(6), Ru(1)-C(4) = 1.946(11), 1.933(10), Ru(1)-H(01) = 1.582(10), 1.581(10), O(1)-C(1) = 1.287(12), 1.257(12), C(4)-

C(3) = 1.386(16), 1.373(15), C(3)-C(1) = 1.369(15), 1.414(14) Å; P(1)-Ru(1)-P(2) = 153.25(9), 153.50(9), P(1)-Ru(1)-O(2) = 80.77(15), 81.23(15), P(2)-Ru(1)-O(2) = 80.45(15), 80.69(16), O(1)-Ru(1)-H(01) = 174(4), 167(3), O(2)-Ru(1)-C(4) = 174.2(4), 172.1(4), O(1)-Ru(1)-C(4) = 77.7(4), 76.9(4).

The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of **12** and **13**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 3 and with those of their osmium counterparts. In the ^{1}H NMR spectra, the most noticeable feature is the hydride resonance, which appears at -15.35 ppm for **12** and at -15.96 ppm for **13** as a triplet with a H-P coupling constant of about 26 Hz. The ^{13}C{^{1}H} NMR spectra reveal that the metalafuran character is more marked for ruthenium than for osmium. Thus, the metalated resonance of the activated ketone is observed at 255.0 ppm for **12** and at 245.6 ppm for **13**, shifted about 30 ppm towards lower field with regard to those of **10** and **11**. These signals are observed as triplets with C-P coupling constants of about 7 Hz. The ^{31}P{^{1}H} NMR spectra contain a singlet at 63.2 ppm for **12** and at 71.5 ppm for **13**.

The osmium complex **1** and the ruthenium derivative **4** activate an *ortho*-C-H bond of aromatic ketones and a vinylic C_β-H bond of α,β-unsaturated ketones. To study the preference between these processes, we have also investigated their reactions with benzylidenacetophenone (Scheme 4), a substrate containing both functions bonded to the carbonyl unit.



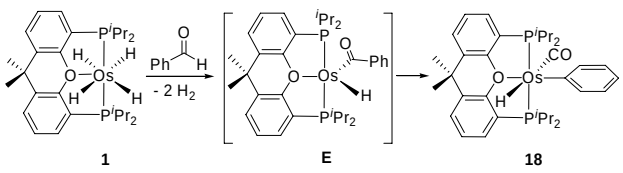
Scheme 4

Treatment of toluene solutions of **1** with 1.0 equiv of this substrate, under reflux, overnight gives rise to a 2:1 mixture of the osmaisobenzofuran derivative OsH{κ^2-C,O-[C_6H_4C(CH=CHPh)O]}{xant(P^{i}Pr$_2$)$_2$} (**14**) and the osmafuran compound OsH{κ^2-C,O-[C(Ph)CHC(Ph)O]}{xant(P^{i}Pr$_2$)$_2$} (**15**). The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the mixture, in benzene-d_6, at room temperature strongly support the formation of both species. In agreement with **2**, **3**, **7**, and **8**, the ^{1}H NMR spectrum of **14** contains a hydride resonance at -18.09 ppm, which is observed as a triplet with a H-P coupling constant of 23.0 Hz. The metalated aryl carbon atom displays at 185.4 ppm a triplet with a C-P coupling constant of 4.3 Hz, in the ^{13}C{^{1}H} NMR spectrum. The ^{31}P{^{1}H} NMR spectrum shows at 47.0 ppm a singlet. Characteristic features of **15** are a triplet ($J_{H\text{-}P}$ = 23.7 Hz) at -16.37 ppm in the ^{1}H NMR spectrum, a triplet ($J_{C\text{-}P}$ = 2.8 Hz) at 223.3 ppm in the ^{13}C{^{1}H} NMR spectrum, and a singlet at 47.5 ppm in the ^{31}P{^{1}H} NMR spectrum, corresponding to the hydride ligand, the metalated carbon atom of the activated substrate, and the equivalent P^{i}Pr$_2$ groups, respectively. These spectroscopic data agree well with those of **10** and **11**.

The *ortho*-C-H bond activation is the favored process for the Os{xant(P^{i}Pr$_2$)$_2$} skeleton, according to the molar ratio of the obtained mixture. On the other hand, the Ru{xant(P^{i}Pr$_2$)$_2$} moiety does not show any preference. Thus, in contrast to the osmium case, the treatment of toluene solutions of **4** with 2.0 equiv of benzylidenacetophenone in the presence of 1.0 equiv of 2-propanol, under reflux overnight, yields a 1:1 mixture of the ruthenaisobenzofuran complex RuH{κ^2-C,O-[C_6H_4C(CH=CHPh)O]}{xant(P^{i}Pr$_2$)$_2$} (**16**) and the ruthenafuran derivative RuH{κ^2-C,O-[C(Ph)CHC(Ph)O]}{xant(P^{i}Pr$_2$)$_2$} (**17**), in addition to 1.0 equiv of saturated ketone. The ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of **16** in benzene-d_6, at room temperature, agree well with those of the ruthenaisobenzofuran compounds **5**, **6**, and **9** whereas the spectra of **17** are in accordance with those of the ruthenafuran derivatives **12** and **13**. Characteristic features of **16** are: a triplet ($J_{H\text{-}P}$ = 24.0 Hz) at -16.30 ppm in the ^{1}H NMR spectrum, a triplet ($J_{C\text{-}P}$ = 9.1 Hz) at 209.9 ppm in the ^{13}C{^{1}H} NMR spectrum, and a singlet at 62.4 ppm in the ^{31}P{^{1}H} NMR spectrum, whereas the related parameters of **17** are: a triplet ($J_{H\text{-}P}$ = 26.1 Hz) at -14.46 ppm in the ^{1}H NMR spectrum, a triplet ($J_{C\text{-}P}$ = 6.7 Hz) at 255.0 ppm in the ^{13}C{^{1}H} NMR spectrum, and a singlet at 64.1 ppm in the ^{31}P{^{1}H} NMR spectrum.

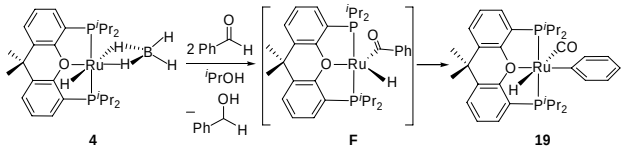
4. Aldehydes. Aldehydes are ketone counterparts with the carbonyl group bonded to a hydrogen atom. The activation of this bond is of great relevance in connection with the catalytic decarbonylation of these substrates[28] and by its importance in organometallic[29] and organic synthesis.[30] The OC-H bond is about 23 kcal·mol^{-1} weaker than the C-H bond of a phenyl group. As a consequence, the OC-H cleavage and the *ortho*-C-H bond activation in aromatic aldehydes are competitive processes. Thus, depending upon the metal precursor, products of both types of reactions have been isolated and characterized.[31] Being nterested in knowing the capacity of the Os{xant(P^{i}Pr$_2$)$_2$} and Ru{xant(P^{i}Pr$_2$)$_2$} skeletons for discerning between both types of bonds, we have also studied the reactions of precursors **1** and **4** with benzaldehyde.

Treatment of toluene solutions of **1** with 1.2 equiv of benzaldehyde, under reflux, for 15 h leads to the aryl-hydride-carbonyl derivative OsH(Ph)(CO){xant(P^{i}Pr$_2$)$_2$} (**18**), which was isolated as a white solid in 71% yield. Its formation involves the activation of the OC-H bond to afford an unsaturated hydride-acyl intermediate **E**, which evolves by deinsertion of the phenyl group (Scheme 5). The presence of the hydride ligand in **18** is revealed by a triplet ($J_{H\text{-}P}$ = 21.3 Hz) at -6.96 ppm in the ^{1}H NMR spectrum, which agrees well with those of OsH(Ph)(CO)$_2$(P^{i}Pr$_3$)$_2$ (δ -6.59)[31] and OsH(Ph)(CO){dbf(P^{i}Pr$_2$)$_2$} (δ -8.07),[12b] where the hydride and carbonyl ligands are also disposed *trans*. In the ^{13}C{^{1}H} NMR spectrum, the carbonyl and metalated aryl resonances appear at 186.9 (t, $J_{C\text{-}P}$ = 7.6 Hz) and 156.2 ppm (t, $J_{C\text{-}P}$ = 8.0 Hz), respectively. In agreement with the ^{13}C{^{1}H} NMR spectrum, the IR shows a ν(CO) band at 1871 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum contains at 53.0 ppm a singlet.



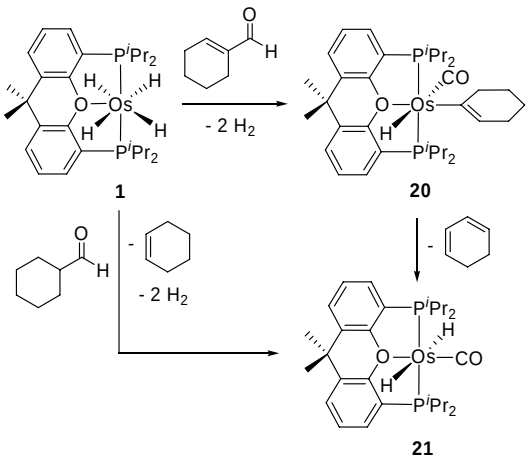
Scheme 5

The ruthenium skeleton Ru{xant(P^iPr_2)$_2$} also favors the OC-H bond activation over the cleavage of an *ortho*-C-H bond of the phenyl substituent. Treatment of toluene solutions of **4** with 2.0 equiv of benzaldehyde, in the presence of 1.0 equiv of 2-propanol, at 80 ºC, for 14 h gives rise to the ruthenium counterpart RuH(Ph)(CO){xant(P^iPr_2)$_2$} (**19**), via the unsaturated hydride-acyl intermedate **F** (Scheme 6). Complex **19** was isolated as a pale brown solid in 69% yield. Characteristic spectroscopic features of **19** are a triplet (J_{H-P} = 19.2 Hz) at -13.71 ppm, in the ^{1}H NMR spectrum, due to the hydride ligand; triplets at 208.5 (J_{C-P} = 6.5 Hz) and 156.0 ppm (J_{C-P} = 8.1 Hz), in the ^{13}C{^{1}H} NMR spectrum, assigned to the carbonyl group and the metalated carbon atom, respectively; a singlet at 69.5 ppm, in the ^{31}P{^{1}H} NMR spectrum, corresponding to the equivalent P^iPr_2 groups of the diphosphine; and a ν(CO) band at 1926 cm^{-1} in the IR.



Scheme 6

The OC-H bond activation is also preferred over the vinylic C-H bond activation in α,β-unsaturated aldehydes. Thus, similarly to benzaldehyde, treatment of toluene solutions of **1** with 1.2 equiv of 1-cyclohexene-1-carboxaldehyde, under reflux, for 14 h leads to OsH(C_6H_9)(CO){xant(P^iPr_2)$_2$} (**20**), the cyclohexenyl counterpart of **18**, although in this case, the OC-H activation-deinsertion product is contaminated with the dihydride-carbonyl derivative OsH_2(CO){xant(P^iPr_2)$_2$} (**21**), which is generated as a consequence of the release of 1,3-cyclohexadiene from **20** (Scheme 7). In agreement with **18**, the ^{1}H NMR spectrum of **20**, in benzene-d_6, at room temperature shows the hydride resonance at -7.23 ppm as a triplet with a H-P coupling constant of 21.2 Hz, whereas the carbonyl and metalated alkenyl resonances are observed at 187.3 and 157.4 ppm, respectively, in the ^{13}C{^{1}H} NMR spectrum. A singlet at 52.1 ppm, in the ^{31}P{^{1}H} NMR spectrum, and a ν(CO) band at 1872 cm^{-1} in the IR are also characteristic features of this compound.



Scheme 7

The dehydrogenation of the substituent of the aldehyde is favored for alkyl with regard to alkenyl. Thus, the dihydride complex **21** was obtained as a pure organometallic species, along with cyclohexene, from the reaction of **1** with cyclohexane carboxaldehyde, in toluene, under reflux. This dihydride derivative was isolated as yellow crystals in 72% yield and characterized by X-ray diffraction analysis. Its structure (Figure 4) proves the dehydrogenative decarbonylation of the substrate. In agreement with **2**, **10**, and **13** the Os{xant(P^iPr_2)$_2$} skeleton is *mer*-coordinated with P(1)-Os-P(2), P(1)-Os-O(1), and P(2)-Os-O(1) angles of 162.14(5)º, 81.56(8)º, and 81.03(9)º, respectively. Thus, the coordination geometry around the osmium atom can be rationalized as a distorted octahedron with *trans* hydrides (H(01)-Os-H(02) = 178(2)º) and the carbonyl group *trans* to the oxygen atom of the diphosphine (O(1)-Os-C(28) = 178.0(2)º). According to the *trans*-dihydride and carbonyl nature of the compound, its IR contains ν(Os-H) and ν(CO) bands at 1688 and 1878 cm^{-1}, respectively. As expected for equivalent hydrides, the ^{1}H NMR spectrum, in benzene-d_6, at room temperature contains only one hydride resonance, which is observed at -4.08 ppm as a triplet with a H-P coupling constant of 17.7 Hz. In the ^{13}C{^{1}H} NMR spectrum, the most noticeable feature is the signal due to the carbonyl ligand, which appears at 186.0 ppm as a triplet with a C-P coupling constant of 7.8 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 70.8 ppm.

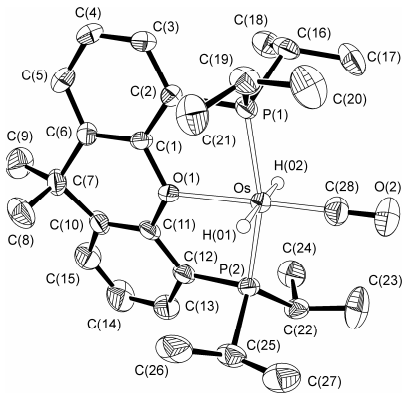


Figure 4. ORTEP diagram of complex **21** (50% probability ellipsoids). Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å) and angles (º): Os-P(1) = 2.2854(13), Os-P(2) = 2.2918(13), Os-O(1) = 2.253(3), Os-C(28) = 1.798(6), Os-H(01) = 1.586(10), Os-H(02) = 1.592(10); P(1)-Os-P(2) = 162.14(5), P(1)-Os-O(1) = 81.56(8), P(2)-Os-O(1) = 81.03(9), O(1)-Os-C(28) = 178.0(2), H(01)-Os-H(02) = 178(2).

CONCLUDING REMARKS

This study has revealed that the tetrahydride osmium complex OsH_4{xant(P^iPr_2)$_2$} and its ruthenium counterpart RuH(η^2-H_2BH_2){xant(P^iPr_2)$_2$} promote the *ortho*-C-H bond activation of aromatic and fluorinated aromatic ketones, the C_β-H bond activation of α,β-unsaturated ketones, and the OC-H bond activation of aldehydes to afford metalaisobenzofuran, metalafuran, hydride-phenyl-carbonyl, hydride-alkenyl-carbonyl and dihydride-carbonyl derivatives depending upon the nature of the substrates. Because the ruthenium precursor reduces C-O and C-C double bonds, 1.0 equiv of sacrificial substrate is necessary for the activation in this case.

Isotope labeling results suggest that the origin of the selectivity of the *ortho*-C-H bond activation of aromatic ketones is only thermodynamic, since the activations of the C-H bonds in

meta and *para* positions are kinetically preferred. In aromatic α,β-unsaturated ketones, the *ortho*-C-H bond activation is slightly favored over the C_β-H bond activation, from a thermodynamic point of view, for osmium whereas ruthenium does not show any preference. In contrast, both osmium and ruthenium favor the OC-H bond activation over the cleavage of an *ortho*-C-H bond in aromatic aldehydes. In this case, the C-H bond activation is the initial step for the decarbonylation of the substrate. Alkyl aldehydes undergo dehydrogenation of the substituent in addition to the decarbonylation process.

In conclusion, the M{xant(P^iPr_2)$_2$} (M = Os, Ru) fragments allow to generate species able of activating C-H bonds of carbonyl derivatives and to stabilize metalaisobenzofuran and metalafuran derivatives, among other interesting organometallic compounds.

EXPERIMENTAL SECTION

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Methanol was dried and distilled under argon. Other solvents were obtained oxygen- and water-free from an MBraun solvent purification apparatus. NMR spectra were recorded on a Varian Gemini 2000, a Bruker ARX 300 MHz, a Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}) or external standard (^{31}P{^{1}H} to 85 % H_3PO_4 and ^{19}F to $CFCl_3$). Coupling constants J and N ($N = J$(PH) + J(P'H) for ^{1}H and $N = J$(PC) + J(P'C) for ^{13}C{^{1}H}) are given in hertz. ^{13}C{^{1}H} NMR assignments were made with HSQC and HMBC spectra. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Elemental analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra (HRMS) were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). All reagents were purchased from commercial sources and used as received. OsH$_4${xant(P^iPr_2)$_2$} (**1**),[12d] RuH(η^2-H$_2$BH$_2$){xant(P^iPr_2)$_2$} (**4**)[12f] and 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant(P^iPr_2)$_2$)[12a] were prepared according to the published methods.

Reaction of OsH$_4${xant(P^iPr_2)$_2$} (1) with Benzophenone: Preparation of OsH{κ^2-C,O-[C$_6$H$_4$C(Ph)O]}{xant(P^iPr_2)$_2$} (2). A solution of **1** (63 mg, 0.099 mmol) in toluene (6 mL) was treated with the stoichiometric amount of benzophenone (18 mg, 0.099 mmol) and the resulting mixture was heated to reflux overnight. During this time the color of the mixture changed from colorless to deep purple. After being cooled at room temperature, the solution was evaporated to afford a purple residue. Addition of methanol (2 mL) at -78 ºC (dry ice/^{i}PrOH bath) afforded a purple solid that was washed with methanol (2 x 2 mL) and dried *in vacuo*. Yield: 60 mg (73%). Anal. Calcd. for $C_{40}H_{50}O_2OsP_2$: C, 58.95; H, 6.18. Found: C, 59.32; H, 6.02. HRMS (electrospray, *m/z*): calcd. for $C_{40}H_{49}O_2OsP_2$ [M – H]$^+$: 815.2820, found: 815.2838. IR (cm^{-1}): ν(Os-H) 2047 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.56 (d, J_{H-H} = 8.0, 1H, CH$_{arom}$), 8.11 (d, J_{H-H} = 8.1, 1H, CH$_{arom}$), 7.98 (d, J_{H-H} = 7.0, 2H, CH$_{arom}$), 7.21-7.09 (m, 5H, CH$_{arom}$-xant(P^iPr_2)$_2$ and CH$_{arom}$), 6.97 (dd, J_{H-H} = 7.5, J_{H-H} = 1.2, 2H, CH$_{arom}$-xant(P^iPr_2)$_2$), 6.87 (t, J_{H-H} = 7.5, 2H, CH$_{arom}$-xant(P^iPr_2)$_2$), 6.76 (t, J_{H-H} = 6.9, 1H, CH$_{arom}$), 6.66 (t, J_{H-H} = 8.1, 1H, CH$_{arom}$), 2.41 (m, 2H, PC*H*(CH$_3$)$_2$), 2.23 (m, 2H, PC*H*(CH$_3$)$_2$), 1.36 (s, 3H, CH$_3$), 1.34 (dvt, J_{H-H} = 6.7, N = 16.6, 6H, PCH(C*H*$_3$)$_2$), 1.18 (dvt, J_{H-H} = 7.0, N = 14.5, 6H, PCH(C*H*$_3$)$_2$), 1.11 (s, 3H, CH$_3$), 0.89 (dvt, J_{H-H} = 6.9, N = 14.1, 6H, PCH(C*H*$_3$)$_2$), 0.72 (dvt, J_{H-H} = 6.9, N = 15.6, 6H, PCH(C*H*$_3$)$_2$), -17.03 (t, J_{H-P} = 23.6, 1H, OsH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 205.3 (t, J_{C-P} = 2.2, CO), 187.4 (t, J_{C-P} = 4.3, OsC), 159.3 (vt, N = 12.8, C$_{arom}$-xant(P^iPr_2)$_2$), 149.8 (s, CH$_{arom}$), 140.6, 140.2 (both s, C$_{arom}$), 133.8 (s, CH$_{arom}$), 132.6 (vt, N = 5.3, C$_{arom}$-xant(P^iPr_2)$_2$), 129.8, 129.5, 129.3 (all s, CH$_{arom}$), 129.1 (s, CH$_{arom}$-xant(P^iPr_2)$_2$), 128.8 (vt, N = 28.7, C$_{ipso}$-xant(P^iPr_2)$_2$), 128.1 (s, CH$_{arom}$), 125.8 (s, CH$_{arom}$-xant(P^iPr_2)$_2$), 124.8 (vt, N = 4.4, CH$_{arom}$-xant(P^iPr_2)$_2$), 115.2 (s, CH$_{arom}$), 34.8 (s, C(CH$_3$)$_2$), 34.6 (s, *C*(CH$_3$)$_2$), 30.1 (vt, N = 18.1, PC*H*(CH$_3$)$_2$), 29.4 (vt, N = 33.9, PC*H*(CH$_3$)$_2$), 25.9 (s, C(*C*H$_3$)$_2$), 20.1 (vt, N = 6.8, PCH(*C*H$_3$)$_2$), 20.1 (s, PCH(*C*H$_3$)$_2$), 18.7 (vt, N = 7.5, PCH(*C*H$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 47.0 (s).

Reaction of OsH$_4${xant(P^iPr_2)$_2$} (1) with Perdeuterated Benzophenone. This reaction was carried out analogously as described for **2**, starting from **1** (75 mg, 0.118 mmol) and perdeuterated benzophenone (22.6 mg, 0.118 mmol). Purple solid. Yield: 65 mg. ^{1}H NMR (300 MHz, C_6D_6, 298 K, aromatic region, integrals with respect to one of the PC*H*(CH$_3$)$_2$ signals (2H)): δ 8.57 (d, J_{H-H} = 8.0, 0.8H, CH$_{arom}$), 8.12 (d, J_{H-H} = 8.1, 0.6H, CH$_{arom}$), 8.00 (d, J_{H-H} = 7.0, 1.2H, CH$_{arom}$).

Reaction of OsH$_4${xant(P^iPr_2)$_2$} (1) with Acetophenone: Preparation of OsH{κ^2-C,O-[C$_6$H$_4$C(CH$_3$)O]}{xant(P^iPr_2)$_2$} (3). This complex was prepared analogously as described for **2** starting from **1** (75 mg, 0.118 mmol) and acetophenone (15 μL, 0.118 mmol). Dark red solid. Yield: 61 mg (69%). Anal. Calcd. for $C_{35}H_{48}O_2OsP_2$: C, 55.83; H, 6.43. Found: C, 55.44; H, 6.12. HRMS (electrospray, *m/z*): calcd. for $C_{35}H_{47}O_2OsP_2$ [M – H]$^+$: 753.2662, found: 753.2959. IR (cm^{-1}): ν(Os-H) 2047 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.58 (d, J_{H-H} = 7.8, 1H, CH$_{arom}$), 7.81 (d, J_{H-H} = 7.8, 1H, CH$_{arom}$), 7.32 (m, 2H, CH$_{arom}$-xant(P^iPr_2)$_2$), 6.97 (dd, J_{H-H} = 7.8, J_{H-H} = 1.5, 2H, CH$_{arom}$-xant(P^iPr_2)$_2$), 6.87 (t, J_{H-H} = 7.5, 2H, CH$_{arom}$-xant(P^iPr_2)$_2$), 6.91 (t, J_{H-H} = 7.8, 1H, CH$_{arom}$), 6.80 (t, J_{H-H} = 7.8, 1H, CH$_{arom}$), 2.78 (s, 3H, COCH$_3$), 2.52 (m, 2H, PC*H*(CH$_3$)$_2$), 2.35 (m, 2H, PC*H*(CH$_3$)$_2$), 1.48 (s, 3H, CH$_3$), 1.45 (dvt, J_{H-H} = 9.6, N = 16.5, 6H, PCH(C*H*$_3$)$_2$), 1.29 (dvt, J_{H-H} = 7.5, N = 14.4, 6H, PCH(C*H*$_3$)$_2$), 1.23 (s, 3H, CH$_3$), 1.05 (dvt, J_{H-H} = 6.6, N = 13.5, 6H, PCH(C*H*$_3$)$_2$), 0.85 (dvt, J_{H-H} = 8.4, N = 15.3, 6H, PCH(C*H*$_3$)$_2$), -18.01 (t, J_{H-P} = 23.1, 1H, OsH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 206.9 (t, J_{C-P} = 1.8, CO), 184.3 (t, J_{C-P} = 4.4, OsC), 159.1 (vt, N = 13.5, C$_{arom}$-xant(P^iPr_2)$_2$), 149.3 (s, CH$_{arom}$), 141.9 (s, C$_{arom}$), 132.2 (vt, N = 5.5, C$_{arom}$-xant(P^iPr_2)$_2$), 131.4, 129.6 (both s, CH$_{arom}$), 128.8 (vt, N = 27.8, C$_{ipso}$-xant(P^iPr_2)$_2$), 128.8, 125.4 (both s, CH$_{arom}$-xant(P^iPr_2)$_2$), 124.5 (vt, N = 4.8, CH$_{arom}$-xant(P^iPr_2)$_2$), 114.1 (s, CH$_{arom}$), 34.6 (s, C(*C*H$_3$)$_2$), 34.2 (t, J_{C-P} = 0.8, *C*(CH$_3$)$_2$), 29.5 (vt, N = 17.9, P*C*H(CH$_3$)$_2$), 29.2 (vt, N = 32.9, P*C*H(CH$_3$)$_2$), 25.6 (s, C(*C*H$_3$)$_2$), 22.5 (t, J_{C-P} = 1.0, CO*C*H$_3$), 19.9 (vt, N = 6.9, PCH(*C*H$_3$)$_2$), 19.8 (s, PCH(*C*H$_3$)$_2$), 18.5 (vt, N = 6.8, PCH(*C*H$_3$)$_2$), 18.5 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 46.3 (s).

Reaction of RuH(η^2-H$_2$BH$_2$){xant(P^iPr_2)$_2$} (4) with Benzophenone: Preparation of RuH{κ^2-C,O-[C$_6$H$_4$C(Ph)O]}{xant(P^iPr_2)$_2$} (5). A solution of **4** (70 mg, 0.125 mmol) in toluene (10 mL) was treated with benzophenone (45 mg, 0.250 mmol) and 2-propanol (10 μL, 0.125 mmol). The mixture was stirred at 80 ºC for 6 h, and the color of the mixture changed from yellow to purple. After this time the mixture was cooled to room temperature and the solvent was dried *in vacuo* and dissolved in diethyl ether. The resulting purple solution is filtered through an alumina column and the filtrate is evaporated to dryness. Methanol (2 mL) was added to afford a purple solid that was washed with methanol (3 x 2 mL), and finally was dried *in vacuo*. Yield: 55 mg (61 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of diphenylmethanol. Anal. Calcd. for $C_{40}H_{50}O_2P_2Ru$: C, 66.19; H, 6.94. Found: C, 65.82; H, 7.10. IR (cm^{-1}): ν(Ru-H) 1944 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.54 (d, J_{H-H} = 8.0, 1H, CH$_{arom}$), 8.00 (d, J_{H-H} = 8.0, 1H, CH$_{arom}$), 7.94 (d, J_{H-H} = 6.9, 2H, CH$_{arom}$), 7.28–6.88 (m, 10H, CH$_{arom}$ and CH$_{arom}$-xant(P^iPr_2)$_2$), 6.69 (t, J_{H-H} = 6.9, 1H, CH$_{arom}$), 2.42 (m, 2H, PC*H*(CH$_3$)$_2$), 2.10 (m, 2H, PC*H*(CH$_3$)$_2$), 1.37 (s, 3H, CH$_3$), 1.36 (dvt, J_{H-H} = 6.8, N = 16.4, 6H, PCH(C*H*$_3$)$_2$), 1.23 (dvt, J_{H-H} = 6.8, N = 14.3, 6H, PCH(C*H*$_3$)$_2$), 1.10 (s, 3H, CH$_3$), 0.92 (dvt, J_{H-H} = 7.1, N = 13.7, 6H, PCH(C*H*$_3$)$_2$), 0.76 (dvt, J_{H-H} = 6.9, N = 15.3, 6H, PCH(C*H*$_3$)$_2$), -15.42 (t, J_{H-P} = 26.1, 1H, RuH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 212.4 (t, J_{C-P} = 8.4, RuC), 195.7 (s, CO), 158.0 (vt, N = 14.3, *C*$_{arom}$-xant(P^iPr_2)$_2$), 147.7 (s, CH$_{arom}$), 144.9, 138.8 (both s, *C*$_{arom}$), 133.8 (s, CH$_{arom}$), 132.7 (vt, N = 4.4, *C*$_{arom}$-xant(P^iPr_2)$_2$), 132.1 (s, *C*H$_{arom}$-xant(P^iPr_2)$_2$), 129.4, 129.3, 128.7 (all s, CH$_{arom}$), 128.1 (this resonance is masked by the resonance of C_6D_6, *C*$_{ipso}$-xant(P^iPr_2)$_2$), 127.5 (s, *C*H$_{arom}$-xant(P^iPr_2)$_2$), 125.7 (s, CH$_{arom}$), 124.4 (vt, N = 3.9, *C*H$_{arom}$-xant(P^iPr_2)$_2$), 116.0 (s, CH$_{arom}$), 34.8 (s, *C*(CH$_3$)$_2$), 34.6 (s, C(*C*H$_3$)$_2$), 29.3 (vt, N = 12.8, P*C*H(CH$_3$)$_2$), 28.9 (vt, N = 27.9,

P*C*H(CH$_3$)$_2$), 25.6 (s, C(*C*H$_3$)$_2$), 20.1, 20.0 (both s, PCH(*C*H$_3$)$_2$), 19.0 (vt, *N* = 9.2, PCH(*C*H$_3$)$_2$), 18.8 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 62.8 (s).

Reaction of RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (4) with Perdeuterated Benzophenone. This reaction was carried out analogously as described for **5**, starting from **4** (70 mg, 0.125 mmol) and perdeuterated benzophenone (48.1 mg, 0.250 mmol). Purple solid. Yield: 50 mg. ^{1}H NMR (300 MHz, C_6D_6, 298 K, aromatic and hydride region, integrals with respect to one of the PC*H*(CH$_3$)$_2$ signals (2H)): δ 8.54 (d, $J_{H\text{-}H}$ = 8.0, 0.6H, CH$_{arom}$), 8.00 (d, $J_{H\text{-}H}$ = 8.1, 0.2H, CH$_{arom}$), 7.95 (d, $J_{H\text{-}H}$ = 7.0, 0.4H, CH$_{arom}$), -15.42 (t, $J_{H\text{-}P}$ = 26.1, 0.5H, RuH).

Reaction of RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (4) with Acetophenone: Preparation of RuH{κ^2-C,O-[C$_6$H$_4$C(CH$_3$)O]}{xant(P^{i}Pr$_2$)$_2$} (6). This complex was prepared analogously as described for **5** starting from **4** (75 mg, 0.134 mmol), acetophenone (31 μL, 0.268 mmol) and 2-propanol (10 μL, 0.134 mmol). Dark red solid. Yield: 46 mg (52 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of 1-phenylethanol. Anal. Calcd. for $C_{35}H_{48}O_2P_2Ru$: C, 63.06; H, 6.35. Found: C, 62.75; H, 6.51. HRMS (electrospray, *m*/*z*): calcd. for $C_{35}H_{47}O_2P_2Ru$ [M - H]$^+$: 663.2099, found: 663.2052. IR (cm^{-1}): ν(Ru-H) 2030 (s).^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.43 (d, $J_{H\text{-}H}$ = 8.1, 1H, CH$_{arom}$), 7.75 (m, 1H, CH$_{arom}$), 7.66 (d, $J_{H\text{-}H}$ = 8.1, 1H, CH$_{arom}$), 7.23 (m, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 7.14-6.87 (m, 4H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.71 (t, $J_{H\text{-}H}$ = 8.1, 1H, CH$_{arom}$), 2.50 (t, $J_{H\text{-}P}$ = 1.5, 3H, COCH$_3$), 2.40 (m, 2H, PC*H*(CH$_3$)$_2$), 1.91 (m, 2H, PC*H*(CH$_3$)$_2$), 1.37 (s, 3H, CH$_3$), 1.33 (dvt, $J_{H\text{-}H}$ = 6.9, *N* = 16.2, 6H, PCH(C*H*$_3$)$_2$), 1.20 (dvt, $J_{H\text{-}H}$ = 6.9, *N* = 14.4, 6H, PCH(C*H*$_3$)$_2$), 1.10 (s, 3H, CH$_3$), 0.95 (dvt, $J_{H\text{-}H}$ = 6.9, *N* = 13.2, 6H, PCH(C*H*$_3$)$_2$), 0.76 (dvt, $J_{H\text{-}H}$ = 7.2, *N* = 15.3, 6H, PCH(C*H*$_3$)$_2$), -16.36 (t, $J_{H\text{-}P}$ = 27.0, 1H, RuH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 209.0 (t, $J_{C\text{-}P}$ = 8.6, RuC), 201.8 (t, $J_{C\text{-}P}$ = 2.1, CO), 158.1 (vt, *N* = 16.6, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 147.6 (s, CH$_{arom}$), 142.9 (s, C$_{arom}$), 132.6 (vt, *N* = 4.3, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 131.2 (s, CH$_{arom}$), 129.1, 128.7 (both s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 128.2 (this resonance is masked by the resonance of C_6D_6, C$_{ipso}$-xant(P^{i}Pr$_2$)$_2$), 126.3 (s, CH$_{arom}$), 124.3 (s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 115.5 (s, CH$_{arom}$), 34.7 (s, *C*(CH$_3$)$_2$), 34.6 (s, C(*C*H$_3$)$_2$), 30.5 (s, CO*C*H$_3$), 29.2 (vt, *N* = 12.1, P*C*H(CH$_3$)$_2$), 28.9 (vt, *N* = 27.9, P*C*H(CH$_3$)$_2$), 26.1 (s, C(*C*H$_3$)$_2$), 20.1 (vt, *N* = 7.5, PCH(*C*H$_3$)$_2$), 19.9 (s, PCH(*C*H$_3$)$_2$), 19.1 (vt, *N* = 9.8, PCH(*C*H$_3$)$_2$), 18.8 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 62.1 (s).

Reaction of OsH$_4$(xant(P^{i}Pr$_2$)$_2$} (1) with 2-Fluoroacetophenone: Preparation of OsH{κ^2-C,O-[C$_6$H$_3$FC(Me)O]}{xant(P^{i}Pr$_2$)$_2$} (7). This complex was prepared analogously as described for **2** starting from **1** (80 mg, 0.126 mmol) and 2-fluoroacetophenone (16 μL, 0.126 mmol). Dark red solid. Yield: 29 mg (30%). Anal. Calcd. for $C_{35}H_{47}FO_2OsP_2$: C, 54.53; H, 6.14. Found: C, 54.32; H, 6.38. HRMS (electrospray, *m*/*z*): calcd. for $C_{35}H_{46}FO_3OsP_2$ [M – H + O]$^+$: 787.2517, found: 787.2638. IR (cm^{-1}): ν(Os-H) 2034 (s). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 8.17 (d, $J_{H\text{-}H}$ = 8.1, 1H, CH$_{arom}$), 7.16-6.96 (m, 4H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.88 (t, $J_{H\text{-}H}$ = 7.6, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.61 (dt, $J_{H\text{-}H}$ = 6.8, $J_{H\text{-}F}$ = 7.6, 1H, CH$_{arom}$), 6.33 (dd, $J_{H\text{-}H}$ = 7.6, $J_{H\text{-}F}$ = 12.4, 1H, CH$_{arom}$), 3.09 (d, $J_{H\text{-}F}$ = 3.6, 3H, COCH$_3$), 2.40 (m, 2H, PC*H*(CH$_3$)$_2$), 2.19 (m, 2H, PC*H*(CH$_3$)$_2$), 1.36 (s, 3H, CH$_3$), 1.29 (dvt, $J_{H\text{-}H}$ = 8.4, *N* = 16.0, 6H, PCH(C*H*$_3$)$_2$), 1.16 (dvt, $J_{H\text{-}H}$ = 7.2, *N* = 14.4, 6H, PCH(C*H*$_3$)$_2$), 1.10 (s, 3H, CH$_3$), 0.91 (dvt, $J_{H\text{-}H}$ = 6.8, *N* = 13.6, 6H, PCH(C*H*$_3$)$_2$), 0.74 (dvt, $J_{H\text{-}H}$ = 8.4, *N* = 15.2, 6H, PCH(C*H*$_3$)$_2$), -17.83 (t, $J_{H\text{-}P}$ = 22.8, 1H, OsH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ 205.5 (s, CO), 188.5 (dt, $J_{C\text{-}F}$ = 4.2, $J_{C\text{-}P}$ = 4.1, OsC), 166.5 (d, $J_{C\text{-}F}$ = 256.3, C-F), 159.3 (vt, *N* = 13.1, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$) 145.6 (d, $J_{C\text{-}F}$ = 2.5, CH$_{arom}$), 132.5 (vt, *N* = 5.3, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 131.1 (d, $J_{C\text{-}F}$ = 5.1, C$_{arom}$), 130.8 (d, $J_{C\text{-}F}$ = 9.6, CH$_{arom}$), 129.1 (s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 128.6 (vt, *N* = 28.7, C$_{ipso}$-xant(P^{i}Pr$_2$)$_2$), 125.8 (s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 124.8 (vt, *N* = 4.6, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 99.1 (d, $J_{C\text{-}F}$ = 21.9, CH$_{arom}$), 34.8 (s, C(*C*H$_3$)$_2$), 34.5 (s, *C*(CH$_3$)$_2$), 29.5 (vt, *N* = 18.7, P*C*H(CH$_3$)$_2$), 29.1 (vt, *N* = 33.3, P*C*H(CH$_3$)$_2$), 27.7 (d, $J_{C\text{-}F}$ = 9.1, CO*C*H$_3$), 25.8 (s, C(*C*H$_3$)$_2$), 19.9 (s, PCH(*C*H$_3$)$_2$), 19.8 (vt, *N* = 6.4, PCH(*C*H$_3$)$_2$), 18.7 (vt, *N* = 7.4, PCH(*C*H$_3$)$_2$), 18.5 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 46.2 (s). ^{19}F{^{1}H} NMR (282.33 MHz, C_6D_6, 298 K): δ -113.4 (s).

Reaction of OsH$_4$(xant(P^{i}Pr$_2$)$_2$} (1) with 2,6-Difluorobenzophenone: Preparation of OsH{κ^2-C,O-[C$_6$H$_4$C(C$_6$H$_3$F$_2$)O]}{xant(P^{i}Pr$_2$)$_2$} (8). This complex was prepared analogously as described for **2** starting from **1** (60 mg, 0.094 mmol) and 2,6-difluorobenzophenone (18 μL, 0.094 mmol). Purple solid. Yield: 58 mg (72%). Anal. Calcd. for $C_{40}H_{48}F_2O_2OsP_2$: C, 56.42; H, 5.69. Found: C, 56.12; H, 6.02. HRMS (electrospray, *m*/*z*): calcd. for $C_{40}H_{47}F_2O_2OsP_2$ [M - H]$^+$: 851.2631, found: 851.2669. IR (cm^{-1}): ν(Os-H) 2096 (m). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.50 (d, $J_{H\text{-}H}$ = 7.5, 1H, CH$_{arom}$), 7.69 (d, $J_{H\text{-}H}$ = 7.5, 1H, CH$_{arom}$), 7.18 (m, 2H, 2 CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.96 (d, $J_{H\text{-}H}$ = 7.5, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.86 (t, $J_{H\text{-}H}$ = 7.5, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.71 (t, $J_{H\text{-}H}$ = 7.5, 1H, CH$_{arom}$), 6.57 (m, 4H, CH$_{arom}$), 2.47 (m, 2H, PC*H*(CH$_3$)$_2$), 2.25 (m, 2H, PC*H*(CH$_3$)$_2$), 1.37 (s, 3H, CH$_3$), 1.29 (dvt, $J_{H\text{-}H}$ = 8.7, *N* = 16.2, 6H, PCH(C*H*$_3$)$_2$), 1.21 (dvt, $J_{H\text{-}H}$ = 7.5, *N* = 14.7, 6H, PCH(C*H*$_3$)$_2$), 1.06 (s, 3H, CH$_3$), 1.00 (dvt, $J_{H\text{-}H}$ = 6.6, *N* = 13.4, 6H, PCH(C*H*$_3$)$_2$), 0.88 (dvt, $J_{H\text{-}H}$ = 8.4, *N* = 15.6, 6H, PCH(C*H*$_3$)$_2$), -17.33 (t, $J_{H\text{-}P}$ = 23.9, 1H, OsH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 194.5 (t, $J_{C\text{-}P}$ = 2.2, CO), 188.1 (t, $J_{C\text{-}P}$ = 3.7, OsC), 161.0 (dd, $J_{C\text{-}F}$ = 249.1, $J_{C\text{-}P}$ = 7.3, C-F), 160.0 (m, C$_{arom}$ and C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 149.6 (s, CH$_{arom}$), 142.6 (s, C$_{arom}$), 133.2 (s, CH$_{arom}$), 133.1 (s, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 130.1 (t, $J_{C\text{-}F}$ = 19.7, CH$_{arom}$), 129.7 (s, CH$_{arom}$), 128.9 (s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$ 127.9 (this resonance is masked by the resonance of C_6D_6, C$_{ipso}$-xant(P^{i}Pr$_2$)$_2$), 125.3 (s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 124.9 (vt, *N* = 4.6, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 115.4 (s, CH$_{arom}$), 111.5 (d, $J_{C\text{-}F}$ = 25.4, CH$_{arom}$), 34.8 (s, C(*C*H$_3$)$_2$), 34.3 (s, *C*(CH$_3$)$_2$), 28.7 (vt, *N* = 18.1, P*C*H(CH$_3$)$_2$), 28.5 (vt, *N* = 29.5, P*C*H(CH$_3$)$_2$), 24.1 (s, C(*C*H$_3$)$_2$), 20.0 (s, PCH(*C*H$_3$)$_2$), 19.6 (vt, *N* = 16.4, PCH(*C*H$_3$)$_2$), 18.8 (vt, *N* = 8.6, PCH(*C*H$_3$)$_2$), 18.2 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 48.5 (s). ^{19}F NMR (282.33 MHz, C_6D_6, 298 K): δ -109.2 (s).

Reaction of RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (4) with 2-Fluoroacetophenone: Preparation of RuH{κ^2-C,O-[C$_6$H$_3$FC(Me)O]}{xant(P^{i}Pr$_2$)$_2$} (9). This complex was prepared analogously as described for **5** starting from **4** (70 mg, 0.125 mmol), 2-fluoroacetophenone (30 μL, 0.250 mmol) and 2-propanol (10 μL, 0.125 mmol). Red solid. Yield: 32 mg (38 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of 1-(2-fluorophenyl)ethanol. Anal. Calcd. for $C_{35}H_{47}FO_2P_2Ru$: C, 61.66; H, 6.95. Found: C, 61.28; H, 6.81. HRMS (electrospray, *m*/*z*): calcd. for $C_{35}H_{46}FO_2P_2Ru$ [M - H]$^+$: 681.2005, found: 681.2014. IR (cm^{-1}): ν(Ru-H) 2016 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.14 (d, $J_{H\text{-}H}$ = 7.8, 1H, CH$_{arom}$), 7.21 (m, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 7.02 (dd, $J_{H\text{-}H}$ = 7.6, $J_{H\text{-}H}$ = 1.5, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.90 (t, $J_{H\text{-}H}$ = 7.5, 2H, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 6.77 (dt, $J_{H\text{-}F}$ = 6.0, $J_{H\text{-}H}$ = 7.8, 1H, CH$_{arom}$), 6.33 (dd, $J_{H\text{-}H}$ = 7.8, $J_{H\text{-}F}$ = 12.5, 1H, CH$_{arom}$), 2.89 (dt, $J_{H\text{-}F}$ = 4.8, $J_{H\text{-}P}$ = 1.6, 3H, CH$_3$), 2.40 (m, 2H, PC*H*(CH$_3$)$_2$), 2.07 (m, 2H, PC*H*(CH$_3$)$_2$), 1.36 (s, 3H, CH$_3$), 1.29 (dvt, $J_{H\text{-}H}$ = 6.9, *N* = 16.5, 6H, PCH(C*H*$_3$)$_2$), 1.21 (dvt, $J_{H\text{-}H}$ = 7.2, *N* = 14.7, 6H, PCH(C*H*$_3$)$_2$), 1.08 (s, 3H, CH$_3$), 0.94 (dvt, $J_{H\text{-}H}$ = 6.9, *N* = 13.5, 6H, PCH(C*H*$_3$)$_2$), 0.77 (dvt, $J_{H\text{-}H}$ = 6.9, *N* = 15.6, 6H, PCH(C*H*$_3$)$_2$), -16.11 (t, $J_{H\text{-}P}$ = 25.6, RuH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 213.7 (dt, $J_{C\text{-}F}$ = 6.0, $J_{C\text{-}P}$ = 8.3, RuC), 200.0 (dt, $J_{C\text{-}F}$ = 6.0, $J_{C\text{-}P}$ = 1.5, CO), 165.7 (d, $J_{C\text{-}F}$ = 259.0, C-F), 158.1 (vt, *N* = 14.3, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 143.3 (d, $J_{C\text{-}F}$ = 2.3, CH$_{arom}$), 132.7 (vt, *N* = 5.3, C$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 131.2 (d, $J_{C\text{-}F}$ = 4.5, C$_{arom}$), 130.4 (s, CH$_{arom}$), 129.1, 128.7 (both s, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 127.1 (vt, *N* = 20.4, C$_{ipso}$-xant(P^{i}Pr$_2$)$_2$), 124.4 (vt, *N* = 3.8, CH$_{arom}$-xant(P^{i}Pr$_2$)$_2$), 100.9 (d, $J_{C\text{-}F}$ = 22.7, CH$_{arom}$), 34.7 (s, *C*(CH$_3$)$_2$), 34.5 (s, C(*C*H$_3$)$_2$), 29.2 (d, $J_{C\text{-}F}$ = 9.6, CO*C*H$_3$), 29.0 (vt, *N* = 12.9, P*C*H(CH$_3$)$_2$), 28.6 (vt, *N* = 27.8, P*C*H(CH$_3$)$_2$), 25.4 (s, C(*C*H$_3$)$_2$), 20.0 (s, PCH(*C*H$_3$)$_2$), 19.9 (vt, *N* = 7.6, PCH(*C*H$_3$)$_2$), 19.0 (vt, *N* = 9.0, PCH(*C*H$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 62.1 (s). ^{19}F NMR (282.33 MHz, C_6D_6, 298 K): δ -109.1 (m).

Reaction of OsH$_4$(xant(P^{i}Pr$_2$)$_2$} (1) with Benzylideneacetone: Preparation of OsH{κ^2-C,O-[C(Ph)CHC(Me)O]}{xant(P^{i}Pr$_2$)$_2$} (10). A solution of **1** (80 mg, 0.126 mmol) in toluene (10 mL) was treated with benzylideneacetone (37 mg, 0.251 mmol) and the resulting mixture was heated to reflux overnight, getting a dark green solution. After being cooled at room temperature, the solution was

evaporated to afford an oily residue. While cooling on a dry ice/ ^{i}PrOH bath, addition of pentane (2 mL) afforded a dark green solid that was washed with pentane (2 x 2 mL) and dried *in vacuo*. Yield: 88 mg (90%). Anal. Calcd. for $C_{37}H_{50}O_2OsP_2$: C, 57.05; H, 6.47. Found: C, 56.84; H, 6.41. HRMS (electrospray, *m/z*): calcd. for $C_{37}H_{49}O_3OsP_2$ $[M - H + O]^+$: 795.2768, found: 795.2732. IR (cm^{-1}): ν(Os-H) 2050 (w). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.73 (d, J_{H-H} = 7.3, 2H, CH_{arom}), 7.48 (t, J_{H-H} = 6.0, 1H, CH_{arom}), 7.45 (s, OsC=CH), 7.36–7.27 (m, 4H, CH_{arom} and CH_{arom}-xant(P^iPr_2)$_2$), 7.09 (dd, J_{H-H} = 7.5, J_{H-H} = 1.2, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 6.98 (t, J_{H-H} = 7.5, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 2.65 (m, 2H, PC*H*(CH_3)$_2$), 2.59 (t, J_{H-P} = 1.5, 3H, $COCH_3$) 2.49 (m, 2H, PC*H*(CH_3)$_2$), 1.45, 1.20 (both s, 3H, CH_3), 1.26-1.02 (dvts, overlapping, 24H, PCH(C*H*$_3$)$_2$), -17.11 (t, J_{H-P} = 23.4, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 224.7 (t, J_{C-P} = 3.2, OsC), 194.5 (t, J_{C-P} = 1.7, CO), 158.0 (vt, *N* = 13.1, C_{arom}-xant(P^iPr_2)$_2$), 156.7 (s, C_{arom}), 131.8 (vt, *N* = 5.4, C_{arom}-xant(P^iPr_2)$_2$), 130.3 (s, CH_{arom}), 129.2 (s, CH_{arom}-xant(P^iPr_2)$_2$), 128.4 (s, CH_{arom}), 127.9 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^iPr_2)$_2$), 127.2 (s, CH_{arom}), 126.3 (s, CH_{arom}-xant(P^iPr_2)$_2$), 124.6 (s, OsC*C*H), 124.4 (vt, *N* = 4.9, CH_{arom}-xant(P^iPr_2)$_2$), 34.7 (s, C(*C*H$_3$)$_2$), 34.1 (s, *C*(CH$_3$)$_2$), 29.1 (vt, *N* = 20.0, P*C*H(CH$_3$)$_2$), 28.7 (vt, *N* = 33.4, P*C*H(CH$_3$)$_2$), 27.2 (s, C(*C*H$_3$)$_2$), 23.9 (s, CO*C*H$_3$), 18.7 (s, PCH(*C*H$_3$)$_2$), 18.5 (vt, *N* = 4.6, PCH(*C*H$_3$)$_2$), 18.1 (vt, *N* = 7.7, PCH(*C*H$_3$)$_2$), 17.9 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 46.8 (s).

Reaction of OsH_4{xant(P^iPr_2)$_2$} (1) with Methyl Vinyl Ketone: Preparation of OsH{κ^2-C,O-[C(H)CHC(Me)O]}{xant(P^iPr_2)$_2$} (11). This complex was prepared analogously as described for **10** starting from **1** (80 mg, 0.126 mmol) and methyl vinyl ketone (20 μL, 0.126 mmol). Dark green solid. Yield: 57 mg (64%). Anal. Calcd. for $C_{31}H_{46}O_2OsP_2$: C, 52.97; H, 6.60. Found: C, 52.52; H, 7.07. HRMS (electrospray, *m/z*): calcd. for $C_{31}H_{45}O_2OsP_2$ $[M - H]^+$: 703.2506, found: 703.2522. IR (cm^{-1}): ν(Os-H) 2035 (w). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 14.05 (dd, J_{H-H} = 6.3, J_{H-H} = 1.5, 1H, OsCH), 7.17 (m, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 7.00–6.96 (m, 3H, CH_{arom}-xant(P^iPr_2)$_2$ and OsCHC*H*), 6.91(t, J_{H-H} = 7.2, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 2.58 (t, J_{H-P} = 1.2, 3H, $COCH_3$), 2.44 (m, 2H, PC*H*(CH_3)$_2$), 2.26 (m, 2H, PC*H*(CH_3)$_2$), 1.48 (s, 3H, CH_3), 1.52-1.35 (dvts, overlapping, 12H, PCH(C*H*$_3$)$_2$), 1.20 (s, 3H, CH_3), 1.26-1.07 (dvts, overlapping, 12H, PCH(C*H*$_3$)$_2$), -17.81 (dt, J_{H-H} = 1.5, J_{H-P} = 23.1, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 213.8 (t, J_{C-P} = 3.0, OsCH), 193.5 (s, CO), 158.7 (vt, *N* = 13.7, C_{arom}-xant(P^iPr_2)$_2$), 132.6 (vt, *N* = 5.3, C_{arom}-xant(P^iPr_2)$_2$), 128.9 (s, CH_{arom}-xant(P^iPr_2)$_2$), 127.9 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^iPr_2)$_2$), 125.5 (s, OsCH*C*H), 125.4 (s, CH_{arom}-xant(P^iPr_2)$_2$), 124.7 (vt, *N* = 4.3, CH_{arom}-xant(P^iPr_2)$_2$), 34.5 (s, *C*(CH$_3$)$_2$), 34.4 (s, C(*C*H$_3$)$_2$), 31.3 (vt, *N* = 19.9, P*C*H(CH$_3$)$_2$), 27.6 (vt, *N* = 34.9, P*C*H(CH$_3$)$_2$), 24.6 (s, C(*C*H$_3$)$_2$), 23.3 (s, CO*C*H$_3$), 20.5 (vt, *N* = 9.8, PCH(*C*H$_3$)$_2$), 19.5 (s, PCH(*C*H$_3$)$_2$), 18.7 (vt, *N* = 7.0, PCH(*C*H$_3$)$_2$), 18.5 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 57.7 (s).

Reaction of RuH(η^2-H_2BH_2){xant(P^iPr_2)$_2$} with Benzylideneacetone: Preparation of RuH{κ^2-C,O-[C(Ph)CHC(Me)O]}{xant(P^iPr_2)$_2$} (12). This complex was prepared analogously as described for **5** starting from **4** (80 mg, 0.143 mmol), benzylidenacetone (42 mg, 0.286 mmol) and 2-propanol (11 μL, 0.143 mmol). Dark green solid. Yield: 74 mg (75 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of 4-phenyl-2-butanone Anal. Calcd. for $C_{37}H_{50}O_2P_2Ru$: C, 64.42; H, 7.31. Found: C, 64.28; H, 6.91. HRMS (electrospray, *m/z*): calcd. for $C_{37}H_{49}O_2P_2Ru$ $[M - H]^+$: 689.2256, found: 689.2247. IR (cm^{-1}): ν(Ru-H) 1949 (w). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.50 (d, J_{H-H} = 7.1, 2H, CH_{arom}), 7.34 (t, J_{H-H} = 7.2, 2H, CH_{arom}), 7.29 (s, 1H, RuCCH), 7.23–6.98 (m, 5H, CH_{arom}), 6.90 (t, J_{H-H} = 7.5, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 2.37, 2.30 (both m, 4H, PC*H*(CH_3)$_2$), 1.56 (s, 3H, $COCH_3$), 1.35 (s, 3H, CH_3), 1.13 (dvt, J_{H-H} = 6.9, *N* = 12.3, 6H, PCH(C*H*$_3$)$_2$), 1.12 (s, 3H, CH_3), 1.10–0.95 (3 dvt overlapped, 18H, PCH(C*H*$_3$)$_2$), -15.35 (t, J_{H-P} = 26.1, 1H, RuH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 255.0 (t, J_{C-P} = 6.3, RuC), 192.7 (t, J_{C-P} = 2.3, CO), 156.8 (vt, *N* = 15.1, C_{arom}-xant(P^iPr_2)$_2$), 153.6 (s, C_{arom}), 132.0 (vt, *N* = 5.4, C_{arom}-xant(P^iPr_2)$_2$), 130.0 (s, CH_{arom}-xant(P^iPr_2)$_2$), 129.5, 127.3, 126.6 (all s, CH_{arom}), 126.4 (s, CH_{arom}-xant(P^iPr_2)$_2$), 126.3 (vt, *N* = 20.2, C_{ipso}-xant(P^iPr_2)$_2$), 124.2 (vt, *N* = 4.2, CH_{arom}-xant(P^iPr_2)$_2$), 123.6 (s, RuC*C*H), 34.8 (s, C(*C*H$_3$)$_2$), 34.5 (s, *C*(CH$_3$)$_2$), 28.5 (vt, *N* = 14.3, P*C*H(CH$_3$)$_2$), 28.3 (vt, *N* = 27.9, P*C*H(CH$_3$)$_2$), 27.6 (s, C(*C*H$_3$)$_2$), 25.4 (s, CO*C*H$_3$), 19.0 (vt, *N* = 5.7, PCH(*C*H$_3$)$_2$), 18.9 (s, PCH(*C*H$_3$)$_2$), 18.7 (vt, *N* = 9.1, PCH(*C*H$_3$)$_2$), 18.4 (vt, *N* = 2.5, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 63.2 (s).

Reaction of RuH(η^2-H_2BH_2){xant(P^iPr_2)$_2$} (4) with Methyl Vinyl Ketone: Preparation of RuH{κ^2-C,O-[C(H)CHC(Me)O]}{xant(P^iPr_2)$_2$} (13). This complex was prepared analogously as described for **5** starting from **4** (90 mg, 0.161 mmol), methyl vinyl ketone (26 μL, 0.322 mmol) and 2-propanol (12 μL, 0.161 mmol). Dark yellow solid. Yield: 51 mg (52 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of 2-butanone. Anal. Calcd. for $C_{31}H_{46}O_2P_2Ru$: C, 60.67; H, 7.55. Found: C, 60.35; H, 7.82. IR (cm^{-1}): ν(Os-H) 1924 (w). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 12.67 (dd, J_{H-H} = 6.0, J_{H-H} = 1.0, 1H, RuCH), 7.12 (m, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 7.07–7.00 (m, 3H, CH_{arom}-xant(P^iPr_2)$_2$ y RuCHC*H*), 6.91 (t, J_{H-H} = 7.5, 2H, CH_{arom}-xant(P^iPr_2)$_2$), 2.38 (t, J_{H-P} = 1.8, 3H, $COCH_3$), 2.22 - 2.10 (both m, 4H, PC*H*(CH_3)$_2$), 1.40 (dvt, J_{H-H} = 6.9, *N* = 18.0, 6H, PCH(C*H*$_3$)$_2$), 1.36, 1.29 (both s, 3H, CH_3), 1.11–1.01 (3 dvts overlapped, 18H, PCH(C*H*$_3$)$_2$), -15.96 (t, J_{H-P} = 26.1, 1H, RuH). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 245.6 (t, J_{C-P} = 7.4, RuC), 191.6 (s, CO), 157.9 (vt, *N* = 15.7, C_{arom}-xant(P^iPr_2)$_2$), 133.0 (vt, *N* = 5.6, C_{arom}-xant(P^iPr_2)$_2$), 128.7 (s, CH_{arom}-xant(P^iPr_2)$_2$), 126.8 (vt, *N* = 25.5, C_{ipso}-xant(P^iPr_2)$_2$), 126.1 (s, RuCH*C*H), 125.5 (s, CH_{arom}-xant(P^iPr_2)$_2$), 124.4 (vt, *N* = 4.3, CH_{arom}-xant(P^iPr_2)$_2$), 34.8 (s, *C*(CH$_3$)$_2$), 34.4 (s, C(*C*H$_3$)$_2$), 30.8 (vt, *N* = 13.9, P*C*H(CH$_3$)$_2$), 27.4 (vt, *N* = 29.8, P*C*H(CH$_3$)$_2$), 25.0 (s, CO*C*H$_3$), 24.5 (s, C(*C*H$_3$)$_2$), 20.7 (vt, *N* = 11.8, PCH(*C*H$_3$)$_2$), 19.9 (s, PCH(*C*H$_3$)$_2$), 19.3 (vt, *N* = 8.4, PCH(*C*H$_3$)$_2$), 18.9 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 71.5 (s).

Reaction of OsH_4{xant(P^iPr_2)$_2$} (1) with Benzylideneacetophenone: Preparation of OsH{κ^2-C,O-[C_6H_4C(CH=CHPh)O]}{xant(P^iPr_2)$_2$} (14) and OsH{κ^2-C,O-[C(Ph)CHC(Ph)O]}{xant(P^iPr_2)$_2$} (15). These complexes were prepared analogously as described for **2** starting from **1** (75 mg, 0.118 mmol) and benzylideneacetophenone (25 mg, 0.118 mmol). Dark red solid. ^{1}H and ^{31}P{^{1}H} NMR spectroscopies show a 2:1 mixture of complexes **14** and **15**. Yield: 63 mg (64%). Anal. Calcd. for $C_{42}H_{52}O_2OsP_2$: C, 59.98; H, 6.23. Found: C, 59.65; H, 5.82. HRMS (electrospray, *m/z*): calcd. for $C_{42}H_{51}O_2OsP_2$ $[M - H]^+$: 841.2976, found: 841.3110. IR (cm^{-1}): ν(Os-H) 2047 (w).

Spectroscopic data for OsH{κ^2-C,O-[C_6H_4C(CH=CHPh)O]}{xant(P^iPr_2)$_2$} (**14**): ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.46 (d, J_{H-H} = 8.0, 1H, C*H*=CHPh), 8.39 (d, J_{H-H} = 7.2, 2H, CH_{arom}), 7.79 (m, 1H, CH_{arom}), 7.38–6.65 (13H, CH_{arom}, CH=C*H*Ph and CH_{arom}-xant(P^iPr_2)$_2$), 2.41 (m, 2H, PC*H*(CH_3)$_2$), 2.21 (m, 2H, PC*H*(CH_3)$_2$), 1.39 (s, 3H, CH_3), 1.30 (dvt, 6H, J_{H-H} = 5.0, *N* = 16.5, PCH(C*H*$_3$)$_2$), 1.15 (dvt, overlapped, 6H, PCH(C*H*$_3$)$_2$), 1.12 (s, 3H, CH_3), 1.04 (dvt, 6H, J_{H-H} = 6.0, *N* = 15.0, PCH(C*H*$_3$)$_2$), 0.86 (dvt, overlapped, 6H, PCH(C*H*$_3$)$_2$), -18.09 (t, J_{H-P} = 23.0, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 189.6 (t, J_{C-P} = 1.6, CO), 185.4 (t, J_{C-P} = 4.3, OsC), 159.5 (vt, *N* = 13.4, C_{arom}-xant(P^iPr_2)$_2$), 149.8 (s, *C*H=CHPh), 142.6 (s, *C*CO), 141.3 (s, C_{arom}), 132.6 (vt, *N* = 5.1, C_{arom}-xant(P^iPr_2)$_2$), 131.2 (s, CH_{arom}), 130.3 (s, CH_{arom}-xant(P^iPr_2)$_2$), 129.7, 129.5, 128.7, 128.6 (all s, CH_{arom}), 128.1, 127.8 (these resonances are masked by the resonance of C_6D_6, C_{ipso}-xant(P^iPr_2)$_2$ and CH_{arom}), 127.6 (s, CH_{arom}), 126.7 (s, CH_{arom}-xant(P^iPr_2)$_2$), 124.8 (vt, *N* = 4.2, CH_{arom}-xant(P^iPr_2)$_2$), 114.3 (s, CH=*C*HPh), 34.7 (s, C(*C*H$_3$)$_2$), 34.6 (s, *C*(CH$_3$)$_2$), 29.6 (vt, *N* = 18.0, P*C*H(CH$_3$)$_2$), 29.1 (vt, *N* = 33.1, P*C*H(CH$_3$)$_2$), 25.6 (s, C(*C*H$_3$)$_2$), 20.1 (s, PCH(*C*H$_3$)$_2$), 18.9 (vt, *N* = 7.5, PCH(*C*H$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$), 18.2 (vt, *N* = 7.3, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 47.0 (s).

Spectroscopic data for OsH{κ^2-C,O-[C(Ph)CHC(Ph)O]}{xant(P^iPr_2)$_2$} (**15**): ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.67 (d, J_{H-H} = 7.5, 2H, CH_{arom}), 7.76 (m, 1H, CH_{arom}), 7.99 (s, OsCCH), 7.38–6.65 (m, 13H, CH_{arom} and CH_{arom}-xant(P^iPr_2)$_2$), 2.43 (m, 2H, PC*H*(CH_3)$_2$), 2.36 (m, 2H, PC*H*(CH_3)$_2$), 1.36 (s, 3H, CH_3),

1.19 (dvt, overlapped, 6H, PCH(CH_3)$_2$), 1.13 (s, 3H, CH_3), 0.93 (dvt, 6H, $J_{H\text{-}H}$ = 7.5, N = 13.5, PCH(CH_3)$_2$), 0.86 (dvt, overlapped, 6H, PCH(CH_3)$_2$), 0.74 (dvt, $J_{H\text{-}H}$ = 7.5, N = 16.5, 6H, PCH(CH_3)$_2$), -16.37 (t, $J_{H\text{-}P}$ = 23.7, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 223.3 (t, $J_{C\text{-}P}$ = 2.8, OsC), 208.8 (t, $J_{C\text{-}P}$ = 1.6, CO), 158.3 (vt, N = 13.1, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 157.5, 140.3 (both s, C_{ipso} Ph), 132.2 (vt, N = 5.2, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 132.5, 130.6 (both s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 129.0, 128.8, 128.7, 128.4 (all s, CH_{arom}), 127.7 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^{i}Pr$_2$)$_2$), 127.4, 126.1, 125.6 (all s, CH_{arom}), 122.5 (s, CO*C*H), 34.8 (s, C(*C*H$_3$)$_2$), 30.4 (s, *C*(CH$_3$)$_2$), 29.2 (vt, N = 19.1, P*C*H(CH$_3$)$_2$), 28.6 (vt, N = 33.8, P*C*H(CH$_3$)$_2$), 27.2 (s, C(*C*H$_3$)$_2$), 19.9 (vt, N = 6.7, PCH(*C*H$_3$)$_2$), 18.9, 18.6, 18.0 (all s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 47.5 (s).

Reaction of RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (4) with Benzylideneacetophenone: Preparation of RuH{κ^2-C,O-[C$_6$H$_4$C(CH=CHPh)O]}{xant(P^{i}Pr$_2$)$_2$} (16) and RuH{κ^2-C,O-[C(Ph)CHC(Ph)O]}{xant(P^{i}Pr$_2$)$_2$} (17). This complex was prepared analogously as described for **5** starting from **4** (75 mg, 0.134 mmol), benzylideneacetophenone (56 mg, 0.268 mmol) and 2-propanol (10 μL, 0.134 mmol). Dark green solid. ^{1}H and ^{31}P{^{1}H} NMR spectroscopies show a 1:1 mixture of complexes **16** and **17**. Yield: 88 mg (90 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of 1,3-diphenyl-1-propanone. Anal. Calcd. for $C_{42}H_{52}O_2P_2Ru$: C, 67.09; H, 6.97. Found: C, 66.75; H, 6.72. HRMS (electrospray, *m/z*): calcd. for $C_{42}H_{52}O_2P_2Ru$ [M – H]$^+$: 751.2414, found: 751.2393. IR (cm^{-1}): ν(Ru-H) 2054, 1950 (w).

Spectroscopic data for RuH{κ^2-C,O-[C$_6$H$_4$C(CH=CHPh)O]}{xant(P^{i}Pr$_2$)$_2$} (**16**)**:** ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.46 (d, $J_{H\text{-}H}$ = 6.0, 1H, C*H*=CHPh), 8.38 (d, $J_{H\text{-}H}$ = 6.0, 2H, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 7.74 (m, 1H, CH_{arom}), 7.28-6.84 (m, 12H, CH_{arom}), 6.73 (t, $J_{H\text{-}H}$ = 6.0, 1H, CH_{arom}), 2.42 (m, 2H, PC*H*(CH$_3$)$_2$), 2.24 (m, 2H, PC*H*(CH$_3$)$_2$), 1.33 (s, 3H, CH$_3$), 1.32 (dvt, 6H, $J_{H\text{-}H}$ = 6.0, N = 14.5, PCH(C*H*$_3$)$_2$), 1.24 (dvt, 6H, $J_{H\text{-}H}$ = 6.0, N = 15.0, PCH(C*H*$_3$)$_2$), 1.11 (s, 3H, CH$_3$), 1.07-089 (m, 12H, PCH(C*H*$_3$)$_2$), 0.89 (dvt, overlapped, 6H, PCH(C*H*$_3$)$_2$), -16.30 (t, $J_{H\text{-}P}$ = 24.0, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 209.9 (t, $J_{C\text{-}P}$ = 9.1, RuC), 186.9 (t, $J_{C\text{-}P}$ = 2.3, CO), 156.9 (vt, N = 15.1, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 147.7 (s, *C*H=CHPh), 142.5 (s, *C*CO), 140.6 (s, C_{arom}), 132.2 (vt, N = 5.3, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 130.8 (s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 129.5, 129.1, 128.8, 128.7 (all s, CH_{arom}), 128.3 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^{i}Pr$_2$)$_2$), 127.5 (s, CH_{arom}), 126.3 (s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 124.3 (vt, N = 4.5, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 115.7 (s, CH=*C*HPh), 34.8 (s, *C*(CH$_3$)$_2$), 34.5 (s, C(*C*H$_3$)$_2$), 28.6 (vt, N = 27.9, P*C*H(CH$_3$)$_2$), 28.1 (vt, N = 14.3, P*C*H(CH$_3$)$_2$), 27.5 (s, C(*C*H$_3$)$_2$), 20.1 (s, PCH(*C*H$_3$)$_2$), 19.9 (vt, N = 7.6, PCH(*C*H$_3$)$_2$), 18.8 and 18.1 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 62.4 (s).

Spectroscopic data for RuH{κ^2-C,O-[C(Ph)CHC(Ph)O]}{xant(P^{i}Pr$_2$)$_2$} (**17**)**:** ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.62 (d, $J_{H\text{-}H}$ = 6.0, 2H, CH_{arom}), 8.09 (s, 1H, COCH), 7.72 (m, 1H, CH_{arom}), 7.39 (t, $J_{H\text{-}H}$ = 6.0, 2H, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 7.28–6.84 (m, 11H, CH_{arom} and CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 2.30 (m, 2H, PC*H*(CH$_3$)$_2$), 2.07 (m, 2H, PC*H*(CH$_3$)$_2$), 1.36 (s, 3H, CH$_3$), 1.14 (dvt, 6H, $J_{H\text{-}H}$ = 6.9, N = 13.5, PCH(C*H*$_3$)$_2$), 1.13 (s, 3H, CH$_3$), 0.99-0.87 (2 dvts, overlapped, 12H, PCH(C*H*$_3$)$_2$), 0.78 (dvt, 6H, $J_{H\text{-}H}$ = 6.9, N = 15.3, PCH(C*H*$_3$)$_2$), -14.46 (t, $J_{H\text{-}P}$ = 26.1, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 255.0 (t, $J_{C\text{-}P}$ = 6.7, OsC), 203.2 (t, $J_{C\text{-}P}$ = 1.8, CO), 158.2 (vt, N = 15.2, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 154.0 (s, C_{ipso} Ph), 137.5 (s, C_{ipso} Ph), 132.8 (vt, N = 5.4, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 132.7, 130.1 (both s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 128.7, 128.6, 128.5 (all s, CH_{arom}), 128.3, 128.1 (these resonances are masked by the resonance of C_6D_6, CH_{arom} and C_{ipso}-xant(P^{i}Pr$_2$)$_2$), 127.5, 126.6 (both s, CH_{arom}), 120.5 (s, CO*C*H), 34.6, 30.5 (both s, C(*C*H$_3$)$_2$), 30.4 (s, *C*(CH$_3$)$_2$), 28.9 (vt, N = 12.2, P*C*H(CH$_3$)$_2$), 27.9 (vt, N = 27.3, P*C*H(CH$_3$)$_2$), 19.2 (vt, N = 8.9, PCH(*C*H$_3$)$_2$), 18.8 and 18.7 (both s, PCH(*C*H$_3$)$_2$), 18.5 (vt, N = 8.6, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 64.1 (s).

Reaction of OsH$_4${xant(P^{i}Pr$_2$)$_2$} (1) with Benzaldehyde: Preparation of OsH(Ph)(CO){xant(P^{i}Pr$_2$)$_2$} (18). A solution of **1** (125 mg, 0.196 mmol) in toluene (12 mL) was treated with benzaldehyde (24 μL, 0.235 mmol) and the resulting mixture was heated to reflux for 15 h. After being cooled at room temperature, the solution was evaporated to afford a white residue. Addition of methanol (2 mL) afforded a white solid that was washed with methanol (2 x 2 mL) and dried *in vacuo*. Yield: 106 mg (71%). Anal. Calcd. for $C_{34}H_{46}O_2OsP_2$: C, 55.27; H, 6.27. Found: C, 54.95; H, 6.42. HRMS (electrospray, *m/z*): calcd. for $C_{34}H_{45}O_2OsP_2$ [M – H]$^+$: 739.2506, found: 739.2493. IR (cm^{-1}): ν(C≡O) 1871 (s). ^{1}H NMR (300 MHz, C_7D_8, 253 K): δ 8.75 (d, $J_{H\text{-}H}$ = 7.2, 1H, CH_{arom}), 7.34 (d, $J_{H\text{-}H}$ = 7.2, 1H, CH_{arom}), 7.12-6.78 (m, 9H, CH_{arom} and CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 2.29 (m, 2H, PC*H*(CH$_3$)$_2$), 2.04 (m, 2H, PC*H*(CH$_3$)$_2$), 1.51 (dvt, $J_{H\text{-}H}$ = 7.1, N = 15.6, 6H, PCH(C*H*$_3$)$_2$), 1.43 (dvt, $J_{H\text{-}H}$ = 7.2, N = 15.3, 6H, PCH(C*H*$_3$)$_2$), 1.33 (s, 3H, C*H*$_3$), 1.26 (s, 3H, C*H*$_3$), 0.97 (dvt, $J_{H\text{-}H}$ = 7.0, N = 14.9, 6H, PCH(C*H*$_3$)$_2$), 0.58 (dvt, $J_{H\text{-}H}$ = 7.1, N = 14.9, 6H, PCH(C*H*$_3$)$_2$), -6.96 (t, $J_{H\text{-}P}$ = 21.3, 1H, OsH). ^{13}C{^{1}H} NMR (75 MHz, C_7D_8, 253 K): δ 186.9 (t, $J_{C\text{-}P}$ = 7.6, CO), 156.3 (vt, N = 14.4, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 156.2 (t, $J_{C\text{-}P}$ = 8.0, OsC), 145.7, 134.4 (both s, CH_{arom}), 131.2 (s, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 131.1, 128.0 (both s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 127.5 (s, CH_{arom}), 127.0 (vt, N = 28.8, C_{ipso}-xant(P^{i}Pr$_2$)$_2$), 125.7 (s, CH_{arom}), 125.3 (vt, N = 4.5, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 120.1 (s, CH_{arom}), 36.7 (s, C(*C*H$_3$)$_2$), 33.7 (s, *C*(CH$_3$)$_2$), 32.1 (vt, N = 26.0, P*C*H(CH$_3$)$_2$), 30.8 (vt, N = 35.6, P*C*H(CH$_3$)$_2$), 28.0 (s, C(*C*H$_3$)$_2$), 21.1 (vt, N = 8.0, PCH(*C*H$_3$)$_2$), 20.0, 19.6 (both s, PCH(*C*H$_3$)$_2$), 19.5 (vt, N = 6.5, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 53.0 (s).

Reaction of RuH(η^2-H$_2$BH$_2$){xant(P^{i}Pr$_2$)$_2$} (4) with Benzaldehyde: Preparation of RuH(Ph)(CO){xant(P^{i}Pr$_2$)$_2$} (19). This complex was prepared analogously as described for **5** starting from **4** (120 mg, 0.214 mmol), benzaldehyde (45 μL, 0.430 mmol) and 2-propanol (16 μL, 0.214 mmol). Pale brown solid. Yield: 96 mg (69 %). ^{1}H NMR spectra of the crude reaction mixture showed the presence of benzylic alcohol. Anal. Calcd. for $C_{34}H_{46}O_2P_2Ru$: C, 62.85; H, 7.13. Found: C, 62.43; H, 7.02. IR (cm^{-1}): ν(CO) 1926 (s). ^{1}H NMR (300 MHz, C_7D_8, 298 K): δ 7.18–6.87 (m, 11H, CH_{arom} and CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 2.76 (m, 2H, PC*H*(CH$_3$)$_2$), 2.21 (m, 2H, PC*H*(CH$_3$)$_2$), 1.65 (dvt, $J_{H\text{-}H}$ = 7.5, N = 16.5, 6H, PCH(C*H*$_3$)$_2$), 1.58 (dvt, $J_{H\text{-}H}$ = 6.9, N = 15.9, 6H, PCH(C*H*$_3$)$_2$), 1.32 (dvt, $J_{H\text{-}H}$ = 6.9, N = 17.1, 6H, PCH(C*H*$_3$)$_2$), 1.26 (s, 3H, CH$_3$), 1.10 (s, 3H, CH$_3$), 0.89 (dvt, $J_{H\text{-}H}$ = 6.9, N = 15.6, 6H, PCH(C*H*$_3$)$_2$), -13.71 (t, $J_{H\text{-}P}$ = 19.2, 1H, RuH). ^{13}C{^{1}H} NMR (75 MHz, C_7D_8, 298 K): δ 208.5 (t, $J_{C\text{-}P}$ = 6.5, CO), 156.0 (t, $J_{C\text{-}P}$ = 8.1, OsC), 155.9 (vt, N = 15.2, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 133.7 (s, CH_{arom}), 132.0 (vt, N = 6.0, C_{arom}-xant(P^{i}Pr$_2$)$_2$), 131.0 and 128.7 (both s, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 128.3 and 128.1 (these resonances are masked by the resonance of C_6D_6, C_{ipso}-xant(P^{i}Pr$_2$)$_2$ and CH_{arom}), 124.9 (vt, N = 5.2, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 126.4 (s, CH_{arom}), 35.5 (s, C(*C*H$_3$)$_2$), 34.8 (s, *C*(CH$_3$)$_2$), 30.0 (vt, N = 21.6, P*C*H(CH$_3$)$_2$), 28.2 (vt, N = 29.1, P*C*H(CH$_3$)$_2$), 28.1 (s, C(*C*H$_3$)$_2$), 22.6 (vt, N = 3.3, PCH(*C*H$_3$)$_2$), 20.1, 20.0 (both s, PCH(*C*H$_3$)$_2$), 19.8 (vt, N = 4.8, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.43 MHz, C_6D_6, 298 K): δ 69.5 (s).

Reaction of OsH$_4${xant(P^{i}Pr$_2$)$_2$} (1) with 1-Cyclohexene-1-carboxaldehyde. A solution of **1** (100 mg, 0.157 mmol) in toluene (12 mL) was treated with 1-cyclohexene-1-carboxaldehyde (22 μL, 0.193 mmol) and the resulting mixture was heated to reflux for 15 h. After being cooled at room temperature, the solution was evaporated to afford a yellow residue. Addition of methanol (2 mL) afforded a yellow solid that was washed with methanol (2 x 2 mL) and dried *in vacuo*. ^{1}H and ^{31}P{H} NMR both before and after isolation indicated a 1:1 mixture of complexes **20** and **21**. GC analysis of the crude reaction mixture showed the presence of 1,3-cyclohexadiene.

Spectroscopic data for OsH(C$_6$H$_9$)(CO){xant(P^{i}Pr$_2$)$_2$} (**20**): HRMS (electrospray, *m/z*): calcd. for $C_{34}H_{50}O_2OsP_2$ [M]$^+$: 743.2897, found: 743.2744. IR (cm^{-1}): ν(CO) 1872 (s). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.18-6.87 (6H, CH_{arom}-xant(P^{i}Pr$_2$)$_2$), 6.49 (br, 1H, OsCCH), 2.68 (m, 4H, PC*H*(CH$_3$)$_2$ and CH$_2$), 2.17 (m, 2H, PC*H*(CH$_3$)$_2$), 1.81 (m, 2H, CH$_2$), 1.47 (dvt, $J_{H\text{-}H}$ = 6.9, N = 14.6, 6H, PCH(C*H*$_3$)$_2$), 1.31 (dvt, $J_{H\text{-}H}$ = 7.2, N = 14.1, 6H, PCH(C*H*$_3$)$_2$), 1.29 (s, 3H, CH$_3$), 1.19 (s, 3H, CH$_3$), 1.13 (overlapped, 6 H, PCH(C*H*$_3$)$_2$), 0.94 (dvt, $J_{H\text{-}H}$ = 6.9, N = 14.7, 6H, PCH(C*H*$_3$)$_2$), -7.23 (t, $J_{H\text{-}P}$ = 21.2, 1H, OsH); resonances corresponding to 4 protons of the cyclohexenyl group are overlapped in the aliphatic region. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 253 K): δ

187.3 (t, $J_{C\text{-}P}$ = 7.3, CO), 157.4 (overlapped, OsC), 157.3 (vt, N = 14.3, C_{arom}-xant(P^iPr_2)$_2$), 134.5 (t, $J_{C\text{-}P}$ = 3.5, OsC*C*H), 131.8 (s, C_{arom}-xant(P^iPr_2)$_2$), 131.2, 129.3 (both s, CH_{arom}-xant(P^iPr_2)$_2$), 128.3 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^iPr_2)$_2$), 125.4 (vt, N = 4.6, CH_{arom}-xant(P^iPr_2)$_2$), 36.8 (s, C(*C*H$_3$)$_2$), 34.2 (s, *C*(CH$_3$)$_2$), 31.6 (vt, N = 24.5, P*C*H(CH$_3$)$_2$), 31.3 (s, CH$_2$), 28.0 (vt, N = 18.6, P*C*H(CH$_3$)$_2$), 27.7 (s, C(*C*H$_3$)$_2$), 27.1, 24.2 (both s, CH$_2$), 21.5 (br, PCH(*C*H$_3$)$_2$), 20.6 (br, PCH(*C*H$_3$)$_2$), 20.0, 19.8 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.43 MHz, C_6D_6, 298 K): δ 52.1 (s, br).

Reaction of OsH$_4${xant(P^iPr_2)$_2$} (1) with Cyclohexane Carboxaldehyde: Preparation of OsH$_2$(CO){xant(P^iPr_2)$_2$} (21). This complex was prepared analogously as described for **18** starting from **1** (100 mg, 0.157 mmol) and cyclohexane carboxaldehyde (24 μL, 0.198 mmol). Yellow solid. Yield: 76 mg (72%). GC analysis of the crude reaction mixture showed the presence of cyclohexene. Anal. Calcd. for $C_{28}H_{42}O_2OsP_2$: C, 50.74; H, 6.39. Found: C, 50.42; H, 6.37. HRMS (electrospray, *m/z*): calcd. for $C_{28}H_{42}O_2OsP_2$ $[M]^+$: 663.2192; found 663.2167. IR (cm^{-1}): ν(CO): 1878 (s), ν(Os-H) 1688 (s). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.16 (m, 2H, CH_{arom}), 6.85-6.82 (m, 4H, CH_{arom}), 2.28 (m, 4H, PC*H*(CH$_3$)$_2$), 1.65 (dvt, $J_{H\text{-}H}$ = 6.9, N = 14.9, 12H, PCH(C*H*$_3$)$_2$), 1.25 (dvt, $J_{H\text{-}H}$ = 7.0, N = 15.0, 12H, PCH(C*H*$_3$)$_2$), 1.15 (s, 6H, CH$_3$), -4.08 (t, $J_{H\text{-}P}$ = 17.7, 2H, OsH). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ 186.0 (t, $J_{C\text{-}P}$ = 7.8, CO), 156.6 (vt, N = 14.3, C_{arom}-xant(P^iPr_2)$_2$), 130.5 (vt, N = 5.5, C_{arom}-xant(P^iPr_2)$_2$), 130.1 (s, CH_{arom}-xant(P^iPr_2)$_2$), 128.0 (this resonance is masked by the resonance of C_6D_6, C_{ipso}-xant(P^iPr_2)$_2$), 127.7 (s, CH_{arom}-xant(P^iPr_2)$_2$), 124.9 (vt, N = 5.1, CH_{arom}-xant(P^iPr_2)$_2$), 33.3 (s, *C*(CH$_3$)$_2$), 32.7 (s, C(*C*H$_3$)$_2$), 30.2 (vt, N = 30.7, P*C*H(CH$_3$)$_2$), 20.8 (vt, N = 8.9, PCH(*C*H$_3$)$_2$), 19.5 (s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.43 MHz, C_6D_6, 298 K): δ 70.8 (s, t under *off-resonance* conditions).

Structural Analysis of Complexes 2, 10, 13, and 21. Crystals were obtained from saturated solutions in methanol (**2** and **10**) or in benzene (**21**), or from slow diffusion of methanol into saturated solutions of **13** in toluene. X-ray data were collected on a Bruker Smart APEX DUO CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (**2**, **10**, **13**) or 30 mA (**21**). Data were collected over the complete sphere. Each frame exposure time was 10 s (**21**), 20 s (**2**), 30 s (**10**) and 60 s (**13**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[32] The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F^2 with SHELXL97,[33] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms (except hydrides) were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model. Hydrogens bonded to metal atoms were observed in the last cycles of refinement but refined too close to metals, so a restricted refinement model was used for all of them (d(M-H= 1.59(1) Å).

Crystal data for **2**: $C_{40}H_{50}O_2OsP_2{\cdot}0.5CH_3OH$, M_W 830.96, orange, irregular block (0.13 x 0.11 x 0.10), orthorhombic, space group Pbca, *a*: 16.6453(13) Å, *b*: 18.6334(15) Å, *c*: 23.6385(19) Å, *V* = 7331.7(10) Å^3, *Z* = 8, *Z'* = 1, D_{calc}: 1.506 g cm^{-3}, F(000): 3368, T = 100(2) K, μ 3.601 mm^{-1}. 56496 measured reflections (2θ: 3-58°, ω scans 0.3°), 8952 unique (R_{int} = 0.0733); min./max. transm. Factors 0.710/0.862. Final agreement factors were R^1 = 0.0541 (6453 observed reflections, I > 2σ(I)) and wR^2 = 0.0919; data/restraints/parameters 8952/1/439; GoF = 1.131. Largest peak and hole 2.821 (close to osmium atom) and -1.344 e/ Å^3.

Crystal data for **10**: $C_{37}H_{50}O_2OsP_2$, M_W 778.91, orange, irregular block (0.13 x 0.08 x 0.06), triclinic, space group P$\bar{1}$, *a*: 11.7401(14) Å, *b*: 12.0479(14) Å, *c*: 27.560(3) Å, *a*: 78.724(2)°, *β*: 83.870(2)°, *γ*: 60.9790(10)°, *V* = 3342.6(7) Å^3, *Z* = 4, *Z'* = 2, D_{calc}: 1.548 g cm^{-3}, F(000): 1576, T = 100(2) K, μ 1.548 mm^{-1}. 33626 measured reflections (2θ: 3-51°, ω scans 0.3°), 12408 unique (R_{int} = 0.0654); min./max. transm. Factors 0.636/0.862. Final agreement factors were R^1 = 0.0599 (9138 observed reflections, I > 2σ(I)) and wR^2 = 0.1369; data/restraints/parameters 12408/22/792; GoF = 1.100. Largest peak and hole 3.239 (close to osmium atoms) and -2.415 e/ Å^3.

Crystal data for **13**: $C_{31}H_{46}O_2P_2Ru$, M_W 613.69, red, irregular block (0.15 x 0.10 x 0.02), orthorhombic, space group Pna2$_1$, *a*: 19.813(3) Å, *b*: 9.9286(17) Å, *c*: 31.283(5) Å, *V* = 6153.9(18) Å^3, *Z* = 8, *Z'* = 2, D_{calc}: 1.325 g cm^{-3}, F(000): 2576, T = 100(2) K, μ 0.638 mm^{-1}. 58966 measured reflections (2θ: 3-53°, ω scans 0.3°), 11646 unique (R_{int} = 0.0981); min./max. transm. Factors 0.569/0.745. Final agreement factors were R^1 = 0.0595 (8096 observed reflections, I > 2σ(I)) and wR^2 = 0.1602; data/restraints/parameters 11646/3/678; Flack parameter 0.26(6); GoF = 1.026. Largest peak and hole 1.261 and -0.766e/ Å^3.

Crystal data for **21**: $C_{28}H_{42}O_2OsP_2$, M_W 662.76, yellow, irregular block (0.17 x 0.16 x 0.11), monoclinic, space group P2$_1$/c, *a*: 10.770(3) Å, *b*: 16.065(4) Å, *c*: 16.500(4) Å, *β*: 103.089(4)°, *V* = 2780.8(13) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.583 g cm^{-3}, F(000): 1328, T = 100(2) K, μ 4.723 mm^{-1}. 24464 measured reflections (2θ: 3-58°, ω scans 0.3°), 7839 unique (R_{int} = 0.0573); min./max. transm. Factors 0.656/0.842. Final agreement factors were R^1 = 0.0433 (5322 observed reflections, I > 2σ(I)) and wR^2 = 0.1046; data/restraints/parameters 7839/2/314; GoF = 0.959. Largest peak and hole 2.946 (close to osmium atoms) and -1.460 e/ Å^3.

ASSOCIATED CONTENT

Supporting Information

Figures containing ^1H NMR spectra (aromatic region) of the products of the reactions of complexes **1** and **4** with benzophenone and perdeuterated benzophenone, and a CIF giving crystallographic data for compounds **2**, **10**, **13**, and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* E-mail: maester@unizar.es.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Financial support from the Spanish MINECO (Projects CTQ2014-52799-P and CTQ2014-51912-REDC), the DGA (E35) and the European Social Fund (FSE) is acknowledged. J.A. acknowledges support *via* a pre-doctoral fellowship from the DGA. P.P. acknowledges the Prof. H. J. Backer Foundation and the European Union Erasmus programme for their support.

REFERENCES

(1) (a) Shilov, A. E.; Shul`pin, G. B. *Chem. Rev.* **1997**, *97*, 2879-2932. (b) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507-514. (c) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471-2526. (d) Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *110*, 749-823.

(2) (a) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890-931. (b) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147-1169. (c) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10236-10254.

(3) Alabau, R. G.; Eguillor, B.; Esler, J.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Tsai, J.-Y.; Xia, C. *Organometallics* **2014**, *33*, 5582-5596.

(4) (a) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624-655. (b) Ros, A.; Fernández, R.; Lassaletta, J. M. *Chem. Soc. Rev.* **2014**, *43*, 3229-3243.

(5) (a) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315-1345. (b) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788-802.

(6) (a) Kakiuchi, F.; Murai, S. *Top. Organomet. Chem.* **1999**, *3*, 47-79 (b) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826-834.

(7) (a) Kakiuchi, F.; Matsuura, Y.; Kan, S.; Chatani, N. *J. Am. Chem. Soc.* **2005**, *127*, 5936-5945. (b) Ueno, S.; Mizushima, E.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2006**, *128*, 16516-16517. (c) Gandeepan, P.; Parthasarathy, K.; Cheng, C.-H. *J. Am. Chem. Soc.* **2010**, *132*, 8569-8571. (d) Wencel-Delord, J.; Nimphius, C.; Patureau, F. W.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 2247-2251. (e) Zhao, D.; Li, X.; Han, K.; Li, X.; Wang, Y. *J. Phys. Chem. A* **2015**, *119*, 2989-2997.

(8) See for example: (a) Esteruelas, M. A.; García-Raboso, J.; Oliván, M. *Organometallics* **2011**, *30*, 3844-3852. (b) Bajo, S.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2011**, *30*, 5710-5715. (c) Crespo, O.; Eguillor, B.; Esteruelas, M. A.; Fernández, I.; García-Raboso, J.; Gómez-Gallego, M.; Martín-Ortiz, M.; Oliván, M.; Sierra, M. A. *Chem. Commun.* **2012**, *48*, 5328-5330. (d) Bajo, S.; Esteruelas, M. A. López, A. M.; Oñate, E. *Organometallics* **2014**, *33*, 1851-1858. (e) Bolaño, T.; Esteruelas, M. A.; Fernández, I.; Oñate, E.; Palacios, A.; Tsai, J.-Y.; Xia, C. *Organometallics* **2015**, *34*, 778-789.

(9) (a) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Oñate, E.; Tomàs, J. *Organometallics* **2001**, *20*, 442-452. (b) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2635-2638. (c) Esteruelas, M. A.; Lledós, A.; Oliván, M.; Oñate, E.; Tajada, M. A.; Ujaque, G. *Organometallics* **2003**, *22*, 3753-3765. (d) Esteruelas, M. A.; Hernández, Y.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 5989-6000. (e) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24*, 1428-1438. (f) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680-4690.

(10) (a) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2004**, *23*, 6015-6024. (b) Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Rubio, L. *Organometallics* **2008**, *27*, 799-802.

(11) Eguillor, B.; Esteruelas, M. A.; García-Raboso, J.; Oliván, M.; Oñate, E. *Organometallics* **2009**, *28*, 3700-3709.

(12) (a) Asensio, G.; Cuenca, A. B.; Esteruelas, M. A.; Medio-Simón, M.; Oliván, M.; Valencia, M. *Inorg. Chem.* **2010**, *49*, 8665-8667. (b) Esteruelas, M. A.; Honczek, N.; Oliván, M.; Oñate, E.; Valencia, M. *Organometallics* **2011**, *30*, 2468-2471. (c) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Inorg. Chem.* **2013**, *52*, 5339-5349. (d) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. *Inorg. Chem.* **2013**, *52*, 6199-6213. (e) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Inorg. Chem.* **2013**, *52*, 12108-12119. (f) Alós, J.; Bolaño, T.; Esteruelas, M. A.; Oliván, M.; Oñate, E.; Valencia, M. *Inorg. Chem.* **2014**, *53*, 1195-1209. (g) Esteruelas, M. A.; Oliván, M.; Vélez, A. DOI: 10.1021/acs.organomet.5b00176.

(13) (a) Zuideveld, M. A.; Swennenhuis, B. H. G.; Boele, M. D. K.; Guari, Y.; van Strijdonck, G. P. F.; Reek, J. N. H.; Kamer, P. C. J.; Goubitz, K.; Fraanje, J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **2002**, 2308-2317. (b) van der Vlugt, J. I.; Sablong, R.; Mills, A. M.; Kooijman, H.; Spek, A. L.; Meetsma, A.; Vogt, D. *Dalton Trans.* **2003**, 4690-4699. (c) Fox, D. J.; Duckett, S. B.; Flaschenriem, C.; Brennessel, W. W.; Schneider, J.; Gunay, A.; Eisenberg, R. *Inorg. Chem.* **2006**, *45*, 7197-7209. (d) Grushin, V. V.; Marshall, W. J. *J. Am. Chem. Soc.* **2006**, *128*, 12644-12645. (e) Deb, B.; Borah, B. J.; Sarmah, B. J.; Das, B.; Dutta, D. K. *Inorg. Chem. Commun.* **2009**, *12*, 868-871. (f) Ledger, A. E. W.; Slatford, P. A.; Lowe, J. P.; Mahon, M. F.; Whittlesey, M. K.; Williams, J. M. J. *Dalton Trans.* **2009**, 716-722. (g) Pontiggia, A. J.; Chaplin, A. B.; Weller, A. S. *J. Organomet. Chem.* **2011**, *696*, 2870-2876. (h) Guard, L. M.; Ledger, A. E. W.; Reade, S. P.; Ellul, C. E.; Mahon, M. F.; Whittlesey, M. K. *J. Organomet. Chem.* **2011**, *696*, 780-786. (i) Dallanegra, R.; Chaplin, A. B.; Weller, A. S. *Organometallics* **2012**, *31*, 2720-2728.

(14) See for example: (a) Batuecas, M.; Esteruelas, M. A.; García-Yebra, C.; Oñate, E. *Organometallics* **2010**, *29*, 2166-2175. (b) Varela-Fernández, A.; García-Yebra, C.; Valera, J. A.; Esteruelas, M. A.; Saá, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 4278-4281. (c) Collado, A.; Esteruelas, M. A.; López, F.; Mascareñas, J. L.; Oñate, E.; Trillo, B. *Organometallics* **2010**, *29*, 4966-4974. (d) Collado, A.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2011**, *30*, 1930-1941. (e) Collado, A.; Esteruelas, M. A.; Gulías, M.; Mascareñas, J. L.; Oñate, E. *Organometallics* **2012**, *31*, 4450-4458.

(15) For some relevant papers, see: C,C,C-ligands: (a) Chung, L.-H.; Chan, S.-C.; Lee, W.-C.; Wong, C.-Y. *Inorg. Chem.* **2012**, *51*, 8693-8703. C,N,C-ligands: (b) Wong, C.-Y.; Lai, L.-M.; Pat, P.-K.; Chung, L.-H. *Organometallics* **2010**, *29*, 2533-2539. (c) Esteruelas, M. A.; Fernández, I.; Herrera, A.; Martín-Ortiz, M.; Martínez-Álvarez, R.; Oliván, M.; Oñate, E.; Sierra, M. A.; Valencia, M. *Organometallics* **2010**, *29*, 976-986. (d) Chung, L.-H.; Cho, K.-S.; England, J.; Chan, S.-C.; Wieghardt, K.; Wong, C.-Y. *Inorg. Chem.* **2013**, *52*, 9885-9896. C,N,N-ligands: (e) Baratta, W.; Benedetti, F.; Del Zotto, A.; Fanfoni, L.; Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. *Organometallics* **2010**, *29*, 3563-3570. C,N,O-ligands: (f) Gupta, P.; Butcher, R. J.; Bhattacharya, S. *Inorg. Chem.* **2003**, *42*, 5405-5411. (g) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 3082-3084. P,C,P-ligands: (h) Wen, T. B.; Cheung, Y. K.; Yao, J.; Wong, W.-T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803-3809. (i) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2001**, *20*, 1001-1007. (j) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2001**, *20*, 1719-1724. (k) Liu, S. H.; Lo, S. T.; Wen, T. B.; Williams, I. D.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Inorg. Chim. Acta* **2002**, *334*, 122-130. (l) Gusev, D. G.; Maxwell, T.; Dolgushin, F. M.; Lyssenko, M.; Lough, A.J. *Organometallics* **2002**, *21*, 1095-1100. (m) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 2601-2603. (n) Wen, T. B.; Zhou, Z. Y.; Jia, G. *Organometallics* **2003,** *22*, 4947-4951. (o) Gusev, D. G.; Fontaine, F.-G.; Lough, A. J.; Zargarian, D. *Angew. Chem. Int. Ed.* **2003**, *42*, 216-219. (p) Wen, T. B.; Zhou, Z. Y.; Jia, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 5842-5846. (q) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Chem. Eur. J.* **2007**, *13*, 1382-1393. (r) Kuznetsov, V. F.; Gusev, D. G. *Organometallics* **2007**, *26*, 5661-5666. P,N,P-ligands: (s) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, *16*, 3941-3949. (t) Liu, S. H.; Lo, S. T.; Wen, T. B.; Zhou, Z. Y.; Lau, C. P.; Jia, G. *Organometallics* **2001**, *20*, 667-672. (u) Lee, J.-H.; Fan, H.; Pink, M.; Caulton, K. G. *New J. Chem.* **2007**, *31*, 838-840. (v) Lee, J.-H.; Pink, M.; Tomaszewski, J.; Fan, H.; Caulton, K. G. *J. Am. Chem. Soc.* **2007**, *129*, 8706-8707. (w) Tsvetkov, N.; Fan, H.; Caulton, K. G. *Dalton Trans.* **2011**, *40*, 1105-1110. (x) Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem. Int. Ed.* **2012**, *51*, 2772-2775. N,N,N-ligands: (y) Esteruelas, M. A.; Masamunt, A. B.; Oliván, M.; Oñate, E.; Valencia, M. *J. Am. Chem. Soc.* **2008**, *130*, 11612-11613. (z) Müller, A. L.; Wadepohl, H.; Gade, L. H. *Organometallics* **2015**, *34*, 2810-2818.

(16) (a) Lee, J.-H.; Pink, M.; Caulton, K. G. *Organometallics* **2006**, *25*, 802-804. (b) Gruver, B. C.; Adams, J. J.; Arulsamy, N.; Roddick, D. M. *Organometallics* **2013**, *32*, 6468-6475.

(17) See for example: (a) Zhang, X.; Kanzelberger, M.; Emge, T. J.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13192-13193. (b) Feller, M.; Karton, A.; Leitus, G.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2006**, *128*, 12400-12401. (c) Bernskoetter, W. H.; Hanson, S. K.; Buzak, S. K.; Davis, Z.; White, P. S.; Swartz, R.; Goldberg, K.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131*, 8603-8613. (d) Choi, J.; Choily, Y.; Zhang, X.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2009**, *131*, 15627-15629. (e) Whited, M. T.; Zhu, Y.; Timpa, S. D.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V.; Grubbs, R. H. *Organometallics* **2009**, *28*, 4560-4570. (f) Conde, A.; Fandos, R.; Hernández, C.; Otero, A.; Rodriguez, A. *Chem. Eur. J.* **2010**, *16*, 12074-12078. (g) Albrecht, M.; Lindner, M. M. *Dalton Trans.* **2011**, *40*, 8733-8744. (h) Fu, R.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **2011**, *30*, 6751-6765. (i) Zhu, Y.; Smith, D. A.; Herbert, D. E.; Gatard, S.; Ozerov, O. V. *Chem. Commun.* **2012**, *48*, 218-220. (j) Kundu, S.; Choi, J.; Wang, D. Y.; Choliy, Y.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2013**, *135*, 5127-5143. (k) Allen, K. E.; Heinekey, D. M.; Goldman, A. S.; Goldberg, K.I. *Organometallics* **2013**, *32*, 1579-1582. (l) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024-12087. (m) Coetzee, J.; Eastham, G. R.; Slawin, A. M. Z.; Cole-Hamilton, D. J. *Dalton Trans.* **2015**, *44*, 1585-1591.

(18) Matsubara, T.; Koga, N.; Musaev, D. G.; Morokuma, K. *Organometallics* **2000**, *19*, 2318-2329.

(19) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Puerta, M. *Organometallics* **2008**, *27*, 445-450.

(20) (a) Selmeczy, A. D.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1994**, *13*, 522-532. (b) Renkema, K. B.; Bosque, R.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 10895-10907. (c) Carbó, J. J.; Eisenstein, O.; Higgitt, C. L.; Klahn, A. H.; Maseras, F.; Oelckers, B.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **2001**, 1452-1461. (d) Clot, E.; Besora, M.; Maseras, F.; Mégret, C.; Eisenstein, O.; Oelckers, B.; Perutz, R. N. *Chem. Commun.* **2003**, 490-491. (e) Clot, E.; Oelckers, B.; Klahn, A. H.; Eisenstein, O.; Perutz, R. N. *Dalton Trans.* **2003**, 4065-4074. (f) Hatnean, J. A.; Beck, R.; Borrelli, J. D.; Johnson, S. A. *Organometallics* **2010**, *29*, 6077-6091.

(21) (a) Liu, W.; Welch, K.; Trindle, C. O.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2007**, *26*, 2589-2597. (b) Schaub, T.; Fischer, P.; Steffen, A.; Braun, T.; Radius, U.; Mix, A. *J. Am. Chem. Soc.* **2008**, *130*, 9304-9317. (c) Johnson, S. A.; Huff, C. W.; Mustafa, F.; Saliba, M. *J. Am. Chem. Soc.* **2008**, *130*, 17278-17280. (d) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119-2183. (e) Clot, E.; Eisenstein, O.; Jasim, N.; Macgregor, S. A.; McGrady, J. E.; Perutz, R. N. *Acc. Chem. Res.* **2011**, *44*, 333-348. (f) Johnson, S. A.; Mroz, N. M.; Valdizon, R.; Murray, S. *Organometallics* **2011**, *30*, 441-457. (g) Li, B. Z.; Qian, Y. Y.; Liu, J.; Chan, K. S. *Organometallics* **2014**, *33*, 7059-7068. (h) Kalläne, S. I.; Teltewskoi, T.; Braun, T.; Braun, B. *Organometallics* **2015**, *34*, 1156-1169.

(22) (a) Evans, M. E.; Burke, C. L.; Yaibuathes, S.; Clot, E.; Eisenstein, O.; Jones, W. D. *J. Am. Chem. Soc.* **2009**, *131*, 13464-13473. (b) Clot, E.; Mégret, C.; Eisenstein, O.; Perutz, R. N. *J. Am. Chem. Soc.* **2009**, *131*, 7817-7827. (c) Tanabe, T.; Brennessel, W. W.; Clot, E.; Eisenstein, O.; Jones, W. D. *Dalton Trans.* **2010**, *39*, 10495-10509.

(23) Xu, X.; Jia, J.; Sun, H.; Liu, Y.; Xu, W.; Shi, Y.; Zhang, D.; Li, X. *Dalton Trans.* **2013**, *42*, 3417-3428.

(24) Zheng, T.; Sun, H.; Ding, J.; Zhang, Y.; Li, X. *J. Organomet. Chem.* **2010**, *695*, 1873-1877.

(25) For the insertion of the C-C double bond of methyl vinyl ketone into an Os-H bond, see for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034-2043. For an osmium-mediated activation of a terminal C(sp^2)-H bond of methyl vinyl ketone, see for example: (b) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828-3836.

(26) (a) Gong, L.; Lin, Y.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1101-1111. (b) Lin, Y.; Gong, L.; Xu, H.; He, X.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28*, 1524-1533. (c) Esteruelas, M. A.; Larramona, C.; Oñate, E. *Organometallics* **2013**, 82, 2567-2575. (d) Liu, B.; Zhao, Q.; Wang, H.; Zeng, B.; Cao, X.; Xia, H. *Sci. China Chem.* **2013**, *56*, 1105-1111. (e) Zhao, Q.; Cao, X.-Y.; Wen, T. B.; Xia, H. *Chem. Asian J.* **2013**, *8*, 269-275. (f) Cao, X.-Y.; Zhao, Q.; Lin, Z.; Xia, H. *Acc. Chem. Res.* **2014**, *47*, 341-354. (g) Chen, J.; Huang, Z.-A.; Hua, Y.; Zhang, H.; Xia, H. *Organometallics* **2015**, *34*, 340-347. (h) Tsui, W.-K.; Chung, L.-H.; Tsang, W-H.; Yeung, C.-F.; Chiu, C.-H.; Lo, H.-S.; Wong, C.-Y. *Organometallics* **2015**, *34*, 1005-1012.

(27) (a) Stone, K. C.; Jamison, G. M.; White, P. S.; Templeton, J. L. *Organometallics* **2003**, *22*, 3083-3095. (b) Li, X.; Appelhans, L. N.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 3378-3387. (c) Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62-76.

(28) (a) Olsen, E. P. K.; Madsen, R. *Chem. Eur. J.* **2012**, *18*, 16023-16029. (b) Roa, A. E.; Salazar, V.; López-Serrano, J.; Oñate, E.; Paneque, M.; Poveda, M. L. *Organometallics* **2012**, *31*, 716-721. (c) Olsen, E. P. K.; Singh, T.; Harris, P.; Andersson, P. G.; Madsen, R. *J. Am. Chem. Soc.* **2015**, *137*, 834-842.

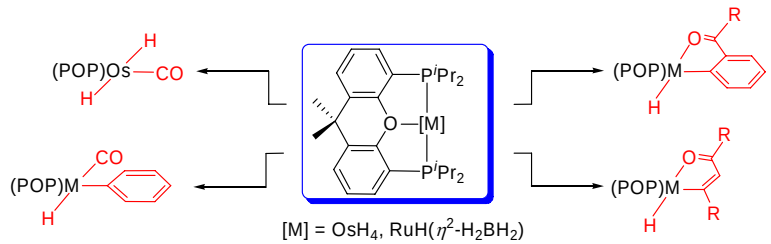
(29) Garralda, M. A. *Dalton Trans.* **2009**, 3635-3645.

(30) Willis, M. C. *Chem. Rev.* **2010**, *110*, 725-748.

(31) For examples of *ortho*-C-H bond activation see references 10a and 10b, whereas for examples of OC-H cleavage see: Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 1340-1348.

(32) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33-37. *SADABS*: Area-Detector absorption correction; Bruker-AXS: Madison, WI, 1996.

(33) *SHELXTL Package*, v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.



[M] = OsH_4, $RuH(\eta^2\text{-}H_2BH_2)$