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Synthesis and Reactivity of the Unusual Five-Coordinate Hydrido−Hydroxo Complex $OsH(OH)(CO)(P^iPr_3)_2$

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The five-coordinate complex $OsHCl(CO)(P^iPr_3)_2$ (**1**) reacts with KOH in methanol to give the hydroxo derivative $OsH(OH)(CO)(P^iPr_3)_2$ (**2**). Treatment of **2** with 1 equiv of dimethyl acetylenedicarboxylate affords $\overline{\text{Os}H\{OC(OCH_3)CHC(CO_2CH_3)\text{O}}\}(CO)(P^iPr_3)_2$ (**3**), which is the result of the *trans* addition of the O−H bond of **2** to the carbon−carbon triple bond of the alkyne. The structure of **3** was determined by an X-ray investigation. The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying apical positions. The equatorial plane is formed by the hydride, the carbonyl group, and the κ^2-O-donor ligand, which has a bite angle of 84.17(7)°. Complex **2** also reacts with methyl acrylate, methyl vinyl ketone, and allyl alcohol. Reaction with methyl acrylate leads to $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (**4**). The structure of **4** was also determined by an X-ray investigation. The coordination geometry around the osmium atom can be rationalized as derived from a highly distorted octahedron with the phosphorus atoms of the triisopropylphosphine ligands occupying *pseudo-trans* positions (P−Os−P = 144.29(3)°) at opposite sides of an ideal coordination plane defined by the carbonyl ligand, disposed *trans* to the hydroxo group and the hydrido ligand disposed *trans* to the olefin. In solution, complex **4** releases the olefin to regenerate **2** and methyl acrylate. The thermodynamic magnitudes involved in the equilibrium were determined in toluene-d_8 by $^{31}P\{^1H\}$ NMR spectroscopy. The values obtained were $\Delta H° = 17.0 \pm 0.5$ kcal mol^{-1} and $\Delta S° = 54.0 \pm 1.2$ cal K^{-1} mol^{-1}. In the presence of methyl vinyl ketone complex **2** affords $\overline{\text{Os}H\{CHCHC(\text{O}})CH_3\}(CO)(P^iPr_3)_2$ (**5**) and water whereas in the presence of allyl alcohol the loss of water affords $OsH(CH_2CH_3)(CO)_2(P^iPr_3)_2$ (**6**). Under a carbon dioxide atmosphere complex **2** gives the bicarbonato derivative $OsH(\kappa^2\text{-}O_2COH)(CO)(P^iPr_3)_2$ (**7**), which, by carbonylation, affords $OsH\{\kappa^1\text{-}OC(O)OH\}(CO)_2(P^iPr_3)_2$ (**8**). Complex **2** also reacts with phenyl isocyanate to give the carbamato derivative $OsH(\kappa^2\text{-}O_2CNHPh)(CO)(P^iPr_3)_2$ (**9**). The reactions of **2** with Lewis bases that are not bulky such as CO, $P(OMe)_3$, and ^tBuNC afford the six-coordinate hydrido−hydroxo compounds $OsH(OH)(CO)L(P^iPr_3)_2$ (L = CO (**10**), $P(OMe)_3$ (**11**), ^tBuNC (**12**)).

Introduction

In 1986, we reported that the treatment of $OsCl_3{\cdot}xH_2O$ with triisopropylphosphine in refluxing methanol leads to the five-coordinate hydrido−chloro complex $OsHCl(CO)(P^iPr_3)_2$ in nearly quantitative yield.[1] Since then it has proved to be one of the most important homogeneous catalysts for the reduction of unsaturated organic substrates and for the addition of silanes to alkynes.[2] Furthermore, this complex has been found to be the master key to the development of an extensive organometallic chemistry related to metal−hydrido[3] and metal−carbon bonds.[4]

We have now observed that the reaction of $OsHCl(CO)(P^iPr_3)_2$ with KOH also leads to the five-coordinate hydrido−hydroxo derivative $OsH(OH)(CO)(P^iPr_3)_2$, which is the starting point of new chemistry related to the M−OH bond.

Although mononuclear hydroxo complexes of transition metals have been postulated as critical intermediates in a number of catalytic reactions involving water as a substrate,[5] there are few examples of isolated compounds of this type.[6] The hydrido−hydroxo deriva-

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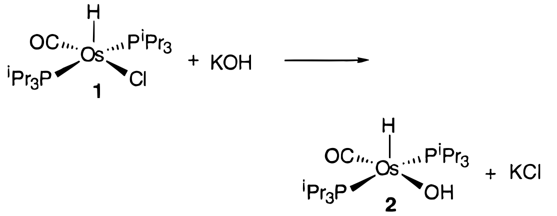
tives are particularly rare,[7] and as far as we know, no osmium−hydrido−hydroxo complexes have been reported.

In this paper, we report the synthesis and characterization of the unusual five-coordinate complex $OsH(OH)(CO)(P^iPr_3)_2$, its reactivity (including O−H insertion and C−H and C−C activation reactions), and the preparation of new six-coordinate osmium−hydrido−hydroxo derivatives.

Results and Discussion

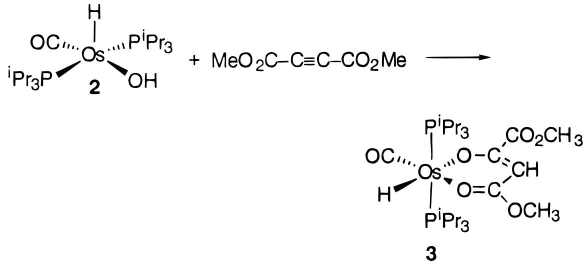
1. Synthesis and Characterization of $OsH(OH)(CO)(P^iPr_3)_2$. Treatment at room temperature of a tetrahydrofuran solution of the chloro−hydrido complex $OsHCl(CO)(P^iPr_3)_2$ (**1**) with the stoichiometric amount of another methanol solution of KOH (0.2 N) gives, after solvent removal, a sticky residue. Toluene extraction of the residue and filtration to remove KCl afford an orange solution from which the five-coordinate hydrido−hydroxo derivative $OsH(OH)(CO)(P^iPr_3)_2$ (**2**) is isolated as an orange solid in 89% yield (eq 1).



(1)

Complex **2** is soluble in most organic solvents except saturated hydrocarbons such as pentane and hexane. Although complex **2** is a very air-sensitive solid, it is stable for up to several months if kept in argon at 0 °C. In solution, it is stable under an argon atmosphere for only a few days.

The presence of the hydroxo ligand in **2** is supported by the IR and the ^1H NMR spectra. The most noticeable features of the IR spectrum in dichloromethane are three bands at 3640, 1960, and 1865 cm^{-1} corresponding to the vibrations ν(O−H), ν(Os−H), and ν(C≡O), respectively. At room temperature, in the low-field region, the ^1H NMR spectrum in toluene-d_8 shows two doublets of virtual triplets at 1.17 and 1.26 ppm for the methyl protons of the phosphines, as a result of the prochirality of the phosphorus atoms, along with the multiplet of the P−CH protons at 2.29 ppm and a very broad resonance at 4.2 ppm assigned to the proton of the hydroxo group. At −60 °C, the latter resonance is converted into a triplet with a P−H coupling constant of 8.1 Hz, which is centered at 4.47 ppm (Figure 1). Although complex **2** is coordinatively unsaturated, the shape of this resonance suggests that it is monomeric in toluene at low temperature. At low (−60 °C) and high (80 °C) temperatures the hydrido ligand gives rise to a triplet at −26.85 ppm with a P−H coupling constant of 12.9 Hz. This, together with the prochirality of the phosphorus atoms of the phosphine ligands, indicates that in solution, between 80 °C and −60 °C, complex **2** has the rigid structure shown in eq 2. In agreement with this, the $^{31}P\{^1H\}$ NMR spectrum, which is temperature invariable between 80 °C and −60 °C, shows a singlet at 46.8 ppm which is split into a doublet under off-resonance conditions.



(2)

The chemical shift of the hydrido ligand and the stretching frequency of the carbonyl group agree well with those previously reported for the starting complex **1** (−31.92 ppm and 1886 cm^{-1} in benzene solution), for which a square-pyramidal arrangement of ligands around the osmium atom has been also proposed.[1] The T-shaped disposition of the hydrido, the carbonyl, and the π-donor ligand (OH) with the carbonyl group disposed *trans* to the hydroxo ligand seems to be the result of an electronic push−pull mechanism between the donor and the acceptor ligands.[7d,8] Furthermore, it has been shown by X-ray diffraction analysis that for this type of compound the triisopropylphosphine ligands favor the

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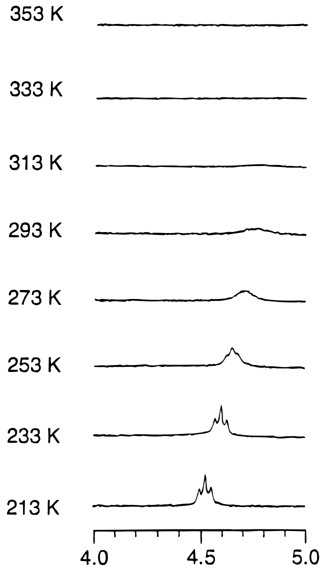

Figure 1. ^{1}H NMR (toluene-d_8) spectrum of $\mathrm{OsH(OH)(CO)(P^iPr_3)_2}$ (**2**) in the OH region as a function of temperature.

square-planar arrangement. The sixth (formally unoccupied) position of the octahedron is well-shielded by 4 of the 12 methyl groups of the phosphine ligands which surround the metal like an umbrella. The shielding effect of the methyl groups produces the bending of the phosphorus−metal−phosphorus angles, which have values of less than 180°.[9]

2. Insertion of $\mathbf{CH_3O_2CC{\equiv}CCO_2CH_3}$ into the O−H bond of 2. The addition of the stoichiometric amount of dimethyl acetylenedicarboxylate to a diethyl ether solution of **2** affords a red solid from which orange-red crystals of the complex $\mathrm{OsH\{OC(OCH_3)CHC(CO_2CH_3)O\}(CO)(P^iPr_3)_2}$ (**3** in eq 2) were isolated in 95% yield, after crystallization from pentane at −20 °C.

The formation of the κ^2-O-donor ligand of **3** is a result of the unprecedented *trans* addition of the O−H bond of **2** to the carbon−carbon triple bond of the alkyne. We note that Bergman has previously reported the reaction between the saturated hydroxo compound $\mathrm{Ir(\eta^5\text{-}C_5Me_5)(Ph)(OH)(PMe_3)}$ and dimethyl acetylenedicarboxylate. In the presence of this iridium−hydroxo compound the alkyne undergoes an insertion reaction into the Ir−O bond to afford the enol complex $\mathrm{Ir(\eta^5\text{-}C_5H_5)(Ph)\{(\mathit{Z})\text{-}C(CO_2CH_3){=}C(CO_2CH_3)OH\}(PMe_3)}$ in 76% yield.[6h] Similarly, the reactions of the complexes *trans*-$\mathrm{Pd(C_6H_4\text{-}CH{=}NPh)(NHPh)(PMe_3)_2}$ and *trans*-$\mathrm{Pd(C_6H_5)(NHPh)(PMe_3)_2}$ with dimethyl acetylenedicarboxylate result in the insertion of the acetylene into the Pd−N bonds.[10] In addition, we must point out the different behavior of complex **3** and its precursor **1**, which reacts with dimethyl acetylenedicarboxylate by insertion of the alkyne into the Os−H bond to give the alkenyl derivative $\mathrm{Os\{C[C(O)OCH_3]{=}CHCO_2CH_3\}Cl(CO)(P^iPr_3)_2}$.[2b]

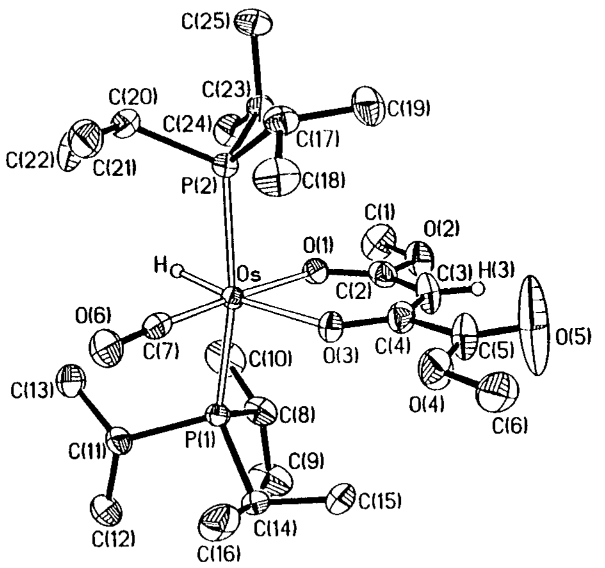

Figure 2. Molecular diagram of $\mathrm{OsH\{OC(OCH_3)CHC(CO_2CH_3)O\}(CO)(P^iPr_3)_2}$ (**3**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $\mathbf{OsH\{OC(OCH_3)CHC(CO_2CH_3)O\}(CO)(P^iPr_3)_2}$ (3)

Os−H	1.51(3)	C(3)−H(3)	0.90(4)
Os−P(1)	2.3704(13)	C(3)−C(4)	1.375(4)
Os−P(2)	2.3716(13)	O(3)−C(4)	1.267(3)
Os−C(7)	1.812(3)	C(4)−C(5)	1.532(4)
Os−O(1)	2.160(2)	C(5)−O(4)	1.300(4)
Os−O(3)	2.194(2)	C(5)−O(5)	1.174(4)
C(7)−O(6)	1.171(3)	O(4)−C(6)	1.445(3)
O(1)−C(2)	1.246(3)	C(2)−O(2)	1.353(3)
C(2)−C(3)	1.404(4)	O(2)−C(1)	1.445(4)

P(1)−Os−P(2)	164.74(2)	C(3)−C(4)−O(3)	129.3(3)
C(7)−Os−O(1)	177.66(9)	C(3)−C(4)−C(5)	115.4(2)
H−Os−O(3)	170.7(1)	C(3)−C(2)−O(2)	113.7(2)
O(1)−Os−O(3)	84.17(7)	Os−C(7)−O(6)	177.3(2)
O(1)−C(2)−C(3)	128.3(3)		

The IR spectrum of **3** in Nujol shows the ν(Os−H) absorption at 2142 cm^{-1} along with four ν(CO) bands; the first of them, at 1884 cm^{-1}, corresponds to the ν(C≡O) vibration, whereas the other three at 1729, 1625, and 1521 cm^{-1} are due to the bidentate O-donor ligand. In the ^{1}H NMR spectrum this ligand gives rise to three singlets at 6.15, 3.40, and 3.27 ppm corresponding to the −CH− and the methyl groups, respectively. Furthermore, the spectrum shows a triplet at −16.9 ppm with a P−H coupling constant of 16.5 Hz assigned to the hydrido ligand. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 36.6 ppm, in line with the mutually *trans* disposition of the phosphine ligands.

The definitive characterization of the unusual[11] κ^2-O-donor ligand of **3** was obtained from an X-ray diffraction experiment on a single crystal of this compound. A view of its molecular geometry is shown in Figure 2. Selected bond distances and angles are listed in Table 1.

The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying the apical positions (P(1)−Os−P(2) = 164.74(2)°). The equatorial

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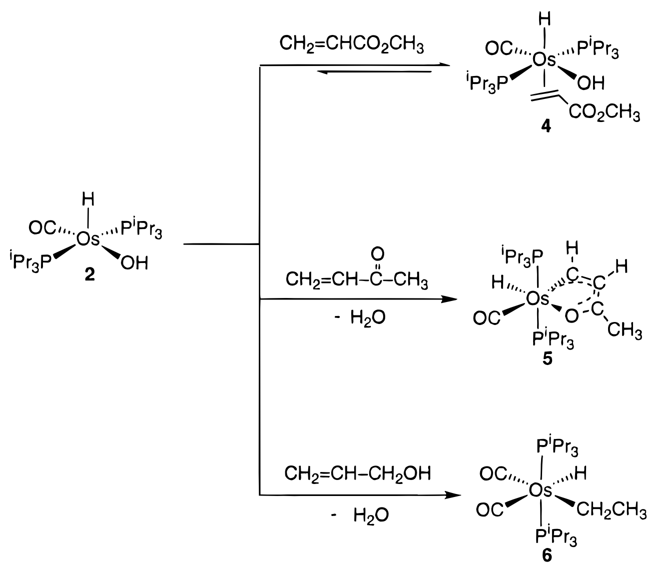
[11] Using the Cambridge Structural Database, we have not detected any transition-metal complex previously reported with this ligand.

Scheme 1



plane is formed by the hydride, the carbonyl group, and the κ^2-O-donor ligand, which has a bite angle O(1)–Os–O(3) of 84.17(7)°.

The bidentate O-donor ligand forms a six-membered, almost planar ring with the osmium atom. The deviations from the best plane are 0.0573(4) (Os), 0.009(2) (O(1)), −0.027(3) (C(2)), 0.006(3) (C(3)), 0.020(3) (C(4)), and −0.007(2) (O(3)) Å. The two Os–O bond lengths are different, the Os–O(3) distance (2.194(2) Å) being approximately 0.3 Å longer than the Os–O(1) distance (2.160(2) Å). Within the κ^2-O-donor ligand, the structural parameters for the sequence O(1)–C(2)–C(3)–C(4)–O(3) (1.246(3), 1.404(4), 1.375(4), 1.267(3) Å) suggest that, although there is some intraligand π-conjugation, the bond sequence is mainly that proposed in eq 2 (double–single–double–single). This is also supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows singlets at 170.2, 164.7, and 86.2 ppm for C(2), C(4), and C(3), respectively.

3. Reactions of 2 with Olefins. The hydrido–chloro complex **1** coordinates activated olefins to give six-coordinate, hydrido–olefin compounds of the $OsHCl(\eta^2\text{-}CH_2{=}CHR)(CO)(P^iPr_3)_2$ type, which are stable and do not evolve by insertion of the olefin into the osmium–hydrido bond.[1] Similarly, the treatment of a tetrahydrofuran solution of **2** with 1.2 equiv of methyl acrylate affords the six-coordinate complex $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (**4**), which was isolated as a white solid in 85% yield (Scheme 1).

Figure 3 shows a representation of the molecule of **4**. Selected bond distances and angles are listed in Table 2. The coordination geometry around the osmium atom could be rationalized as being derived from a highly distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying *pseudo-trans* positions ((P(1)–Os–P(2) = 144.29(3)°), at opposite sides of an ideal coordination plane defined by the carbonyl ligand disposed *trans* to the hydroxo group (O(1)–Os–C(5) = 178.8(2)°) and the hydrido ligand disposed *trans* to the midpoint (M) of the carbon–carbon double bond of the olefin (M–Os–H = 177.9(16)°). The strong deviation of the P(1)–Os–P(2) angle from the ideal value of 180° is most probably a result of the large steric hindrance that occurs between the phosphines and the olefin. The methyl acrylate lies almost parallel to the phosphorus-phosphorus vector, the dihedral angle between the P(1)–Os–P(2) and C(1)–Os–C(2) planes being 21.4°.

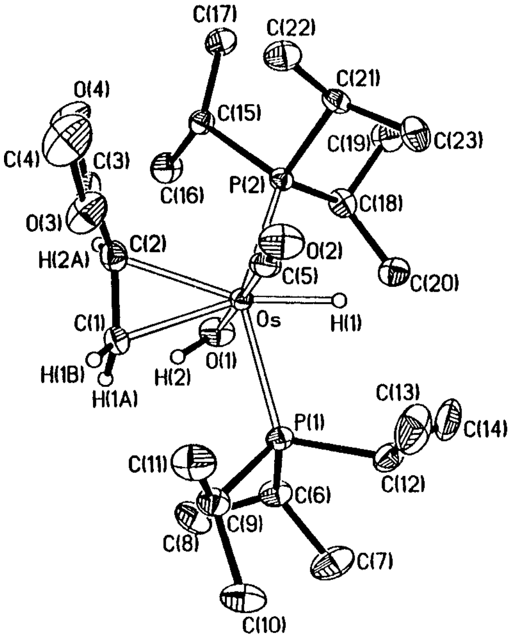


Figure 3. Molecular diagram of $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (**4**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (4)

Os–H(1)	1.66(5)	O(1)–H(2)	0.71(10)
Os–C(5)	1.844(4)	C(1)–C(2)	1.418(5)
Os–O(1)	2.111(3)	C(2)–C(3)	1.464(5)
Os–C(1)	2.169(3)	C(5)–O(2)	1.163(5)
Os–C(2)	2.210(4)	C(1)–H(1A)	0.93(5)
Os–P(1)	2.3881(9)	C(1)–H(1B)	1.09(4)
Os–P(2)	2.4169(8)	C(2)–H(2A)	0.83(4)
P(1)–Os–P(2)	144.29(3)	Os–O(1)–H(2)	90(8)
C(5)–Os–O(1)	178.76(12)	C(3)–C(2)–Os	116.8(3)
C(1)–Os–C(2)	37.77(13)	H(2A)–C(2)–C(3)	111(4)
C(5)–Os–C(1)	96.5(2)	H(1A)–C(1)–H(1B)	113(4)
C(5)–Os–C(2)	94.9(2)		

The intrinsic asymmetry of the olefin produces a loss of symmetry in the molecule, which is seen in the structural parameters by the two different Os–P distances. The Os–P(2) bond length (2.4169(8) Å) is approximately 0.03 Å longer than the Os–P(1) bond length (2.3881(9) Å). This fact can be also observed in the $^{31}P\{^1H\}$ NMR spectrum, which shows an AB spin system at 18.0 and 9.7 ppm, with an A–B coupling constant of 165 Hz.

The osmium–methyl acrylate coordination exhibits Os–C distances of 2.169(3) Å (Os–C(1)) and 2.210(4) Å (Os–C(2)), which agree well with those found in other osmium-olefin complexes (between 2.15 and 2.28 Å).[12] Similarly, the olefinic bond distance C(1)–C(2) (1.418(5) Å) is within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).[13]

It is also interesting to note the relatively small Os–O(1)–H(2) angle of 90(8)° and the orientation of the

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(12) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 636.

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

hydroxo proton. The Os−O(1)−H(2) angle, which is significantly smaller than the normal tetrahedral value, agrees well with that previously determined by X-ray diffraction for the iridium complex $[\text{IrH(OH)(PMe}_3)_4]^+$ (91(±7)°).[14] However, unlike this compound, the O−H ligand points away from the hydrido ligand. A similar arrangement has been found for the S−H group of the related complex $[\text{IrH(SH)(PMe}_3)_4]^+$.[7c]

The spectroscopic data obtained for **4** are in accordance with the structure shown in Figure 3. Thus, in the ^{1}H NMR spectrum at room temperature methyl acrylate gives rise to three multiplets at 2.60, 3.36, and 3.58 ppm corresponding to the olefinic protons and a singlet at 3.64 ppm due to the protons of the methyl group. The spectrum also contains a broad resonance at −4.50 ppm, assigned to the hydroxo proton,[15] and a triplet at −4.27 ppm with a P−H coupling constant of 29.9 Hz due to the hydrido ligand. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonances are two singlets at 176.3 and 50.3 ppm corresponding to C(3) and C(4) and, at 46.8 and 44.1 ppm, two triplets with P−C coupling constants of 5.7 and 6.2 Hz, which were assigned to the olefinic carbon atoms C(2) and C(1), respectively.

In solution, complex **4** releases the olefin to give **2** and methyl acrylate. The constants of the dissociation equilibrium were calculated between 253 and 323 K by ^{31}P{^{1}H} NMR spectroscopy, on the assumption that in the equilibrium the concentration of **2** is the same as the methyl acrylate concentration. Linear least-squares analysis of ln K versus $1/T$ provides values for $\Delta H°$ and $\Delta S°$ of 17.0 ± 0.5 kcal mol^{-1} and 54.0 ± 1.2 cal K^{-1} mol^{-1}, respectively.

At room temperature complex **2** does not coordinate significant amounts of methyl vinyl ketone. However, in the presence of the α,β-unsaturated ketone it evolves into the derivative $\overline{\text{OsH}\{\text{CHCHC(O}}\text{)CH}_3\}(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**5**) and water after 7 days (Scheme 1).

Complex **5** was isolated as a yellow solid in 42% yield. In the ^{1}H NMR, the CHCHCO protons give rise to signals at 13.66 (Os−CH) and 7.31 (CH) ppm, which appear as doublets with an H−H coupling constant of 8.4 Hz, while the resonance of the protons of the C(O)-CH_3 group is observed at 1.58 ppm, as a singlet. Furthermore, in the high-field region, the spectrum contains a triplet with a P−H coupling constant of 27.4 Hz at −4.87 ppm, which corresponds to the resonance of the hydrido ligand. The resonance of the OsCH carbon atom appears in the ^{13}C{^{1}H} NMR spectrum at 250.8 ppm as a triplet with a P−C coupling constant of 2.3 Hz. The remaining resonances of the carbon atoms of the CHCHC(O)CH_3 ligand were located at 200.0 (OsOC), 130.4 (CH), and 19.6 (CH_3) ppm. The first resonance was observed as a triplet with a P−C coupling constant of 3.0 Hz, whereas the other two appeared as singlets. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 42.1 ppm, indicating the relative *trans* position of the phosphine ligands. The above-mentioned spectroscopic data agree well with those previously reported for the complex $\overline{\text{Os}\{\text{CHCHC(O}}\text{)Ph}\}\text{Cl(CO)}(\text{P}^i\text{Pr}_3)_2$, which was obtained as a byproduct (8% yield) from the reaction of the chloro complex **1** with 1-phenyl-2-propyn-1-ol and in which the presence of the metallacycle unit was established by X-ray investigation of a single crystal of the complex.

The coordination of significant amounts of allyl alcohol to the hydroxo complex **2** was not observed either. However, complex **2** evolves in the presence of the α,β-unsaturated alcohol. In this case, the product formed is the hydrido−ethyl derivative $\text{OsH(CH}_2\text{CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$ (**6**, in Scheme 1). The related complexes $\text{OsH(CH}_3)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2$ and $\text{OsH(CH}_2\text{OMe)(CO)}_2(\text{P}^i\text{Pr}_3)_2$ have been previously prepared from the reactions of the tetrahydride $\text{OsH}_4(\text{CO})(\text{P}^i\text{Pr}_3)_2$ with ethanol and 2-methoxyethanol, respectively.[4b]

Complex **6** was isolated as a white solid in 58% yield. The relative *cis* positions of the carbonyl ligands were inferred from the IR spectrum, which shows, along with a ν(Os−H) band at 2018 cm^{-1}, two strong ν(CO) absorptions at 1958 and 1876 cm^{-1}. The ^{13}C{^{1}H} NMR spectrum also supports this idea, with two triplets at 191.1 ($J_{\text{P-C}} = 6.0$ Hz) and 183.1 ($J_{\text{P-C}} = 8.1$ Hz) ppm which are attributable to the carbonyl ligands. This spectrum also contains the expected resonances for the ethyl group. At −19.5 ppm the Os-CH_2 carbon atom gives rise to a triplet with a P−C coupling constant of 8.25 Hz, whereas the resonance of the CH_3 group appears at 21.6 ppm as a singlet. The CH groups of the phosphine ligands give a virtual triplet at 25.5 ppm ($N = 25.4$ Hz), which is characteristic of two equivalent phosphine ligands in a relative *trans* positions. This is in agreement with the singlet at 23.1 ppm found in the ^{31}P{^{1}H} NMR spectrum. In the ^{1}H NMR spectrum the most noticeable resonances are a triplet ($J_{\text{P-H}} = 22.8$ Hz) of triplets ($J_{\text{H-H}} = 1.6$ Hz) at −7.78 ppm, a quartet ($J_{\text{H-H}} = 7.8$ Hz) of triplets ($J_{\text{P-H}} = 7.6$ Hz) of doublets ($J_{\text{H-H}} = 1.6$ Hz) at 0.79 ppm, and a triplet ($J_{\text{H-H}} = 7.8$ Hz) at 1.93 ppm, corresponding to the hydrido ligand and the CH_2 and CH_3 protons of the ethyl group, respectively.

We note that Woerpel and Bergman have previously studied the reaction of the iridium−hydroxo complex Ir(η^5-C_5Me_5)(Ph)(OH)(PMe_3) with ethylene. In that case, in contrast to the reactions shown in Scheme 1, the unfunctionalized olefin undergoes an insertion reaction into the Ir−OH bond of the iridium starting material, to give a hydroxyethyl derivative which subsequently evolves into a formylmethyl complex.[6h]

4. Reactions of 2 with CO_2 and PhN=C=O. When a slow stream of carbon dioxide is passed through diethyl ether solutions of **2**, the bicarbonato complex $\text{OsH}(\kappa^2\text{-O}_2\text{COH})(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (**7**) is formed as a white solid in nearly quantitative yield (Scheme 2).

The κ^2 coordination mode of the bicarbonato ligand in **7** is indicated by the IR spectrum in Nujol, which contains bands at 1575 and 1496 cm^{-1} assignable to the symmetric and asymmetric OCO stretching frequencies, respectively.[16] These values agree well with those previously reported for rhodium complexes of the $\text{RhH}_2(\kappa^2\text{-O}_2\text{COH})(\text{PR}_3)_2$ type, which contain a bidentate bicarbonato ligand, as has been confirmed by an X-ray investigation on a single crystal of $\text{RhH}_2(\kappa^2\text{-O}_2\text{COH})(\text{P}^i$-

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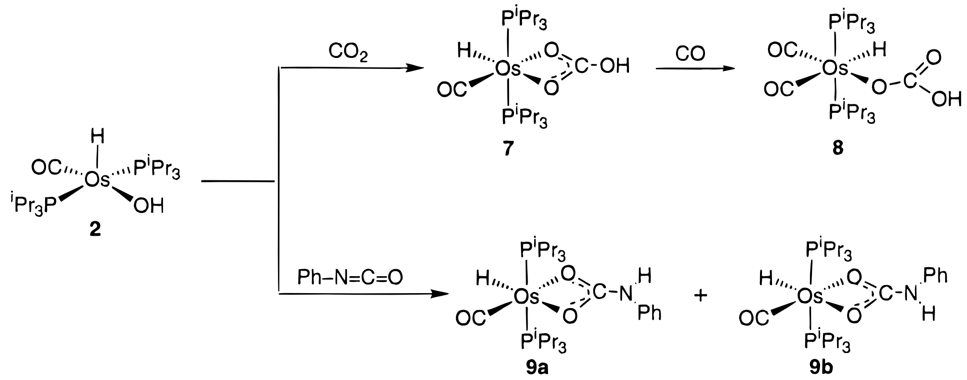
[14] A value of 104.4(7)° has been determined by low-temperature neutron diffraction.[7c]

[15] A similar chemical shift (−1.40 ppm) has been reported for the hydroxo proton of the complex $[\text{IrH(OH)(PMe}_3)_4]^+$.[7b]

[16] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978.

Scheme 2



$Pr_3)_2$.[17] In the ^1H NMR spectrum the most noticeable resonances are two broad signals at −21.94 and 11.30 ppm, assigned to the hydrido ligand and the proton of the bicarbonato group. This ligand gives rise to a singlet at 161.3 ppm in the $^{13}C\{^1H\}$ NMR spectrum. A broad singlet at 39.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of **7**.

The broadness of the resonance of the hydrido ligand as well as that observed in the $^{31}P\{^1H\}$ NMR spectrum suggests that, in solution, complex **7** is in rapid equilibrium[18] with a five-coordinate species containing a κ^1-bicarbonato ligand. This concurs with the way in which the *cis*-dicarbonyl complex $OsH\{\kappa^1\text{-}OC(O)OH\}(CO)_2(P^iPr_3)_2$ (**8**) is formed by passing a slow stream of carbon monoxide through a diethyl ether suspension of **7** (Scheme 2).

Complex **8** was isolated as a white solid in 82% yield. In accordance with the mutually *cis* disposition of the two carbonyl ligands, the IR spectrum of **8** in Nujol shows two ν(CO) absorptions at 1972 and 1912 cm^{-1}. Furthermore, the spectrum reflects the conversion of the bicarbonato group from bidentate to monodentate. Thus, the symmetric and asymmetric ν(OCO) stretchings appear at 1616 and 1350 cm^{-1} ($\Delta\nu = 266$ cm^{-1}), in line with those of monodentate bicarbonato species.[19] In the ^1H NMR spectrum, at room temperature the most noticeable signal is that due to the hydrido ligand, which appears at −3.86 ppm as a triplet with a P−H coupling constant of 21.0 Hz. At this temperature the resonance of the bicarbonato proton was not observed. It was located at 8.95 ppm, as a broad signal, at −60 °C. The $^{13}C\{^1H\}$ NMR spectrum confirms the presence of two carbonyl ligands in the complex, showing two triplets at 190.6 and 181.5 ppm, with P−C coupling constants of 5.2 and 8.1 Hz, respectively. The carbon atom of the bicarbonato group gives rise to a singlet at 162.4 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 37.2 ppm.

Complex **2** also reacts with phenyl isocyanate. Interestingly, the reaction product is the carbamato derivative $OsH(\kappa^2\text{-}O_2CNHPh)(CO)(P^iPr_3)_2$ (**9**), which is the result of adding the O−H bond of **2** to the C=N double bond of the heteroallene (Scheme 2). Similar behavior has been observed for the organic alcohols.[20]

Complex **9** was isolated as a yellow solid in 79% yield. The bidentate coordination of the carbamato ligand is supported by the IR spectrum in Nujol, which shows bands at 1620 and 1518 cm^{-1}, corresponding to the OCO group. The ^1H NMR spectrum in benzene-d_6 shows the presence, in a 1:0.8 molar ratio, of the two possible conformers (**9a**,**b**), ascribed to hindered rotation about the C−N axis. The spectrum thus contains two hydrido resonances at −21.0 and −20.8 ppm, which appear as triplets with P−H coupling constants of 15.5 and 16.0 Hz, respectively. The presence of the conformers **9a**,**b** is also supported by the $^{31}P\{^1H\}$ NMR spectrum, which shows two singlets at 39.4 and 39.2 ppm. However, the $^{13}C\{^1H\}$ NMR spectrum only shows resonances of one type, suggesting that the carbon atoms of both conformers are isochronous. The most noticeable resonance of the spectrum is a singlet at 162.6 ppm, corresponding to the central carbon atom of the carbamato ligand. The chemical shift of this resonance compares well with those previously reported for related compounds (δ 170−160).[21]

5. Synthesis of Six-Coordinate Hydrido−Hydroxo Compounds. Compounds of this type can be easily prepared by the reaction of **2** with nonbulky Lewis bases such as CO, $P(OMe)_3$ and ^tBuNC. When a slow stream of carbon monoxide is passed through a toluene solution of **2**, the *cis*-dicarbonyl complex $OsH(OH)(CO)_2(P^iPr_3)_2$ (**10**) is formed as a white solid in 60% yield. Similarly, treatment of tetrahydrofuran and diethyl ether solutions of **2** with stoichiometric amounts of trimethyl phosphite and *tert*-butyl isocyanide, respectively, affords the compounds $OsH(OH)(CO)\{P(OMe)_3\}(P^iPr_3)_2$ (**11**) and $OsH(OH)(CO)(^tBuNC)(P^iPr_3)_2$ (**12**), which were isolated as white solids in 78% (**11**) and 47% (**12**) yield (eq 3).

The relative *cis* positions of the carbonyl ligands in **10** was inferred from the IR spectrum which shows two strong ν(CO) absorptions at 1965 and 1890 cm^{-1}. As in the case of **4**, the resonances of the hydroxo protons of the three compounds appear in the high-field region of the ^1H NMR spectra, at −3.14 (**10**), −3.71 (**11**), and −4.25 (**12**) ppm. In this region, the ^1H NMR spectra of **10** and **12** also contain a triplet at −4.14 (**10**) and −6.07 (**12**) ppm, with P−H coupling constants of 20.9 and 21.3 Hz, respectively, which correspond to the hydrido

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(18) Attempts to study the equilibrium were unsuccessful due to the low solubility of the complex.

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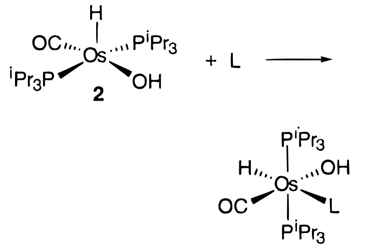

L = CO (**10**), $P(OMe)_3$ (**11**), ^tBuNC (**12**) (3)

ligands. In agreement with the *trans* disposition of the hydrido and trimethyl phosphite ligands, the hydrido resonance of **11** is observed as a doublet of triplets with P−H coupling constants of 157.2 and 24.3 Hz. The $^{31}P\{^1H\}$ NMR spectra of **10** and **12** show singlets at 32.7 (**10**) and 31.6 (**12**) ppm, whereas the $^{31}P\{^1H\}$ NMR spectrum of **11** contains a doublet at 23.8 (P^iPr_3) ppm and a triplet at 107.9 ($P(OMe)_3$) ppm. In accordance with the *cis* disposition of the trimethyl phosphite with respect to both phosphine ligands, the value of the P−P coupling constant is 17.6 Hz.

Concluding Remarks

We report overwhelming evidence of the versatility of the chemistry of the five-coordinate hydrido−hydroxo complex $OsH(OH)(CO)(P^iPr_3)_2$ (**2**), which can be easily prepared from $OsHCl(CO)(P^iPr_3)_2$ by reaction with KOH in methanol, in which it is stable. According to the spectroscopic data obtained for **2**, a square-pyramidal arrangement of ligands around the osmium atom, with a T-shaped arrangement for the hydrido, carbonyl and hydroxo groups can also be proposed.

This arrangement appears to determine the reactivity of **2**, which is characterized by (i) the inertia of the hydrido ligand as a result of its *trans* disposition to the coordination vacancy and the rigidity of the structure in solution, (ii) the tendency of unsaturated organic molecules such as dimethyl acetylenedicarboxylate and heteroallenes to undergo insertion reactions into the O−H bonds, most probably, as a result of an electronic push−pull mechanism between the carbonyl and hydroxo ligands (mutually *trans* disposed), which strengthens the Os−O bond while it weakens the O−H bond, and (iii) the formation of six-coordinate hydrido−hydroxo compounds of the $OsH(OH)(CO)L(P^iPr_3)_2$ type, as a result of the tendency shown by the osmium atom to add Lewis bases that are not bulky.

Reactions of particular interest take place when complex **2** is treated with methyl vinyl ketone and allyl alcohol. Under these conditions the compounds formed, $OsH\{CHCHC(O)CH_3\}(CO)(P^iPr_3)_2$ and $OsH(CH_2CH_3)(CO)_2(P^iPr_3)_2$, involve the loss of a water molecule and C−H and C−C activation processes, respectively.

In conclusion, this study has revealed that the unusual five-coordinate hydrido−hydroxo complex $OsH(OH)CO)(P^iPr_3)_2$ has chemical behavior completely different from that previously reported for known late-transition-metal−hydroxo derivatives.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by known procedures and distilled prior to use. $OsHCl(CO)(P^iPr_3)_2$ (**1**) was prepared by a published method.[1]

Physical Measurements. Infrared spectra were run on either a Perkin-Elmer 883 or a Nicolet 550 spectrometer as either solids (Nujol mulls or polyethylene sheets) or solutions (NaCl cell windows). Mass spectra analyses were performed with a VG Autospec instrument operating in the positive mode; ions were produced with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on either a Varian UNITY 300 or on a Bruker 300 AXR spectrometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and (85%) H_3PO_4 (^{31}P). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^1H and $N = J(CP) + J(CP')$ for ^{13}C) are given in hertz.

Preparation of $OsH(OH)(CO)(P^iPr_3)_2$ (2). A solution of **1** (450 mg, 0.81 mmol) in tetrahydrofuran (15 mL) was treated with a methanol KOH solution (0.2024 N, 4.0 mL, 0.81 mmol). After the orange mixture was stirred for 10 min, the solvent was removed *in vacuo*. The orange residue was treated with toluene (10 mL) and the resulting suspension filtered through Kieselguhr. The filtrate was evaporated to dryness and the residue washed twice with 2 mL of cold pentane and dried *in vacuo*. The product is an orange solid: yield 526 mg (89%). IR (CH_2Cl_2, cm^{-1}): ν(O−H) 3640 w, ν(Os−H) 1960 w, ν(C≡O) 1865 s. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −26.85 (t, 1H, J(PH) = 12.9 Hz, Os−H), 1.17 (dvt, 18H, J(HH) = 6.6 Hz, N = 12.6 Hz, $PCHCH_3$), 1.26 (dvt, 18H, J(HH) = 7.2 Hz, N = 13.5 Hz, $PCHCH_3$), 2.29 (m, 6H, $PCHCH_3$), 4.25 (br, 1H, OH).[22] $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 46.8 (s, d in off-resonance). Anal. Calcd for $C_{19}H_{44}O_2OsP_2$: C, 40.99; H, 7.97. Found: C, 40.70; H, 7.40.

Preparation of $OsH\{OC(OCH_3)CHC(CO_2CH_3)O\}(CO)(P^iPr_3)_2$ (3). A solution of **2** (292 mg, 0.52 mmol) in diethyl ether (10 mL) was treated with dimethyl acetylenedicarboxylate (65 μL, 0.53 mmol). The mixture was stirred then for 90 min; the solvent was removed *in vacuo* to afford an orange-red solid, which was crystallized from pentane at −20 °C. The product is an orange microcrystalline solid: yield 349 mg (95%). IR (Nujol, cm^{-1}): ν(Os−H) 2142 m, ν(C≡O) 1884 s, ν(C=O) 1615 s and 1521 s. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −16.90 (t, 1H, J(PH) = 16.5 Hz, Os−H), 1.23 (dvt, 18H, J(HH) = 6.3 Hz, N = 12.6 Hz, $PCHCH_3$), 1.30 (dvt, 18H, J(HH) = 6.6 Hz, N = 13.2 Hz, $PCHCH_3$), 2.29 (m, 6H, $PCHCH_3$), 3.27 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 6.15 (s, 1H, CH). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 36.6 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6): δ 184.3 (t, J(PC) = 9.0 Hz, Os−CO), 172.5 (s, CO_2CH_3), 170.2 ($OsOCOCH_3$), 164.7 (s, $OC(CO_2CH_3)$), 86.2 (s, CH), 51.9 and 51.3 (s, both OCH_3), 25.3 (dvt, N = 23.7 Hz, PCH), 19.9 and 19.5 (s, $PCHCH_3$). Anal. Calcd for $C_{25}H_{50}O_6OsP_2$: C, 42.97; H, 7.21. Found: C, 42.72; H, 6.76.

Preparation of $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (4). A solution of **2** (131 mg, 0.24 mmol) in tetrahydrofuran (8 mL) was treated with methyl acrylate (25 μL, 0.28 mmol). The mixture was stirred then for 30 min; the solvent was removed *in vacuo* to afford a yellow solid, which was crystallized from pentane at −20 °C. The product is a colorless microcrystalline solid: yield 128 mg (85%). IR (Nujol, cm^{-1}): ν(O−H) 3662 w, ν(Os−H) 2064 w, ν(C≡O) 1907 s, ν(C=O) 1693 m. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −4.50 (br, 1H, OH), −4.27 (t, 1H, J(PH) = 29.9 Hz, Os−H), 1.15 (dvt, 18H, J(HH) = 7.2 Hz, N = 12.6 Hz, $PCHCH_3$), 1.23 (dvt, 18H, J(HH) = 7.6 Hz, N = 13.5 Hz, $PCHCH_3$), 2.50 (m, 6H, $PCHCH_3$), 2.60 (br, 1H, CH=), 3.36 (br, 1H, CH=), 3.58 (br, 1H, CH=), 3.64 (s, 3H, OCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): AB system, δ_A = 18.0, δ_B = 9.7, J(AB) = 165 Hz. $^{13}C\{^1H\}$ NMR

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[22] 4.47 (t, 1H, J(PH) = 8.1 Hz, OH), at −60 °C in toluene-d_8 as solvent.

(75.4 MHz, 293 K, C_6D_6): δ 181.4 (vt, J(PC) + J(P′C) = 16.2 Hz, Os−CO), 176.3 (s, CO_2), 50.3 (s, OCH_3), 46.8 (vt, J(PC) + J(P′C) = 11.0 Hz, CH_2=), 44.1 (vt, J(PC) + J(P′C) = 12.9 Hz, CH=), 26.5 (d, J(PC) = 23.8 Hz, PCH), 26.4 (d, J(PC) = 26.8 Hz, PCH), 20.4 (s, PCHCH_3), 20.2 (s, PCHCH_3). Anal. Calcd for $C_{23}H_{50}O_4OsP_2$: C, 42.98; H, 7.84. Found: C, 42.82; H, 7.53.

Preparation of $\overline{\mathrm{OsH\{CHCHC(O}}\mathrm{)CH_3\}(CO)(P^iPr_3)_2}$ (5). A solution of **2** (156 mg, 0.28 mmol) in tetrahydrofuran (12 mL) was treated with methyl vinyl ketone (35 μL, 0.42 mmol). The mixture was stirred then for 7 days at room temperature, and the solvent was removed *in vacuo*. The residue was treated with dichloromethane (8 mL) and the resulting suspension filtered through Kieselguhr. The solvent of the filtrate was again evaporated to dryness, and the new residue was treated with acetone (8 mL). The resulting suspension was filtered through Kieselguhr and the filtrate solvent was removed *in vacuo* to afford a yellow solid, which was washed five times with 1.5 mL of methanol and dried *in vacuo*. The product is a yellow solid: yield 71 mg (42%). IR (Nujol, cm^{-1}): ν(Os−H) 2018 w, ν(C≡O) 1890. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −4.87 (t, 1H, J(PH) = 27.4 Hz, Os−H), 1.05 (dvt, 18H, J(HH) = 7.1 Hz, N = 13.8 Hz, PCHCH_3), 1.22 (dvt, 18H, J(HH) = 7.0 Hz, N = 13.3 Hz, PCHCH_3), 1.53 (s, 3H, OCCH_3), 2.07 (m, 6H, PCHCH$_3$), 7.31 (d, 1H, J(HH) = 8.4 Hz, CH), 13.66 (d, 1H, J(HH) = 8.4 Hz, OsCH). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 42.1 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6): δ 250.8 (t, J(PC) = 2.3 Hz, OsCH), 200.0 (t, J(PC) = 3.0 Hz, OsOC), 189.2 (t, J(PC) = 9.7 Hz, Os−CO), 130.4 (s, CH), 26.7 (vt, N = 27.2 Hz, PCH), 20.3 (s, PCHCH_3), 19.5 (s, PCHCH_3). Anal. Calcd for $C_{23}H_{48}O_2OsP_2$: C, 45.38; H, 7.95. Found: C, 45.74; H, 7.95. MS (FAB): m/e 609 (M^+ − 1).

Preparation of $OsH(CH_2CH_3)(CO)_2(P^iPr_3)_2$ (6). A solution of **2** (150 mg, 0.24 mmol) in tetrahydrofuran (8 mL) was treated with allyl alcohol (20 μL, 0.29 mmol). The mixture was then stirred for 24 h at room temperature, and the solvent was removed *in vacuo*. The residue was treated with acetone (5 mL) and the resulting suspension filtered through Kieselguhr. The solvent of the yellow filtrate was removed *in vacuo* to afford a yellow solid, which was crystallized from methanol at −20 °C. The product is a colorless microcrystalline solid: yield 94 mg (58%). IR (Nujol, cm^{-1}): ν(Os−H) 2018 w, ν(C≡O) 1858 s and 1876 s. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −7.78 (tt, 1H, J(PH) = 22.8 Hz, J(HH) = 1.6 Hz, Os−H), 0.79 (qtd, 2H, J(HH) = 7.8 Hz, J(PH) = 7.6 Hz, J(HH) = 1.6 Hz, OsCH_2), 1.18 (dvt, 18H, J(HH) = 7.2 Hz, N = 14.4 Hz, PCHCH_3), 1.20 (dvt, 18H, J(HH) = 7.2 Hz, N = 14.1 Hz, PCHCH_3), 1.93 (t, 3H, J(HH) = 7.8 Hz, CH_2CH_3), 2.30 (m, 6H, PCHCH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 23.1 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, C_6D_6): δ 191.9 (t, J(PC) = 6.0 Hz, Os−CO), 183.1 (t, J(PC) = 8.1 Hz, Os−CO), 25.5 (vt, N = 26.8 Hz, PCH), 21.6 (s, $CH_2$$CH_3$), 19.1 (s, PCH$CH_3$), 19.0 (s, PCH$CH_3$), −19.5 (t, J(PC) = 8.3 Hz, OsCH_2). Anal. Calcd for $C_{22}H_{48}O_2OsP_2$: C, 44.28; H, 8.11. Found: C, 43.99; H, 8.08.

Preparation of $OsH(\kappa^2\text{-}O_2COH)(CO)(P^iPr_3)_2$ (7). A slow stream of carbon dioxide was passed through a solution of **2** (105 mg, 0.19 mmol) in diethyl ether (10 mL). After 5 min a yellow suspension formed. The solvent was then decanted and the solid washed twice with 1 mL of diethyl ether. The product was a white solid: yield 106 mg (94%). IR (Nujol, cm^{-1}): ν(O-H) 2644 m, ν(Os-H) 2160 m, ν(C≡O) 1889 s, ν(OCO) 1575 s and 1496 s. ^1H NMR (300 MHz, 293 K, CD_2Cl_2): δ −21.94 (br, 1H, Os−H), 1.27 (dvt, 18H, J(HH) = 6.6 Hz, N = 13.5 Hz, PCHCH_3), 1.29 (dvt, 18H, J(HH) = 7.2 Hz, N = 14.2 Hz, PCHCH_3), 2.42 (m, 6H, PCHCH$_3$), 11.30 (br, 1H, OH). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, CD_2Cl_2): δ 39.7 (br). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, CD_2Cl_2): δ 182.5 (t, J(PC) = 12.0 Hz, Os−CO), 161.3 (s, COH), 25.3 (vt, N = 24.7 Hz, PCH), 20.0 (s, PCHCH_3), 19.3 (s, PCHCH_3). Anal. Calcd for $C_{20}H_{44}O_4OsP_2$: C, 39.99; H, 7.38. Found: C, 40.15; H, 7.33.

Preparation of $OsH\{\kappa^1\text{-}OC(O)OH\}(CO)_2(P^iPr_3)_2$ (8). Carbon monoxide was bubbled through a suspension of **7** (120 mg, 0.20 mmol) in diethyl ether (12 mL). A colorless solution was instantly formed. The solvent was removed *in vacuo* to afford a white solid, which was washed twice with 1 mL of cold pentane and dried *in vacuo*. The product was a white solid: yield 103 mg (82%). IR (Nujol, cm^{-1}): ν(O−H) 2637 m, ν(Os−H) 2043 s, ν(C≡O) 1972 s and 1912 s, ν(OCO) 1616 s and 1350 s. ^1H NMR[23] (300 MHz, 293 K, C_6D_6): δ −3.86 (t, 1H, J(PH) = 21.0 Hz, Os−H), 1.17 (dvt, 18H, J(HH) = 6.6 Hz, N = 13.5 Hz, PCHCH_3), 1.20 (dvt, 18H, J(HH) = 6.9 Hz, N = 13.8 Hz, PCHCH_3), 2.22 (m, 6H, PCHCH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 37.2 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$): δ 190.6 (t, J(PC) = 5.2 Hz, Os−CO), 181.5 (t, J(PC) = 8.1 Hz, Os−CO), 162.4 (s, OCO), 25.1 (vt, N = 13.3 Hz, PCH), 19.3 (s, PCHCH_3), 19.2 (s, PCHCH_3). Anal. Calcd for $C_{21}H_{44}O_5OsP_2$: C, 40.12; H, 7.05. Found: C, 39.94; H, 6.74.

Preparation of $OsH(\kappa^2\text{-}O_2CNHPh)(CO)(P^iPr_3)_2$ (9). A solution of **2** (132 mg, 0.24 mmol) in diethyl ether (10 mL) was treated with phenyl isocyanate (30 μL, 0.28 mmol). The mixture was then stirred for 1 h, and the solvent was removed *in vacuo* to afford a yellow solid, which was crystallized from pentane at −20 °C. The product is a colorless microcrystalline solid: yield 127 mg (79%). IR (Nujol, cm^{-1}): ν(N−H) 3285 m, ν(Os−H) 2190 m, ν(C≡O) 1887 s, ν(OCO) 1620 s and 1518 s. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −21.0 (t, 0.55H, J(PH) = 15.5 Hz, Os−H), −20.8 (t, 0.45H, J(PH) = 16.0 Hz, Os−H), 1.25 (dvt, 18H, J(HH) = 6.9 Hz, N = 12.8 Hz, PCHCH_3), 1.35 (dvt, 18H, J(HH) = 6.9 Hz, N = 13.5 Hz, PCHCH_3), 2.39 (m, 6H, PCHCH$_3$), 6.15 (br, 1H, NH), 6.78 (t, 1H, J(HH) = 6.4 Hz, $H_p(C_6H_5)$), 7.40 (br, 2H, $H_o(C_6H_5)$), 7.50 (br, 2H, $H_m(C_6H_5)$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, CD_2Cl_2): δ 39.4 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (75.4 MHz, 293 K, $CDCl_3$): δ 184.0 (t, J(PC) = 9.2 Hz, Os−CO), 162.6 (s, OCO), 139.0, 128.8, 121.5, and 117.2 (all s, C_6H_5), 25.3 (vt, N = 24.4 Hz, PCH), 19.9 (s, PCHCH_3), 19.1 (s, PCHCH_3). Anal. Calcd for $C_{21}H_{47}NO_3OsP_2$: C, 46.21; H, 7.31; N, 2.07. Found: C, 46.46; H, 7.55; N, 2.35.

Preparation of $OsH(OH)(CO)_2(P^iPr_3)_2$ (10). Carbon monoxide was bubbled through a solution of **2** (103 mg, 0.18 mmol) in toluene (6 mL). After 10 min a yellow solution formed. The solvent was then removed *in vacuo* to afford a pale gray solid, which was crystallized from pentane at −20 °C. The product was a colorless microcrystalline solid: yield 65 mg (60%). IR (CH_2Cl_2, cm^{-1}): ν(O−H) 3650 w, ν(Os−H) 2030 s, ν(C≡O) 1965 s and 1890 s. ^1H NMR[24] (300 MHz, 293 K, C_6D_6): δ −4.14 (t, 1H, J(PH) = 20.8 Hz, Os−H), 1.18 (dvt, 18H, J(HH) = 7.1 Hz, N = 13.5 Hz, PCHCH_3), 1.23 (dvt, 18H, J(HH) = 7.3 Hz, N = 13.9 Hz, PCHCH_3), 2.42 (m, 6H, PCHCH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 32.7 (s, d in off-resonance). Anal. Calcd for $C_{20}H_{44}O_3OsP_2$: C, 41.08; H, 7.58. Found: C, 40.84; H, 7.84.

Preparation of $OsH(OH)\{P(OMe)_3\}(CO)(P^iPr_3)_2$ (11). A solution of **2** (79 mg, 0.14 mmol) in tetrahydrofuran (6 mL) was treated with trimethyl phosphite (17 μL, 0.14 mmol). The mixture was then stirred for 15 min, and the solvent was removed *in vacuo* to afford a gray solid, which was crystallized from pentane at −20 °C. The product was a colorless microcrystalline solid: yield 75 mg (78%). IR (Nujol, cm^{-1}): ν(O−H) 3645 w, ν(Os−H) 2058 s, ν(C≡O) 1903 s. ^1H NMR (300 MHz, 293 K, C_6D_6): δ −6.12 (dt, 1H, J(PH) = 157.2 Hz, J(P′H) = 24.3 Hz, Os−H), −3.69 (br, 1H, OH), 1.33 (dvt, 18H, J(HH) = 6.9 Hz, N = 12.9 Hz, PCHCH_3), 1.36 (dvt, 18H, J(HH) = 7.2 Hz, N = 13.8 Hz, PCHCH_3), 2.66 (m, 6H, PCHCH$_3$), 3.51 (d, 9H, J(PH) = 10.2 Hz, OCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, 293 K, C_6D_6): δ 23.8 (d, 2P, J(PP) = 23.8 Hz, P^iPr_3), 107.9 (t, 1P,

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[23] The resonance of the OH proton was observed at −60 °C in CD_2Cl_2 as solvent: 8.95 (br, 1H, OH).

[24] The resonance of the OH proton was located at −80 °C in toluene-d_8 as solvent: −3.14 (br, 1H, OH).

Table 3. Crystal Data and Data Collection and Refinement for $OsH\{OC(OCH_3)CHC(CO_2CH_3)O\}(CO)(P^iPr_3)_2$ (3) and $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (4)

	3	**4**
	Crystal Data	
formula	$C_{25}H_{50}O_6OsP_2$	$C_{23}H_{50}O_4OsP_2$
mol wt	698.79	642.77
color, habit	orange, irregular prism	yellow, irregular prism
cryst size, mm	0.40 × 0.19 × 0.15	0.38 × 0.35 × 0.28
space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
a, Å	8.899(4)	16.506(2)
b, Å	10.692(5)	10.5560(10)
c, Å	17.393(8)	17.0910(10)
α, deg	104.41(2)	90
β, deg	96.37(2)	114.300(10)
γ, deg	109.28(2)	90
V, Å^3	1478.8(12)	2714.1(4)
Z	2	4
D(calcd), g cm^{-3}	1.553	1.573
	Data Collection and Refinement	
diffractometer	four-circle Siemens-STOE AED	
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry	
monochromator	graphite oriented	
μ, mm^{-1}	4.454	4.841
scan type	ω/2θ	ω/2θ
2θ range, deg	4.2 ≤ 2θ ≤ 50	4.5 ≤ 2θ ≤ 50.1
temp, K	173	153
no. of data collected	6304	4976
no. of unique data	5204 (R_{int} = 0.0138)	4788 (R_{int} = 0.0289)
no. of params refined	329	304
$R(F_o \geq 4.0\sigma(F_o))$[a]	0.0159	0.0221
R_w(all data)[b]	0.0397	0.0586
S[c]	1.076	1.054

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$ (**3**, $a = 0.0170$, $b = 0.90$; **4**, $a = 0.0326$, $b = 2.70$). [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

J(PP) = 23.8 Hz, P(OMe)$_3$). Anal. Calcd for $C_{22}H_{53}O_5OsP_3$: C, 38.81; H, 7.85. Found: C, 38.73; H, 7.84.

Preparation of $OsH(OH)(CO)(^tBuNC)(P^iPr_3)_2$ (12). A solution of **2** (120 mg, 0.22 mmol) in diethyl ether (8 mL) was treated with *tert*-butyl isocyanide (30 μL, 0.27 mmol). The mixture was then stirred for 15 min, and the solvent was removed *in vacuo* to afford a gray solid, which was crystallized from pentane at −20 °C. The product was a colorless microcrystalline solid: yield 65 mg (47%). IR (Nujol, cm^{-1}): ν(O−H) 3652 w, ν(Os−H) 2131 s, ν(C≡O) 1907 s, ν(C=N) 1644 m. ^{1}H NMR (300 MHz, 293 K, C_6D_6): δ −6.07 (t, 1H, J(PH) = 21.3 Hz, Os−H), −3.3 (br, 1H, OH), 1.13 (s, 9H, NCCH$_3$), 1.30 (dvt, 18H, J(HH) = 6.9 Hz, N = 13.2 Hz, PCHCH_3), 1.34 (dvt, 18H, J(HH) = 6.9 Hz, N = 13.8 Hz, PCHCH_3), 2.55 (m, 6H, PCHCH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, 293 K, C_6D_6): δ 31.6 (s, d in off-resonance). Anal. Calcd for $C_{24}H_{53}NO_2OsP_2$: C, 45.05; H, 8.35; N, 2.19. Found: C, 44.78; H, 8.22; N, 2.13.

X-ray Structure Analyses of $OsH\{OC(OCH_3)CHC(CO_2CH_3)O\}(CO)(P^iPr_3)_2$ (3) and $OsH(OH)(CO)(\eta^2\text{-}CH_2{=}CHCO_2CH_3)(P^iPr_3)_2$ (4). Crystals suitable for X-ray diffraction were obtained from saturated solutions of **3** or **4** in pentane at −20 °C. A summary of crystal data, intensity collection procedure, and refinement is reported in Table 3. An orange (**3**) or a yellow (**4**) crystal was glued to a glass fiber and mounted on a Siemens-Stoe AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 24 reflections in the range 18 ≤ 2θ ≤ 25°. Three orientation and intensity standards were monitored along data collection every 55 min of measuring time; no variation was observed. All the recorded reflections, 6304 for **3** and 4976 for **4**, were corrected for Lorentz and polarization effects. Both sets of data were also corrected for absorption by a semiempirical (ψ-scan) method.[25] The structures were solved by Patterson and subsequent Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. The most relevant hydrogen atoms of both structures, that is the hydrido H and H(3) in **3** and the hydride (H(1)), the hydroxo proton (H(2)), and the olefinic hydrogens (H(1A), H(2A) and H(1B)) in **4**, were located in difference Fourier maps and refined as free isotropic atoms. All the remaining hydrogens were calculated (C−H = 0.96 Å) and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were taken from ref 26. Final $R(F, F_o > 4.0\sigma(F_o))$ and $Rw(F^2$, all reflections) values were 0.0159 and 0.0397 in **3** and 0.0220 and 0.0586 in **4**. All calculations were performed by using the SHELXS-86[27] and SHELX93[28] system of computer programs.

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Supporting Information Available: Tables of anisotropic thermal parameters, complete atomic coordinates and thermal parameters, experimental details of the X-ray study, bond distances and angles, and selected least-squares planes and interatomic distances for **3** and **4** (16 pages). Ordering information is given on any current masthead page.

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