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Hydrido-Osmium(II), -Osmium(IV) and -Osmium(VI) Complexes with Functionalized Phosphanes as Ligands

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Dedicated to Professor Michael Lappert on the occasion of his 80th birthday

Keywords: Dioxygen ligands / Hydrido complexes / Hydrogen transfer / Osmium / Phosphane ligands

Reaction of five-coordinate [OsHCl(CO)(P*i*Pr$_3$)$_2$] (**1**) with the chelating phosphane *i*Pr$_2$PCH$_2$CO$_2$Me gave six-coordinate [OsHCl(CO)(P*i*Pr$_3$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=*O*)OMe}] (**2**), which upon treatment with CO and O$_2$ afforded the 1:1 adducts [OsHCl(CO)(L)(P*i*Pr$_3$){κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (**3**, **4**) by partial opening of the chelate ring. The vinyl complex [OsCl(CH=CHPh)(CO)(P*i*Pr$_3$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=*O*)OMe}] (**5**) was obtained from **2** and PhC≡CH by insertion of the alkyne into the Os–H bond. Reaction of **2** with sodium acetate led to metathesis of the anionic ligands and formation of [OsH(η^2-O$_2$CCH$_3$)(CO)(P*i*Pr$_3$){κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (**6**). Osmium(VI) compounds [OsH$_6$(P*i*Pr$_2$R)$_2$] with R = CH$_2$CH$_2$OMe (**12**), CH$_2$CO$_2$Me (**13**) and CH$_2$CO$_2$Et (**14**), and [OsH$_6$(P*i*Pr$_3$){κ(*P*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$}] (**16**) were prepared from osmium(IV) precursors and shown to rapidly react with O$_2$ and primary alcohols. Exploratory studies revealed that the catalytic activity of the hexahydrido complexes in the hydrogen transfer reaction from 2-propanol to cyclohexanone and acetophenone depends on the type of the functionalized phosphane and is best for R = CH$_2$CH$_2$OMe.
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Introduction

In the course of studies to explore the catalytic potential of coordinatively unsaturated hydrido-osmium complexes having a 16-electron count, we reported that five-coordinate [OsHCl(CO)(P*i*Pr$_3$)$_2$] (**1**), in the presence of KOH or NaBH$_4$, serves as catalyst for hydrogen transfer from 2-propanol to cyclohexanone, acetophenone,[1] benzylideneacetone, benzylideneacetophenone,[2] and phenylacetylene.[3] Moreover, under a hydrogen atmosphere, complex **1** also catalyzes the reduction of cyclohexene, 1,3- and 1,4-cyclohexadiene, styrene and phenyl- and diphenylacetylene.[4,5] After we observed that the P*i*Pr$_3$ ligands of **1** can easily be replaced by chiral mono- and bisphosphanes such as P*i*Pr$_2$NHCH(Me)Ph, (*S*,*S*)-Chiraphos and (*S*,*S*)-Diop,[6] we became interested to find out whether a similar substitution reaction would also occur with hemilabile, potentially chelating phosphanes. We note that the chemistry of a manifold of osmium and ruthenium compounds with phosphane ethers, phosphane esters and phosphaneamines as ligands has recently been investigated in our laboratory as well as by others.[7,8]

As a continuation of our earlier work, we report here the synthesis of a series of mono-, di-, tetra- and hexahydrido-osmium complexes mainly with P*i*Pr$_2$CH$_2$CO$_2$Me and P*i*Pr$_2$CH$_2$CH$_2$OMe as the coordinated phosphanes, which were prepared by addition, substitution or insertion reactions. The catalytic activity of some of the title compounds in the hydrogen transfer from 2-propanol to cyclohexanone and acetophenone has also been briefly investigated.

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Results and Discussion

The reaction of the monohydrido-osmium(II) complex **1** (Scheme 1), which was prepared from OsCl$_3$·3H$_2$O and P*i*Pr$_3$ in methanol,[9] with a threefold excess of P*i*Pr$_2$CH$_2$CO$_2$Me in pentane proceeded smoothly at room temperature and afforded the monosubstitution product **2** in almost quantitative yield. The composition of the colorless, air-sensitive solid was determined by elemental analyses and mass spectrometry. The ^{1}H NMR spectrum of **2** displays a broadened signal for the hydrido ligand at room temperature, which resolves at –70 °C into a doublet-of-doublets owing to coupling to two ^{31}P nuclei. We assume that the broadening of the signal is due to an equilibrium between a five-coordinate species with a (*P*)-bonded and a six-coordinate species with a (*P*,*O*)-bonded phosphane ester, which is rapid on the NMR time scale at room temperature. The chemical shift of the hydride resonance of **2** (δ –16.27 ppm) is nearly identical to that of the analogous ruthenium compound [RuHCl(CO)(P*i*Pr$_3$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=*O*)OMe}] (δ = –16.56 ppm).[7c]

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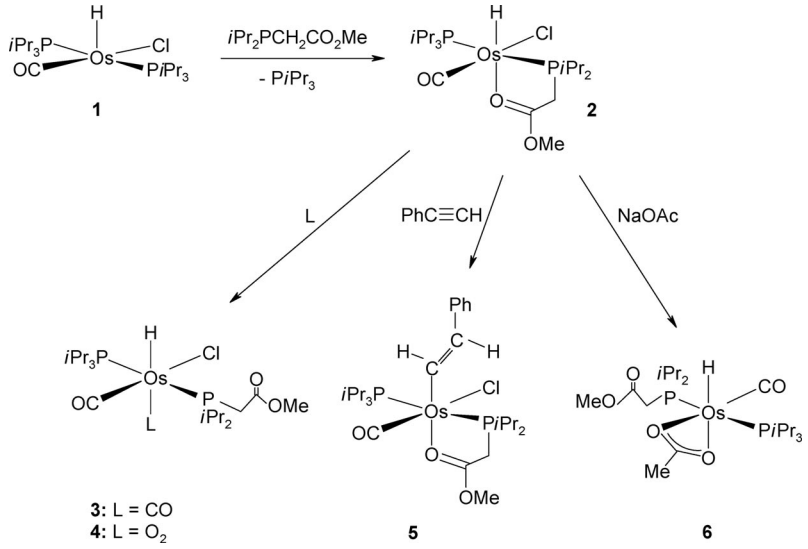

Scheme 1.

The ^{31}P NMR spectrum of **2** displays two signals at δ = 47.0 and 35.8 ppm, which corresponds to an AB spin system. The large $^{31}P,^{31}P$ coupling constant of 256.8 Hz indicates that the two phosphorus atoms are *trans*-disposed.[7m] Since the ν(C=O) stretching mode appears in the IR spectrum of **2** at 1630 cm^{-1} in KBr and is thus shifted by 100 cm^{-1} to lower energy compared with free $PiPr_2CH_2CO_2Me$,[10] we conclude that in the solid state the functionalized phosphane is coordinated in a bidentate fashion. It is worth mentioning that even with a tenfold excess of the phosphane ester, neither the remaining $PiPr_3$ nor the CO ligand of **2** could be replaced by a second $PiPr_2CH_2CO_2Me$ molecule.

Similar to the starting material **1**,[4,9] the substitution product **2** reacts with CO and O_2 at room temperature to give the 1:1 adducts **3** and **4** in excellent yields. Both complexes were isolated as colorless, only slightly air-sensitive solids, for which correct elemental analyses were obtained. The structures of **3** and **4** are related to the structure of **2** insofar, as the entering ligand L (CO or O_2) occupies the same coordination site which in the precursor is taken by the C=O oxygen of the ester group. In agreement with this, the ^{31}P NMR spectra of **3** and **4** show two signals of an AB spin system with $^{31}P,^{31}P$ coupling constants that are typical for *trans* disposed phosphorus atoms.[7m]

The IR spectra of **3** and **4** display one ν(C=O) stretching mode at, respectively, 1728 cm^{-1} (for **3**) and 1720 cm^{-1} (for **4**), confirming that the C=O oxygen atom of the ester unit is not involved in the coordination to the metal.[10] In the IR spectrum of **3**, two bands appear in the ν(CO) region, which indicates that the two carbonyl ligands are in *cis* disposition. The fact that the ν(CO) stretching mode of **4** (observed at 1950 cm^{-1}) is shifted by 70 cm^{-1} to higher wave numbers compared with **1**, is consistent with the well-known π-acceptor properties of the dioxygen unit. We assume that the O_2 ligand is coordinated to the metal in a side-on fashion, as was found in related compounds such as $[OsHCl(CO)(O_2)(PCy_3)_2]$,[11] $[OsHX(CO)(O_2)(PR_3)_2]$ (X = Cl, Br, I, N_3, OPh; PR_3 = $PiPr_3$, $PMetBu_2$),[4,5,12] and $[IrCl(CO)(O_2)(PPh_3)_2]$.[13] This bonding mode is supported by a band at 853 cm^{-1} in the IR spectrum of **4**, which appears at wavelengths that are characteristic for metal peroxo derivatives.[14]

The reaction of **2** with phenylacetylene also proceeded at room temperature and led to the insertion of the alkyne into the Os–H bond. The yield of the insertion product **5**, which like **3** and **4** is a colorless, slightly air-sensitive solid, is virtually quantitative. Typical spectroscopic features of **5** are (1) the signals for the OsC*H* and =C*H*Ph protons at δ = 8.35 and 6.32 ppm in the low-temperature ^1H NMR spectrum, (2) the resonances of the vinylic carbon atoms at δ = 140.0 and 133.8 in the ^{13}C NMR spectrum, and (3) the appearance of an AB spin system with signals at δ = 30.2 and 20.6 ppmin the ^{31}P NMR spectrum. The $^1H,^1H$ coupling constant for the vinyl protons is 16.1 Hz and indicates the formation of the *E*-isomer. We note that in the case of the vinyl osmium complex $[OsCl(CH{=}CHPh)(CO)(PiPr_3)_2]$, the *E*-configuration of the OsCH=CHPh fragment was confirmed by an X-ray diffraction analysis.[15]

Treatment of **2** with NaOAc in THF led to the displacement of chloride by acetate. The proposed structure of **6** (see Scheme 1) is mainly supported by the IR spectrum, which shows two C-O stretching modes at 1520 and 1470 cm^{-1}, that are diagnostic for a bidentate OAc ligand.[16] The presence of the hydride ligand is substantiated by the appearance of a signal at δ –20.63 in the ^1H NMR spectrum, the chemical shift being nearly identical to that of $[OsH(\eta^2\text{-}O_2CCH_3)(CO)(PiPr_3)_2]$.[9] The ^{31}P NMR spectrum of **6** shows the characteristics of a AB spin system with resonances at δ = 39.3 and 34.3. The large $^{31}P,^{31}P$ coupling constant of 264.5 Hz as well as the $^{31}P,^{187}Os$ coupling constants of 188.2 (for δ_A) and 192.5 Hz (for δ_B) confirm the *trans* disposition of the two phosphorus atoms. The ^1H and ^{31}P NMR spectra of **6** are independent of tempera-

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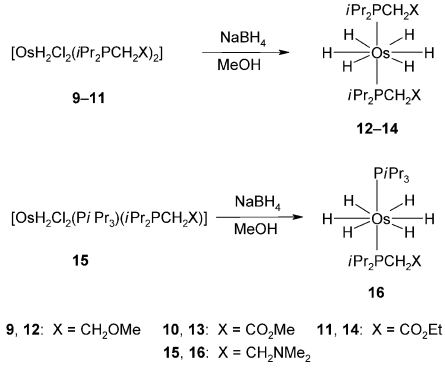
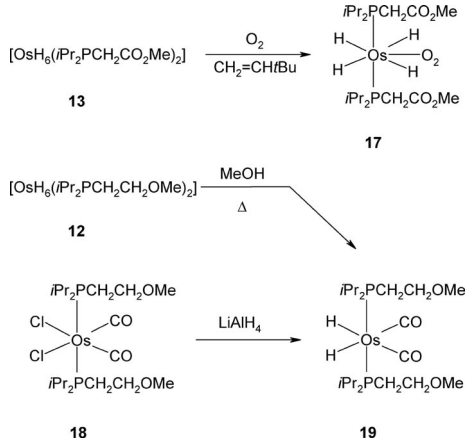
ture, which proves that the molecule is not fluxional in solution.

Following the observation, that the dihydrido-osmium(IV) complex $[OsH_2Cl_2(PiPr_3)_2]$ (**7**) reacts with $NaBH_4$ and methanol to give the hexahydrido-osmium(VI) derivative $[OsH_6(PiPr_3)_2]$ (**8**),[17] we prepared the analogues of **8** with phosphane ethers and phosphane esters as ligands on the same route. With **9**, **10** and **11** as the starting materials,[7m] we obtained the products **12**, **13** and **14** either as a colorless air-sensitive solid (**13**) or air-sensitive oils (**12**, **14**). The related complex **16** with one $PiPr_3$ and one phosphaneamine ligand was obtained analogously (see Scheme 2). The presence of six equivalent hydrido ligands in the osmium(VI) compounds is confirmed by the ^{31}P NMR spectra, which for **12**, **13** and **14** display a singlet and for **16** two doublets at room temperature. In off-resonance, these signals transform into symmetrical septets owing to $^{1}H,^{31}P$ coupling. The ^{1}H NMR spectra of **12**, **13**, **14** and **16** display a high-field resonance at, respectively, δ –9.86 (**12**), –9.61 (**13**), δ –9.64 (**14**) and δ –9.94 (**16**), which is split into a triplet (**12**, **13**, **14**) or a doublet-of-doublets (**16**) through $^{1}H,^{31}P$ coupling. This illustrates that the two phosphorus atoms of the functionalized phosphanes are in *trans*-disposition. At –80 °C in $[D_8]$toluene, the ^{31}P NMR signals of **12**, **13**, **14** and **16** become broader which could be due to an intramolecular rearrangement. For other polyhydrido metal complexes with the coordination number eight, it was previously postulated that the eight ligands can be arranged either in a dodecahedral or square-antiprismatic fashion; the difference in energy probably being small.[18] In the case of $[OsH_6(PiPr_2Ph)_2]$, the molecular structure was determined by X-ray and neutron diffraction methods at low temperature and shown to be dodecahedral.[19]



Scheme 2.

In comparison with **8**, the catalytic activity of **12**, **13** and **14** was probed for the hydrogen transfer reaction from 2-propanol to cyclohexanone and acetophenone. Taken the proposal into account,[17] that the osmium(VI) precursor $[OsH_6(PR_3)_2]$ initiate the catalytic cycle by generating an active osmium(IV) intermediate $[OsH_4(PR_3)_2]$ via elimination of H_2, we were tempted to find out whether the functionalized phosphane could temporarily stabilize the tetrahydrido-osmium(IV) species and thus facilitate the reduction of the ketone. In the course of these studies we first recognized, that even traces of oxygen in the solvents or test tubes led to a facile deactivation of the catalyst. Thus, we reacted **13** with an equimolar amount of O_2 and isolated the tetrahydrido(dioxygen) osmium(IV) compound **17** (Scheme 3). In the presence of CH_2=CH*t*Bu, serving as a hydrogen acceptor, the yield of the dioxygen complex is virtually quantitative. The IR spectrum of **17** shows an absorption for the side-on bonded O_2 ligand at 875 cm^{-1} (see **4**: 853 cm^{-1}) as well as a C=O stretching mode at 1720 cm^{-1}, i.e., at the same wave length as **4**. The ^{31}P NMR spectrum of **17** displays a singlet (split into a quintet in off-resonance), which indicates that the two phosphane ligands occupy equivalent coordination sites.



Scheme 3.

The results of the hydrogen transfer experiments, where the hexahydrido complexes were prepared in situ from the dihydrides $[OsH_2Cl_2(PR_3)_2]$ and $NaBH_4$ in 2-propanol,[17] are listed in Table 1. They indicate that replacing one isopropyl unit of $PiPr_3$ for the ether moiety CH_2CH_2OMe has only a minor effect. If one isopropyl group of $PiPr_3$ is replaced by a CH_2CO_2R unit, the corresponding osmium compounds **13** and **14** are significantly less active than **8** and **12**. We assume that the main reason for the difference is that with $iPr_2PCH_2CO_2Me$ and $iPr_2PCH_2CO_2Et$ as ligands the proposed intermediate $[OsH_4(PR_3)_2]$ is much faster deactivated by 2-propanol than the corresponding tetrahydrido species with PR_3 = $PiPr_3$ and $iPr_2PCH_2CH_2OMe$. Support for this argument comes from the observation that we were unable to identify the osmium containing product formed during the decomposition of **13** and **14** in methanol. With **12** as the precursor, we found that if a solution of this compound in methanol is stirred at 60 °C, the coordinatively and electronically saturated complex *cis*,*cis*,*trans*-$[OsH_2(CO)_2(iPr_2PCH_2CH_2OMe)_2]$ (**19**) is obtained. It is catalytically inactive in the hydrogen transfer reaction. A more convenient procedure for the synthesis of **19** consists in the substitution of chloride in **18** for hydride (see Scheme 3), which affords the dihydrido-osmium(II) compound in excellent yield. The spectroscopic data of **19** are quite similar to those of *cis*,*cis*,*trans*-$[OsH_2(CO)_2(PiPr_3)_2]$, prepared from $[OsH(\eta^2\text{-}BH_4)(CO)(PiPr_3)_2]$ and CO in methanol.[20]

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Table 1. Results of the hydrogen transfer reactions from 2-propanol to cyclohexanone (Cy) and acetophenone (Ac) with the hexahydrido-osmium(VI) complexes **8** and **12**–**14** as the catalyst precursor. The conversion of the ketones (Cy and Ac) into the alcohols (CyH_2 and AcH_2) are given in prozent (%) at a particular reaction time (see the first horizontal line). Reactions conditions are described in the Exp. Section.

Catalyst	*t* [min]:	5	15	30	60	180	360
8	% CyH_2		98				
12	% CyH_2	98					
13	% CyH_2	5		7	9	16	25
14	% CyH_2	4		6	8	16	27
Catalyst	*t* [min]:	5	10	15	45	120	240
8	% AcH_2	10		24	47	60	
12	% AcH_2	21	53			63	
13	% AcH_2	2					4
14	% AcH_2	2					17

In summary, the present work has shown that the six-coordinate complex **2**, containing the functionalized phosphane ester *i*$Pr_2PCH_2CO_2Me$ as ligand, is a useful starting material for the preparation of a series of monohydrido and monovinyl osmium(II) derivatives. Several hexahydrido-osmium(VI) complexes with ether-, ester- and amine-substituted phosphanes were obtained from dihydrido-osmium(IV) precursors. They are rather labile and readily react with oxygen and primary alcohols. The catalytic activity of the hexahydrido compounds $[OsH_6(PiPr_2R)_2]$ (**12**–**14**) in the hydrogen transfer reaction from 2-propanol to cyclohexanone and acetophenone depends on the type of the phosphane ligand and is best for R = CH_2CH_2OMe.

Experimental Section

General: All operations were carried out under argon using Schlenk techniques. The osmium complexes **1**,[9] **7**, **8**,[17] **9**–**11**, **15** and **18**[7m] were prepared as described in the literature. – NMR: Jeol FX 90 Q, Bruker AC 200 and AMX 400. IR: Perkin–Elmer 397 and 1320. – Mass spectra: Varian CH 7 MAT (70 eV). Melting points determined by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet; vt, virtual triplet; br, broadened signal; $N = {}^3J_{P,H} + {}^5J_{P,H}$ or ${}^2J_{P,C} + {}^4J_{P,C}$. The coupling constants ${}^1J_{Os,P}$ were determined from the satellites that belongs to the ^{31}P NMR signals.[21]

[OsHCl(CO)(P*i*Pr$_3$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OMe}] (2): A suspension of **1** (207 mg, 0.31 mmol) in pentane (20 mL) was treated with *i*$Pr_2PCH_2CO_2Me$ (211 μL, 1.08 mmol) and stirred for 4 h at room temperature. A colorless, air-sensitive solid precipitated, which was filtered, washed three times with 10-mL portions of pentane and dried; yield 199 mg (91%); m.p. 96 °C (dec.). MS: *m*/*z*(I$_r$) = 606 (3.4) [M$^+$]; 570 (3.3) [M$^+$ – Cl]. IR (KBr): $\tilde{\nu}$ = 2125 [ν(OsH)], 1880 [ν(CO)], 1630 [ν(C=O)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.74 (s, 3 H, OCH_3), 3.05 (AB part of an ABX spin system, *i*$Pr_2PCH_2CO_2Me$, $J_{A,B}$ = 16.8, $J_{A,X} = J_{B,X}$ = 8.6 Hz, 2 H, A and B = H, X = P of *i*Pr_2P, δ_A = 3.07, δ_B = 3.03), 2.57 (m, 3 H, PC*H*CH_3 of P*i*Pr_3), 2.75, 2.32 (both m, 1 H each, PC*H*CH_3 of *i*Pr_2P), 1.30 (br. m, 27 H, PCHC*H*$_3$ of P*i*Pr_3 and *i*Pr_2P), 1.17 (dd, ${}^3J_{P,H}$ = 15.2, ${}^3J_{H,H}$ = 6.9 Hz, 3 H, PCHC*H*$_3$ of *i*Pr_2P), –17.86 (br., 1 H, OsH) ppm. ^{1}H NMR (90 MHz, $CDCl_3$, –70 °C): δ = –16.27 (dd, ${}^2J_{P,H} = {}^2J_{P',H}$ = 14.9 Hz, 1 H, OsH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 185.9 (dd, ${}^2J_{P,C}$ = 13.4, ${}^3J_{P,C}$ = 4.9 Hz, *C*O_2Me), 183.1 (dd, ${}^2J_{P,C} = {}^2J_{P',C}$ = 8.5 Hz, OsCO), 54.9 (s, CO_2CH_3), 33.0 (d, ${}^1J_{P,C}$ = 23.2 Hz, PCH_2), 25.2 (d, ${}^1J_{P,C}$ = 25.6 Hz, P*C*HCH$_3$ of *i*Pr_2P), 24.4 (d, ${}^1J_{P,C}$ = 23.2 Hz, P*C*HCH$_3$ of P*i*Pr_3), 23.6 (d, ${}^1J_{P,C}$ = 25.6 Hz, P*C*HCH$_3$ of *i*Pr_2P), 19.8, 19.2 (both s, PCH*C*H$_3$ of P*i*Pr_3), 19.4, 18.9, 18.8, 18.4 (all s, PCH*C*H$_3$ of *i*Pr_2P) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$): AB spin system: δ_A = 47.0 (${}^1J_{Os,P}$ = 181.8, ${}^2J_{P,P}$ = 256.8 Hz, d in off-resonance), δ_B = 35.8 (${}^1J_{Os,P}$ = 192.9, ${}^2J_{P,P}$ = 256.8 Hz, d in off-resonance) ppm. $C_{19}H_{41}ClO_3OsP_2$ (605.1): calcd. C 37.71, H 6.83; found C 37.43, H 6.90.

[OsHCl(CO)$_2$(P*i*Pr$_3$){κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (3): A slow stream of CO was passed through a solution of **2** (179 mg, 0.30 mmol) in benzene (5 mL) for 10 min at room temperature. The solvent was evaporated in vacuo, and the oily residue suspended in pentane (2 mL). After the suspension was stirred for 5 min, a colorless solid precipitated, which was filtered, washed three times with 10-mL portions of pentane and dried; yield 165 mg (88%); m.p. 86 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2040 [ν(OsH)], 1970, 1910 [ν(CO)], 1730 [ν(C=O)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3 H, OCH_3), 3.20 (AB part of an ABX spin system, *i*$Pr_2PCH_2CO_2Me$, $J_{A,B}$ = 14.3, $J_{A,X} = J_{B,X}$ = 9.1 Hz, 2 H, A and B = H, X = P of *i*Pr_2P, δ_A = 3.22, δ_B = 3.19), 2.50 (m, 5 H, PC*H*CH_3 of P*i*Pr_3 and *i*Pr_2P), 1.24 (dvt, ${}^3J_{H,H}$ = 6.7, *N* = 13.6 Hz, 18 H, PCHC*H*$_3$ of P*i*Pr_3), 1.15 (m, 12 H, PCHC*H*$_3$ of *i*Pr_2P), –5.17 (dd, ${}^2J_{P,H} = {}^2J_{P',H}$ = 21.2 Hz, 1 H, OsH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 186.6 (dd, ${}^2J_{P,C} = {}^2J_{P',C}$ = 5.4 Hz, OsCO), 178.5 (dd, ${}^2J_{P,C} = {}^2J_{P',C}$ = 8.2 Hz, OsCO), 171.6 (dd, ${}^2J_{P,C}$ = 8.2, ${}^3J_{P,C}$ = 2.3 Hz, *C*O_2Me), 52.5 (s, CO_2CH_3), 28.8 (d, ${}^1J_{P,C}$ = 16.7 Hz, PCH_2), 26.0 (d, ${}^1J_{P,C}$ = 27.9 Hz, P*C*HCH$_3$ of *i*Pr_2P), 25.2 (d, ${}^1J_{P,C}$ = 25.9 Hz, P*C*HCH$_3$ of P*i*Pr_3), 25.0 (d, ${}^1J_{P,C}$ = 27.0 Hz, P*C*HCH$_3$ of *i*Pr_2P), 19.6, 19.5 (both s, PCH*C*H$_3$ of P*i*Pr_3), 18.3 (d, ${}^4J_{P,C}$ = 2.0 Hz, PCH*C*H$_3$ of *i*Pr_2P), 18.2 (d, ${}^4J_{P,C}$ = 2.5 Hz, PCH*C*H$_3$ of *i*Pr_2P), 17.7, 17.6 (both s, PCH*C*H$_3$ of *i*Pr_2P) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$) AB spin system: δ_A = 30.2 (${}^1J_{Os,P}$ = 169.3, ${}^2J_{P,P}$ = 220.8 Hz, d in off-resonance), δ_B = 20.6 (${}^1J_{Os,P}$ = 169.0, ${}^2J_{P,P}$ = 220.8 Hz, d in off-resonance) ppm. $C_{20}H_{41}ClO_4OsP_2$ (633.1): calcd. C 37.94, H 6.53; found C 38.12, H 6.80.

[OsHCl(CO)(O$_2$)(P*i*Pr$_3$){κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (4): A slow stream of O_2 was passed through a solution of **2** (236 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) for 2 min at room temperature. After the solvent was evaporated in vacuo, the oily residue was worked up as described for **3**. Colorless solid; yield 230 mg (88%); m.p. 90 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2110 [ν(OsH)], 1950 [ν(CO)], 1720 [ν(C=O)], 855 [ν(O_2)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.71 (s, 3 H, OCH_3), 3.58 (AB part of an ABX spin system, A and B = H, X = P of *i*Pr_2P, correct coupling constants not determined due to overlap of respective signals, 2 H, *i*$Pr_2PCH_2CO_2Me$), 2.92 (m, 5 H, PC*H*CH_3 of P*i*Pr_3 and *i*Pr_2P), 1.43 (m, 30 H, PCHC*H*$_3$ of *i*Pr_2P and P*i*Pr_3), –2.95 (dd, ${}^2J_{P,H} = {}^2J_{P',H}$ = 31.0 Hz, 1 H, OsH) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$) AB spin system: δ_A = 28.7 (${}^2J_{P,P}$ = 90.8 Hz, d in off-resonance), δ_B = 18.2 (${}^2J_{P,P}$ = 90.8 Hz, d in off-resonance) ppm. $C_{19}H_{41}ClO_5OsP_2$ (637.1): calcd. C 35.82, H 6.49; found C 35.72, H 6.76.

[OsCl(CH=CHPh)(CO)(P*i*Pr$_3$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OMe}] (5): A solution of **2** (150 mg, 0.25 mmol) in benzene (10 mL) was treated with phenylacetylene (45 μL, 0.30 mmol) and stirred for 30 min at room temperature. The solvent was evaporated in vacuo and the residue dissolved in pentane (10 mL). After the solution was stored for 2 h, a colorless solid precipitated. It was filtered, washed three times with 5-mL portions of pentane and dried; yield 156 mg (89%); m.p. 110 °C (dec.). MS: *m*/*z*(I$_r$) = 708 (0.2) [M$^+$];

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604 (0.2) [M^+ – CH=CHPh], 540 (10.7) [M^+ – CO – PhCH=CHCl]. IR (KBr): $\tilde{\nu}$ = 1880 [ν(CO)], 1625 [ν(C=O)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 8.64 (br., 1 H, OsC*H*=CHPh), 7.12, 6.96, 6.67 (all m, 5 H, C_6H_5), 6.61 (br. d, $^3J_{H,H}$ = 16.0 Hz, 1 H, OsCH=C*H*Ph), 2.93 (s, 3 H, OCH_3), 2.65, 2.50 (both m, 7 H, PCH_2 and PC*H*CH_3), 1.05 (dvt, $^3J_{H,H}$ = 7.4, *N* = 12.3 Hz, 18 H, PCHC*H*$_3$ of P*i*Pr_3), 0.75 (m, 12 H, PCHC*H*$_3$ of *i*Pr_2P) ppm. ^1H NMR (200 MHz, $CDCl_3$, –60 °C): δ = 8.35 (d, $^3J_{H,H}$ = 16.1 Hz, 1 H, OsC*H*=CHPh), 6.32 (d, $^3J_{H,H}$ = 16.1 Hz, 1 H, OsCH=C*H*Ph) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 187.6, 185.4 (both br, Os(CO) and *C*O_2Me), 143.6 (s, *ipso*-C of C_6H_5), 140.0 (br., *C*H=CHPh), 133.8 (s, CH=*C*HPh), 128.6, 124.2, 123.4 (all s, C_6H_5), 55.9 (s, CO_2CH_3), 33.4 (d, $^1J_{P,C}$ = 24.0 Hz, PCH_2), 25.8 (d, $^1J_{P,C}$ = 27.9 Hz, P*C*HCH_3 of *i*Pr_2P), 24.9 (d, $^1J_{P,C}$ = 23.4 Hz, P*C*HCH_3 of P*i*Pr_3), 20.0, 19.6 (both s, PCH*C*H_3 of P*i*Pr_3), 19.8, 19.4, 18.9, 18.6 (all s, PCH*C*H_3 of *i*Pr_2P) ppm. ^{31}P NMR (81.0 MHz, $C_6D_5CD_3$, –40 °C) AB spin system: δ_A = 31.4 ($^2J_{P,P}$ = 253.4 Hz, d in off-resonance), δ_B = 16.5 ($^2J_{P,P}$ = 253.4 Hz, d in off-resonance) ppm. $C_{27}H_{47}ClO_3OsP_2$ (707.2): calcd. C 45.86, H 6.70; found C 45.33, H 7.01.

[OsH(η²-O_2CCH_3)(CO)(P*i*Pr_3){κ(*P*)-*i*Pr_2PCH_2CO_2Me}] (6): A solution of **2** (105 mg, 0.17 mmol) in THF (10 mL) was treated with an excess of sodium acetate (ca. 1 g) and stirred for 15 min under reflux. After the solution was cooled to room temperature, the solvent was evaporated in vacuo. The residue was extracted twice with benzene (10 mL each) and the combined extracts were dried in vacuo. A colorless solid was obtained, which was washed three times with 5-mL portions of pentane and dried; yield 81 mg (74%); m.p. 71 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2120 [ν(OsH)], 1880 [ν(CO)], 1715 [ν(C=O)], 1520, 1470 [ν(O_2CCH_3)] cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 3.29 (s, 3 H, OCH_3), 2.96 (AB part of an ABX spin system, *i*Pr_2PC*H*$_2$$CO_2$Me, $J_{A,B}$ = 13.9, $J_{A,X}$ = $J_{B,X}$ = 7.4 Hz, 2 H, A and B = H, X = P of *i*Pr_2P, δ_A = 3.01, δ_B = 2.92), 2.62, 2.50 (both m, 1 H each, PC*H*CH_3 of *i*Pr_2P), 2.30 (m, 3 H, PC*H*CH_3 of P*i*Pr_3), 1.56 (s, 3 H, O_2CCH_3), 1.45 (dd, $^3J_{P,H}$ = 15.5, $^3J_{H,H}$ = 7.1 Hz, 3 H, PCHC*H*$_3$ of *i*Pr_2P), 1.32 (dd, $^3J_{P,H}$ = 14.6, $^3J_{H,H}$ = 6.7 Hz, 3 H, PCHC*H*$_3$ of *i*Pr_2P), 1.27 (dd, $^3J_{P,H}$ = 13.1, $^3J_{H,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$ of P*i*Pr_3), 1.23 (br. d, $^3J_{H,H}$ = 7.1 Hz, 3 H, PCHC*H*$_3$ of *i*Pr_2P), 1.20 (dd, $^3J_{P,H}$ = 12.4, $^3J_{H,H}$ = 7.1 Hz, 9 H, PCHC*H*$_3$ of P*i*Pr_3), 1.15 (dd, $^3J_{P,H}$ = 12.5, $^3J_{H,H}$ = 7.0 Hz, 3 H, PCHC*H*$_3$ of *i*Pr_2P), –20.63 (dd, $^2J_{P,H}$ = $^2J_{P',H}$ = 16.0 Hz, 1 H, OsH) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 184.1 (s, O_2CCH_3), 183.7 (dd, $^2J_{P,C}$ = 16.3, $^2J_{P',C}$ = 8.9 Hz, OsCO), 170.8 (dd, $^2J_{P,C}$ = 8.5, $^3J_{P,C}$ = 2.4 Hz, *C*O_2Me), 51.3 (s, CO_2CH_3), 26.7 (d, $^1J_{P,C}$ = 9.0 Hz, PCH_2), 25.8 (dd, $^1J_{P,C}$ = 24.0, $^3J_{P,C}$ = 2.0 Hz, P*C*HCH_3 of P*i*Pr_3), 25.7 (dd, $^1J_{P,C}$ = 22.6, $^3J_{P,C}$ = 1.5 Hz, P*C*HCH_3 of *i*Pr_2P), 25.3 (s, O_2CCH_3), 20.3, 19.4 (both s, PCH*C*H_3 of P*i*Pr_3), 18.6 (d, $^2J_{P,C}$ = 3.2 Hz, PCH*C*H_3 of *i*Pr_2P), 18.5 (s, PCH*C*H_3 of P*i*Pr_3), 18.0 (d, $^2J_{P,C}$ = 3.6 Hz, PCH*C*H_3 of P*i*Pr_3), 17.4 (d, $^2J_{P,C}$ = 2.2 Hz, PCH*C*H_3 of P*i*Pr_3) ppm. ^{31}P NMR (162.0 MHz, C_6D_6): AB spin system: δ_A = 39.3 ($^1J_{Os,P}$ = 188.2, $^2J_{P,P}$ = 264.5 Hz, d in off-resonance), δ_B = 34.3 ($^1J_{Os,P}$ = 192.5, $^2J_{P,P}$ = 264.5 Hz, d in off-resonance) ppm. $C_{21}H_{44}O_5OsP_2$ (628.7): calcd. C 40.12, H 7.05; found C 40.19, H 7.35.

[OsH_6{κ(*P*)-*i*Pr_2PCH_2CH_2OMe}$_2$] (12): A solution of **9** (66 mg, 0.11 mmol) in benzene (8 mL) was treated with an excess of $NaBH_4$ (ca. 0.5 g) and methanol (1 mL). The mixture was stirred at room temperature until the evolution of gaseous byproducts stopped. The solution was filtered, and the filtrate was evaporated in vacuo. An off-white air-sensitive oil was obtained; yield 54 mg (92%). IR (pentane): $\tilde{\nu}$ = 1965, 1890 [ν(OsH)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.59 (m, 4 H, OCH_2), 3.13 (s, 6 H, OCH_3), 2.01 (m, 4 H, PCH_2), 1.57 (m, 4 H, PC*H*CH_3), 1.04 (dvt, *N* = 15.5, $^3J_{H,H}$ = 7.1 Hz, 12 H, PCHC*H*$_3$), 0.95 (dvt, *N* = 14.6, $^3J_{H,H}$ = 7.1 Hz, 12 H, PCHC*H*$_3$), –9.86 (t, $^2J_{P,H}$ = 9.6 Hz, 6 H, OsH) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 38.4 (s; sept in off-resonance) ppm. $C_{18}H_{48}O_2OsP_2$ (548.72): calcd. C 39.40, H 8.82; found C 40.10, H 9.29.

[OsH_6{κ(*P*)-*i*Pr_2PCH_2CO_2Me}$_2$] (13): This compound was prepared as described for **12**, with **10** (68 mg, 0.11 mmol), an excess of $NaBH_4$ (ca. 0.5 g) and methanol (1 mL) as starting materials. After the solution was filtered and the filtrate evaporated in vacuo, a grey residue remained, which was recrystallized from hexane (1 mL) at –78 °C to give a colorless air-sensitive solid; yield 22 mg (36%); m.p. 50 °C (dec.). IR (pentane): $\tilde{\nu}$ = 1980, 1895 [ν(OsH)], 1725 [ν(C=O)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.29 (s, 6 H, OCH_3), 2.90 (vt, *N* = 8.1 Hz, 4 H, PCH_2), 1.92 (m, 4 H, PC*H*CH_3), 1.13 (dvt, *N* = 16.5, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$), 1.05 (dvt, *N* = 15.0, $^3J_{H,H}$ = 6.7 Hz, 12 H, PCHC*H*$_3$), –9.61 [t, $^2J_{P,H}$ = 9.6 Hz, 6 H, OsH] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 44.6 (s; sept in off-resonance) ppm. $C_{18}H_{44}O_4OsP_2$ (576.7): calcd. C 37.49, H 7.69; found C 37.06, H 7.75.

[OsH_6{κ(*P*)-*i*Pr_2PCH_2CO_2Et}$_2$] (14): This compound was prepared as described for **12**, with **11** (33 mg, 0.05 mmol), an excess of $NaBH_4$ (ca. 0.5 g) and methanol (1 mL) as starting materials. A colorless air-sensitive oil was obtained; yield 28 mg (96%). IR (pentane): $\tilde{\nu}$ = 1965, 1880 [ν(OsH)], 1720 [ν(C=O)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.81 (q, $^3J_{H,H}$ = 6.9 Hz, 4 H, OCH_2CH_3), 2.91 (vt, *N* = 7.9 Hz, 4 H, PCH_2), 1.96 (m, 4 H, PC*H*CH_3), 1.13 (m, 24 H, PCHC*H*$_3$), 1.04 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, OCH_2CH_3), –9.64 (t, $^2J_{P,H}$ = 9.6 Hz, 6 H, OsH) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 44.75 (s, $^1J_{Os,P}$ = 138.0 Hz; sept in off-resonance) ppm. $C_{20}H_{48}O_4OsP_2$ (604.8): calcd. C 39.72, H 8.00; found C 39.64, H 8.35.

[OsH_6(P*i*Pr_3){κ(*P*)-*i*Pr_2PCH_2CH_2NMe$_2$}] (16): This compound was prepared as described for **12**, with **15** (60 mg, 0.10 mmol), an excess of $NaBH_4$ (ca. 0.5 g) and methanol (1 mL) as starting materials. A colorless air-sensitive oil was obtained; yield 41 mg (76%). IR (pentane): $\tilde{\nu}$ = 1965, 1890 [ν(OsH)] cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 2.98 (m, 2 H, C*H*$_2$NMe$_2$), 2.09 (s, 6 H, NCH_3), 2.02, 1.72, 1.56 (all m, 7 H, PCH_2 and PC*H*CH_3), 1.08 (dd, $^3J_{P,H}$ = 13.9, $^3J_{H,H}$ = 7.1 Hz, 18 H, PCHC*H*$_3$ of P*i*Pr_3), 1.00 (dd, $^3J_{P,H}$ = 14.4, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$ of *i*Pr_2P), –9.94 (dd, $^2J_{P,H}$ = $^2J_{P',H}$ = 10.0 Hz, 6 H, OsH), one signal for PCHC*H*$_3$ of *i*Pr_2P not exactly located ppm. ^{31}P NMR (162.0 MHz, C_6D_6): δ = 57.2 (d, $^2J_{P,P}$ = 134.9, $^1J_{Os,P}$ = 131.0 Hz; sept in off-resonance), 41.15 (d, $^2J_{P,P}$ = 134.9, $^1J_{Os,P}$ = 128.8 Hz; sept in off-resonance) ppm. $C_{19}H_{51}NOsP_2$ (545.7): calcd. C 41.81, H 9.42, N 2.57; found C 41.61, H 10.01, N 2.32.

[$OsH_4(O_2)$${κ(*P*)-*i*Pr_2PCH_2CO_2Me}$_2$] (17): A solution of **13** (81 mg, 0.14 mmol) in benzene (5 mL) was treated with CH_2=CH*t*Bu (ca. 0.5 g) and, after a trace of air was passed through, was stirred for 2 h under reflux. The solution was brought to room temperature, and the solvent was evaporated in vacuo. The remaining red-brown oil was washed twice with hexane (1 mL) and dried; yield 80 mg (93%). IR (KBr): $\tilde{\nu}$ = 1935, 1875 [ν(OsH)], 1720 [ν(C=O)], 875 [ν(O_2)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.25 (s, 6 H, OCH_3), 2.92 (d, $^2J_{P,H}$ = 8.4 Hz, 4 H, PCH_2), 2.18 (m, 4 H, PC*H*CH_3), 1.33 (dd, $^3J_{P,H}$ = 16.7, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$), 1.23 (dd, $^3J_{P,H}$ = 15.3, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$), –12.78 (br., 4 H, OsH) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 171.6 (dd, $^2J_{P,C}$ = 9.8 Hz, *C*O_2Me), 51.6 (s, CO_2CH_3), 41.2 (br. m, PCH_2), 30.0 (d, $^1J_{P,C}$ = 45.0 Hz, P*C*HCH_3), 20.3, 20.1 (both s, PCH*C*H_3) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.2 (s; quint in off-resonance) ppm. $C_{18}H_{42}O_6OsP_2$ (606.7): calcd. C 35.64, H 6.98; found C 36.01, H 7.01.

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***cis*,*cis*,*trans*-[$OsH_2(CO)_2${κ(*P*)-*i*$Pr_2PCH_2CH_2OMe$}$_2$] (19):** A solution of **18** (45 mg, 0.07 mmol) in diethyl ether (10 mL) was treated with an excess of $LiAlH_4$ (ca. 0.3 g) and stirred for 2 d under reflux. After the solution was cooled to room temperature, the solvent was evaporated in vacuo, and the residue was extracted twice with benzene (10 mL each). The combined extracts were dried in vacuo, the colorless oily residue was washed with hexane (1 mL) and dried; yield 31 mg (78%). IR (pentane): $\tilde{\nu}$ = 1995, 1975 [ν(CO)], 1915, 1855 [ν(OsH)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 3.70 (m, 4 H, OCH_2), 3.16 (s, 6 H, OCH_3), 2.10 (m, 4 H, PCH_2), 1.77 (m, 4 H, $PCHCH_3$), 1.10 (dvt, N = 16.1, $^3J_{H,H}$ = 7.1 Hz, 12 H, $PCHCH_3$), 0.97 (dvt, N = 14.2, $^3J_{H,H}$ = 6.9 Hz, 12 H, $PCHCH_3$), –9.64 (t, $^2J_{P,H}$ = 22.7 Hz, 2 H, OsH) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 186.8 (t, $^2J_{P,C}$ = 6.3 Hz, OsCO), 71.2 (s, OCH_2), 58.2 (s, OCH_3), 28.2 (vt, N = 16.1 Hz, PCH_2), 20.2 (vt, N = 12.9 Hz, $PCHCH_3$), 19.0, 18.4 (both s, $PCHCH_3$) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 23.5 (s, $^1J_{Os,P}$ = 162.8 Hz; t in off-resonance) ppm. $C_{20}H_{44}O_4OsP_2$ (600.7): calcd. C 40.00, H 7.38; found C 40.37, H 7.71.

Catalytic Studies: The reactions were carried out under argon with magnetic stirring, in a 25 mL round-bottom flask fitted with a condenser and provided with a serum cap. In a typical procedure, a solution of the catalyst precursor $[OsH_6(PR_3)_2]$ (**8**, **12**–**14**) prepared in situ from $[OsH_2Cl_2(PR_3)_2]$ (**7**, **9**–**11**) (0.02 mmol) and $NaBH_4$ (1.0 mmol) in 5 mL of 2-propanol, was stirred for 1 h under reflux, and then a solution of cyclohexanone or acetophenone (2.0 mmol) in 3 mL of 2-propanol was injected. The progress of the reactions were monitored by a Perkin–Elmer 8900 gas chromatograph with a flame ionization detector and an FFAP on Chromosorb GHP 80/100 mesh column (3.6 × 1/8 in.) at 160 °C. The results are summarized in Table 1.

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