A Series of Neutral and Cationic Mesityleneosmium(II) Complexes Containing Bulky Phosphines with Various Functionalities as Ligands

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Received November 6, 1998

Mono- and dihydridoosmium(II) compounds with [(mes)Os{*i*Pr$_2$P(CH$_2$)$_n$Y}] (mes = mesitylene, 1,3,5-trimethylbenzene; n = 2, Y = NMe$_2$, OMe; n = 3, Y = NMe$_2$) as a molecular unit are prepared from the dichloro derivatives [(mes)OsCl$_2${*i*Pr$_2$P(CH$_2$)$_n$Y}] and magnesium amalgam in THF in the presence of ethanol. Upon treatment of [(mes)Os(X)Cl{κ^1(*P*)-*i*Pr$_2$P-(CH$_2$)$_2$Y}] (X = H, Cl) with AgPF$_6$ in CH$_2$Cl$_2$ cationic complexes with *i*Pr$_2$P(CH$_2$)$_2$Y as a chelating ligand are obtained. The compounds with Y = OMe react (for X = Cl) with L = CO and CNMe by opening of the chelate bond to give the PF$_6$ salts [(mes)Os(L)Cl{κ^1(*P*)-*i*Pr$_2$P(CH$_2$)$_2$Y}]PF$_6$ and (for X = H) with KO*t*Bu by fragmentation of the functionalized phosphine to afford the neutral complex [(mes)OsH(OMe)(*i*Pr$_2$PCH=CH$_2$)]. The reaction of the chelate compound [(mes)OsCl{κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(OMe)O}]PF$_6$ with KO*t*Bu leads to the formation of the corresponding uncharged phosphanyl ester enolate−osmium(II) complex by proton abstraction from the PCH$_2$ unit. The ester enolate complex reacts with phenyl isocyanate and diphenylketene by insertion of the heterocumulene into the enolate C−H bond and with water by ester hydrolysis to yield the phosphanyl carboxylate derivative [(mes)-OsCl(κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$CO$_2$)]. The molecular structures of compounds **9**, **11**, **22**, and **23** have been determined by X-ray crystallography.

Introduction

Owing to their important role in homogeneous catalysis,[1,2] the chemistry of functionalized phosphines of the general composition R$_2$P(CH$_2$)$_n$Y and their transition-metal complexes has been an area of active research in recent years.[3] In particular for compounds where Y is OMe, C(O)R′, or CO$_2$R′, the oxygen donor atoms are able to protect temporarily a vacant coordination site and thus allow the addition of other (better) donor ligands to the metal center under fairly mild conditions. Moreover, with β-phosphanyl ketones or esters as starting materials a number of phosphanyl enolate−metal complexes have been prepared and found to be useful starting materials for C−C coupling reactions with activated alkynes and isocyanates[4] as well as for the reversible binding of carbon dioxide.[5]

In a continuation of our work on the behavior of [(mes)OsCl$_2$]$_n$ (**1**) toward trialkylphosphines,[6] we recently reported the synthesis of the monomeric compounds [(mes)OsCl$_2$(L)] with phosphanyl ethers and phosphanyl esters as ligands.[7] We also illustrated that, depending on the reaction conditions, the corresponding complex with L = *i*Pr$_2$PCH$_2$CO$_2$Me reacts with hydride sources to give either the dihydridoosmium(II) derivative [(mes)OsH$_2$(L)] or, by elimination of HCl, the novel phosphanylmethanide compound [(mes)OsCl{κ^2(*P*,*C*)-*i*Pr$_2$PCHCO$_2$Me}].[7] In this paper we describe the preparation of a series of neutral mesityleneosmium(II) complexes with bulky phosphines containing dimethylamino, methoxy, or carbomethoxy functionalities, their conversion into cationic species, and the reactivity of these cations toward nucleophilic and electrophilic

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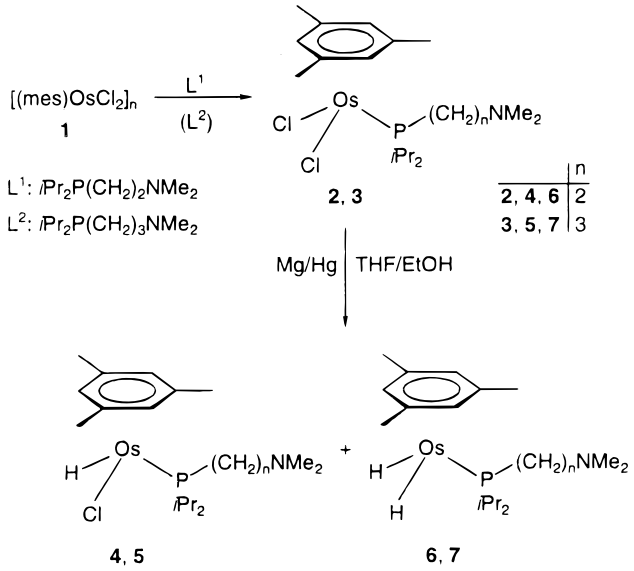
10.1021/om980909e CCC: $18.00
Publication on Web 03/04/1999

Scheme 1



substrates. Part of this work has already been communicated.[8]

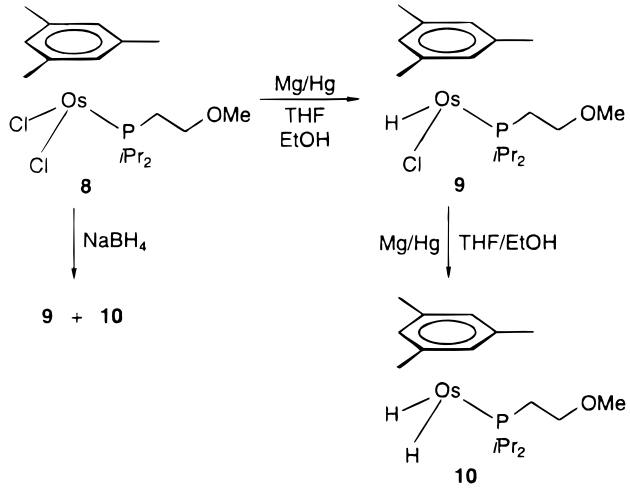
Results and Discussion

1. Mono- and Dihydridoosmium(II) Compounds with [(mes)Os{*i*Pr$_2$P(CH$_2$)$_n$Y}] as a Molecular Unit. Under conditions similar to those with phosphanyl ethers, ketones and esters, the chloro-bridged complex **1** reacts with phosphanylamines *i*Pr$_2$P(CH$_2$)$_n$NMe$_2$ (n = 2, 3) to give the mononuclear products **2** and **3** (Scheme 1) in almost quantitative yield. They are orange solids which are practically air-stable and moderately soluble in polar organic solvents such as CH_2Cl_2 and acetone. While the ^{1}H NMR data of **2** and **3** deserve no further comment, it should be mentioned that the expected singlet in the ^{31}P NMR spectra is associated with two satellites arising from $^1J(^{187}Os^{31}P)$ coupling of ca. 277 Hz.

The experiments aimed at substituting the chloro ligands in **2** and **3** by hydride ions led to some unexpected results. When we tried to prepare the complexes [(mes)OsH$_2$(L)] (**6**, **7**) from the precursors **2**, **3** and Mg/Hg in THF in the presence of EtOH, following the method which we applied to the synthesis of the corresponding dihydridoosmium(II) compounds with L = CO, CNMe,[9] we obtained a mixture of **4** and **6** or **5** and **7**, respectively, in different ratios. Despite several attempts we failed to separate these mixtures by column chromatography or fractional crystallization. Therefore, we characterized the chloro hydrido and dihydrido complexes by spectroscopic techniques. The ^{1}H NMR spectra of **4** and **5** display a hydride signal at ca. δ −9.0 and those of **6** and **7** at ca. δ −12.1, both of which are split into a doublet with a large P−H coupling of 38−44 Hz. The ^{31}P NMR spectra of **4**−**7** show a singlet resonance which under off-resonance conditions is split into either a doublet (**4**, **5**) or a triplet (**6**, **7**).

In contrast to the reactions of **2** and **3**, the reaction of the phosphanyl ether complex **8** with magnesium amalgam in THF/EtOH proceeds very selectively and affords the chlorohydridoosmium(II) derivative **9** (Scheme 2) in 88% isolated yield. Like the related phosphanyl ester

Scheme 2



derivative [(mes)OsHCl(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$CO$_2$Et)],[7] compound **9** forms yellow, slightly air-sensitive crystals which (even under argon) slowly decompose at room temperature but can be stored at −20 °C for weeks. With regard to the spectroscopic data of **9** we note that owing to the chirality of the molecule the protons of the CH_2 units of the functionalized phosphines are diastereotopic and thus four multiplets are observed. The same happens for the CH_3 protons of the isopropyl groups, which give rise to four doublets of doublets in the range δ 1.17−0.95.

The structure of **9** was confirmed by single-crystal X-ray structure analysis. The ORTEP structure plot (Figure 1) reveals that the metal center is coordinated by the mesitylene ring and the three monodentate ligands in a piano-stool fashion. Probably due to the dangling of the phosphanyl ether unit, there is a slight disorder in the CH_2OMe fragment. Although the mesitylene ring is almost planar, the Os−C10 to Os−C15 bond lengths differ by ca. 0.12 Å. The shortest distance Os−C13 (2.168(5) Å) is that to the ring carbon atom which is nearest to the hydride ligand, while the longest distance Os−C10 (2.289(5) Å) is trans to Os−H. Hence,

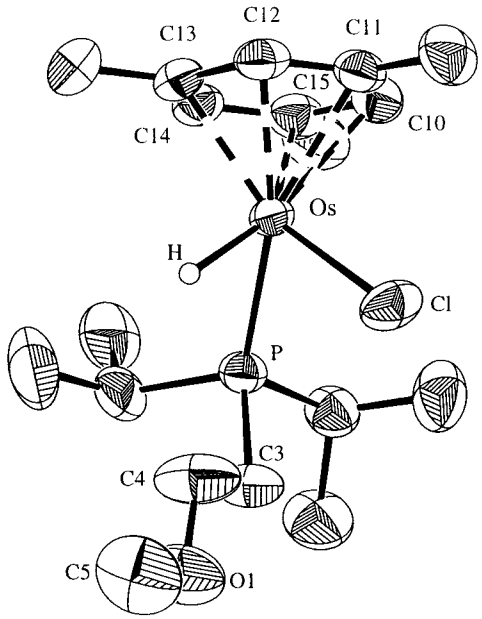
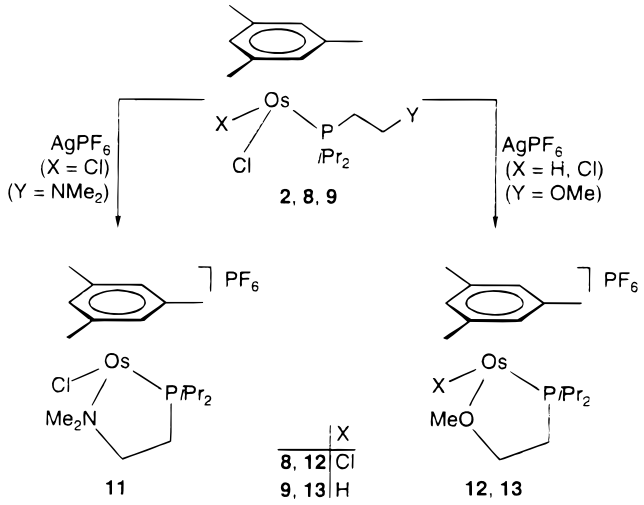


Figure 1. ORTEP drawing of **9**.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 9

	Bond Distances (Å)		
Os−Cl	2.419(2)	Os−C13	2.168(5)
Os−P	2.302(2)	Os−C14	2.197(5)
Os−C10	2.289(5)	Os−C15	2.259(5)
Os−C11	2.274(5)	C3−C4	1.516(8)
Os−C12	2.231(5)	C4−O1	1.344(7)
	Bond Angles (deg)		
Cl−Os−P	87.12(6)	C3−C4−O1	109.4(5)
P−C3−C4	117.6(4)	C4−O1−C5	113.0(5)

Scheme 3



it seems that both steric requirements and eletronic effects (i.e., the trans influence of the hydride) are responsible for the differences in bond lengths. The distances Os−Cl and Os−P (Table 1) are in the expected range[7,10] and thus deserve no further comment.

Treatment of the chloro hydrido complex **9** with a larger excess of Mg/Hg in THF/EtOH produces in part the dihydridoosmium(II) derivative **10**, which can be separated from the starting material **9** by chromatographic techniques. The isolated yield of **10** (a colorless, air-sensitive, and thermally unstable solid) was 58%. The presence of two hydride ligands is indicated by the ^{1}H NMR spectrum, which displays a doublet at δ −12.20 with an intensity of 2H. Under off-resonance conditions, in the ^{31}P NMR spectrum a triplet is observed. Attempts to prepare the dihydrido complex **10** from the dichloro compound **8** and $NaBH_4$ led to a mixture of **9** and **10** in the molar ratio of 1:1, indicating that this method is not an alternative for the synthesis of the OsH_2 species.

Both the dichloro compounds **2** and **8** and the chloro hydrido derivative **9** react with an equimolar amount of $AgPF_6$ in CH_2Cl_2 by abstraction of a chloride ligand to give the cationic complexes **11**−**13** (Scheme 3) in good to excellent yield. Compounds **11**−**13** are yellow solids, the composition of which has been confirmed not only by elemental analysis but also by conductivity measurements. Due to the deshielding effect of the positive charge at the metal center, the signal for the phosphorus

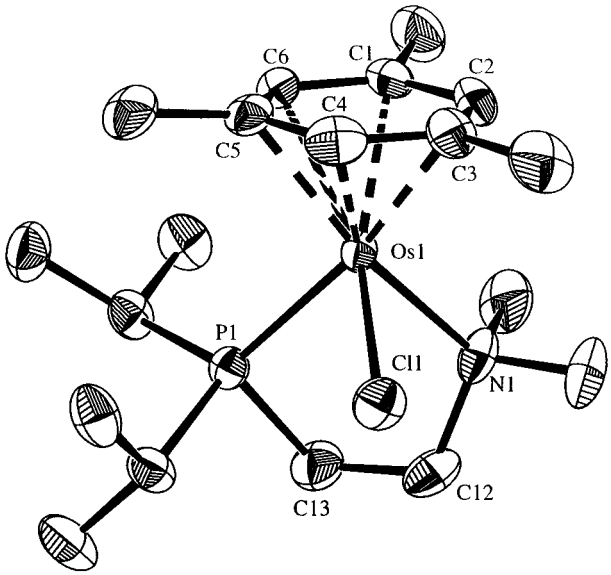


Figure 2. ORTEP drawing of **11**.

Table 2. Selected Bond Distances and Angles with Esd's for Compound 11

	Bond Distances (Å)		
Os1−Cl1	2.4363(11)	Os1−C3	2.254(4)
Os1−P1	2.3544(11)	Os1−C4	2.197(5)
Os1−N1	2.225(3)	Os1−C5	2.245(4)
Os1−C1	2.250(4)	Os1−C6	2.197(4)
Os1−C2	2.252(4)		
	Bond Angles (deg)		
Cl1−Os1−P1	87.19(4)	Os1−N1−C12	110.8(3)
Cl1−Os1−N1	84.22(10)	N1−C12−C13	111.2(4)
P1−Os1−N1	81.74(10)	P1−C13−C12	109.0(3)
Os1−P1−C13	103.20(15)		

nuclei in the ^{31}P NMR spectra of **11**−**13** is shifted to lower field by 35−44 ppm compared with the neutral compounds **2**, **8**, and **9**, respectively. The ^{1}H NMR spectrum of **13** displays the hydride signal at δ −8.29, and this is also at lower field compared with **9** (δ −12.20).

The molecular structure of the cationic complex **11** is shown in Figure 2, and bond distances and angles are given in Table 2. The osmium and the functionalized phosphine form a five-membered chelate ring with a P−Os−N bond angle of 81.74(10)°. This "bite angle" of the phosphanylamine is almost identical with that of the phosphanylethanolate in the related neutral compound [(mes)Os(Ph)(κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$CPh$_2$O)] (81.3(1)°), which was obtained upon treatment of **17** with PhMgBr.[7] The Os−N bond length of **11** (2.225(3) Å) is significantly shorter than in [OsCl(CO)(κ^2(*C*,*P*)-*i*Pr$_2$PCH$_2$CH$_2$NMeCH)(κ^2(*P*,*N*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$)]Cl (2.333(5) Å),[11b] which we assume is due to the steric crowding around the metal center in the non-mesitylene-containing chelate complex.

The reactions of compounds **12** and **13** with some nucleophiles are summarized in Scheme 4. When the stability of cationic carbonylosmium(II) complexes such as [(C_6H_6)OsI(CO)(PR_3)]PF_6 is taken into account,[12] the

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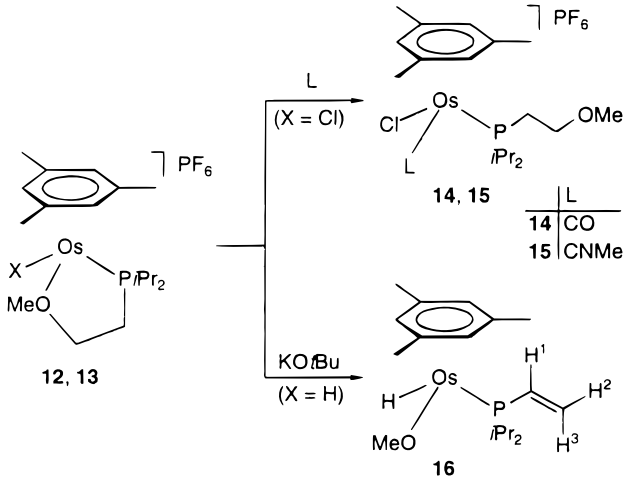
Scheme 4

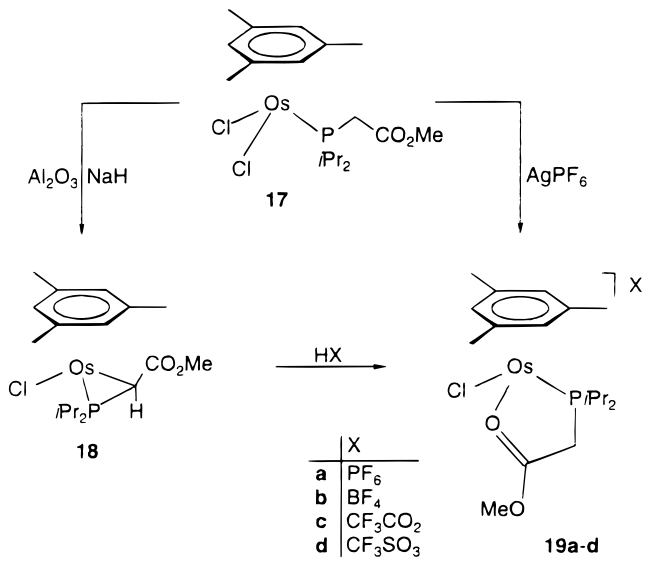


somewhat surprising observation is that the corresponding mesitylene compound **14** is rather labile and decomposes in solution within a few hours. The IR spectrum of **14** (in CH_2Cl_2) shows the ν(CO) frequency at 1990 cm^{-1}, i.e., at a similar position as $[(C_6H_6)OsI(CO)(PiPr_3)]PF_6$.[12b] In contrast to **14**, the related methyl isocyanide derivative **15** is quite stable and can be stored under argon for weeks. We conclude that the increase in the thermodynamic stability when CO is replaced by CNMe is attributed to the stronger donor ability of the isocyanide, which is also reflected in the shift of the phosphorus resonance by ca. 8 ppm to higher field in the ^{31}P NMR spectrum of **15** compared to that of **14**.

The attempt to abstract the coordinated hydride ligand from **13** by KO*t*Bu led to a puzzling result. Instead of generating the compound [(mes)Os(κ^2(*P*,*O*)-*i*$Pr_2PCH_2CH_2OMe$)], a cleavage of the C−OMe bond of the chelate unit occurred and the hydridomethoxyosmium(II) complex **16** with diisopropylvinylphosphine as ligand was formed. The pale yellow oily substance is readily soluble in common organic solvents and decomposes slowly at room temperature. The ^1H NMR spectrum of **16** displays a doublet resonance at δ −8.55 for the hydride and three signals for the vinylic protons H^1, H^2, and H^3 (see Scheme 4) at δ 6.32, 5.59, and 5.44 corresponding to an ABC pattern. These signals appear in the $^1H\{^{31}P\}$ spectrum as doublets of doublets with the expected different H−H coupling for the cis, trans, and geminal protons of the $CH{=}CH_2$ fragment. With regard to the mechanism of formation of **16** we assume that in the initial step the strong base KO*t*Bu abstracts a proton from either the OCH_3 or the PCH_2 moiety of the functionalized phosphine ligand. The coordinated *i*Pr_2PCHCH_2OMe systems, once formed, could be transformed by breaking the H_2C−OMe bond to a methoxy and a vinylphosphine unit, a process that is reminiscent of the fragmentation of dialkyl ethers by $NaNH_2$, organoalkali-metal compounds, or other strong bases.[13]

2. Phosphanyl Ester− and Phosphanyl Ester Enolate−Osmium(II) Complexes. Like the above-mentioned phosphanyl ether and phosphanylamine

Scheme 5



metal derivatives **2**, **8**, and **9**, the related phophanyl ester compound **17**[7] also reacts with $AgPF_6$ in CH_2Cl_2 to give the chelate complex **19a** (Scheme 5) in 85% yield. An alternative route to this compound as well as to the analogous BF_4^-, $CF_3CO_2^-$, and $CF_3SO_3^-$ salts **19b−d** of the $[(mes)OsCl\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(OMe)O\}]^+$ cation consists of the reaction of the phosphanylmethanide complex **18** with acid HX. Compound **18** was obtained by attempting to prepare the phosphanyl ester enolate−osmium(II) derivative $[(mes)OsCl\{\kappa^2(P,O)\text{-}iPr_2PCH{=}C(OMe)O\}]$ from **17** and NaH in the presence of Al_2O_3.[7] With regard to the thermodynamic stability of isomeric complexes such as **18** and **20** (see Scheme 6), it should be noted that recent work from our laboratory has shown that in the corresponding mesitylene ruthenium(II) system a thermodynamic preference for a three- instead of a five-membered chelate ring exists.[14] The IR spectra of the yellow, nearly air-stable solids **19a**,**b** display a C=O stretching frequency at 1595 cm^{-1} (**19a**) and 1604 cm^{-1} (**19b**), which is lowered by ca. 120−130 cm^{-1} if compared with the frequency for **17**.[7] We therefore conclude that the phosphanyl ester ligand in the cationic species **19a−d** is coordinated via the phosphorus and the carbonyl oxygen (but not the methoxy group) to the metal center.

In contrast to **17**, which upon treatment with bases gives **18**, the cationic complex **19a** reacts with KO*t*Bu in THF to afford the phosphanyl ester enolate compound **20** in excellent yield. The structural proposal (Scheme 6) for the yellow, very moisture-sensitive substance is mainly supported by the ^1H NMR spectrum, in which a characteristic signal (doublet) for the PCH proton at δ 3.48 appears. The ^{13}C NMR spectrum of **20** displays two resonances for the O−C−C−P carbon atoms of the chelate ring at δ 184.4 (O−C) and 45.6 (C−P), the chemical shift and the P−C coupling constant of which are quite similar to those of phosphanyl ester enolate−ruthenium(II) and −platinum(II) derivatives.[5a,14]

While compound **20** is inert toward CO_2, it reacts with phenyl isocyanate in benzene to give a mixture of products, among which the neutral complex **21** is the

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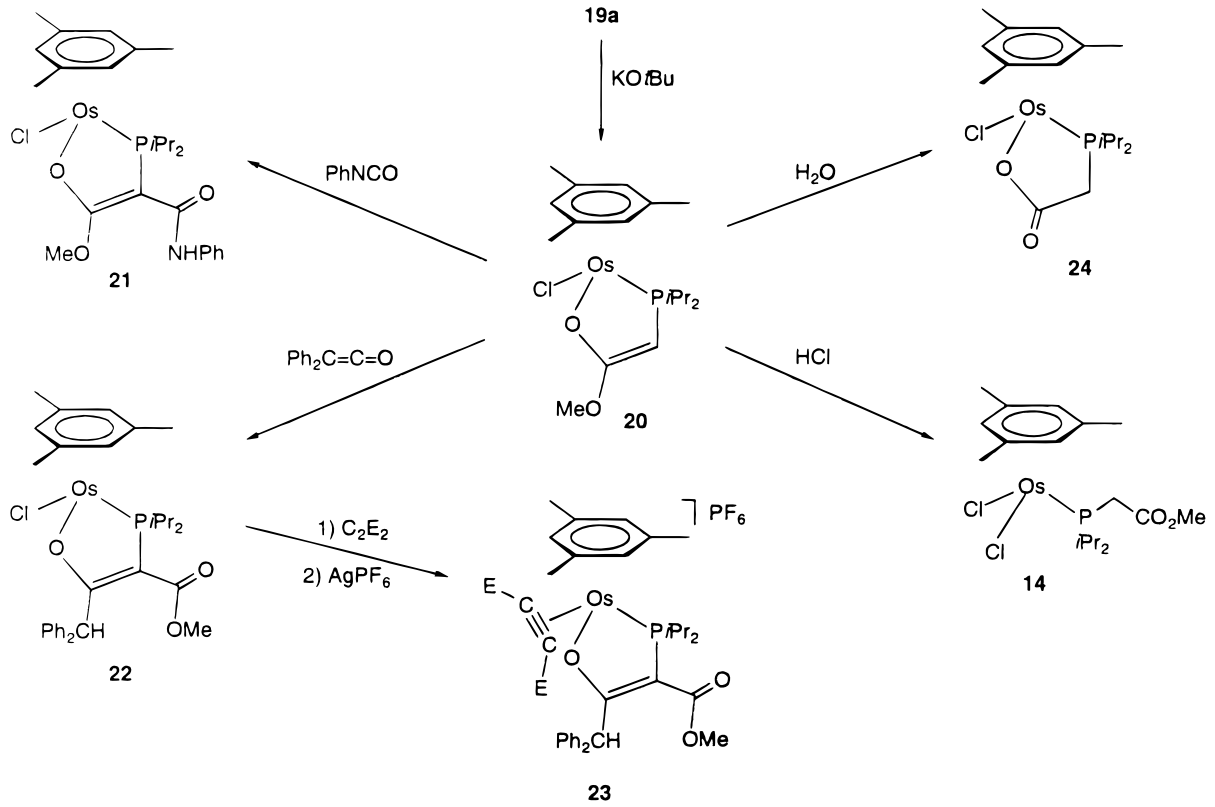
(14) Henig, G.; Schulz, M.; Werner, H. *Chem. Commun.* **1997**, 2349−2350.

Scheme 6[a]



[a] E = CO_2Me.

dominating species. This ring-substituted derivative of **20** formally results from the addition of the C−H bond of the phosphino ester enolate across the C═N bond of the substrate. Insertion reactions of this type are not without precedent and have been studied in detail, particularly by Braunstein, Matt, and their co-workers.[4] Characteristic spectroscopic features of **21** are the N−H stretching frequency at 3405 cm^{-1} in the IR and the signal for the N−H proton at δ 9.13 in the ^1H NMR spectrum.

Not only phenyl isocyanate but also diphenylketene forms the 1:1 adduct **22** with the enolate complex **20**. If the reaction is carried out in hexane/dichloromethane (3:1) and the reaction mixture worked up by column chromatography with basic Al_2O_3, the product is isolated in 63% yield. The composition of the pale yellow, only moderately air- and moisture-sensitive solid was substantiated not only by elemental analysis and spectroscopic techniques but also by X-ray crystallography. The presence of the uncoordinated CO_2Me group is indicated by the C═O absorption in the IR spectrum at 1671 cm^{-1} and the ^{13}C NMR resonance (singlet) at δ 194.6. The signal for the C−O enolate carbon atom appears at δ 182.3 and is split into a doublet due to P−C coupling.

The result of the single-crystal X-ray structure analysis of **22** is shown in Figure 3. The ORTEP diagram (Figure 3) reveals that the molecule possesses a similar piano-stool configuration as the cationic complex **11** with bond angles between the three "legs" of 88.6(1)° (P−Os−Cl), 83.8(2)° (O1−Os−Cl), and 79.6(2)° (O1−Os−P). The five-membered phosphanyl enolate−osmium unit is almost planar, with the carbon atoms C3 and C5 of the substituents lying in the ring plane. While the bond length C1−C2 (1.36(1) Å) is only slightly elongated compared to a normal C═C bond, the distance C2−O1 (1.28(1) Å) lies between that of a C−O single and a C═O double bond, indicating some electron delocalization within the enolate ligand. In analogy to **9** and **11**, the Os−C24 to Os−C29 bond lengths differ by ca. 0.14 Å (Table 3), for which both steric and electronic effects could be responsible.

The reaction of **22** with $C_2(CO_2Me)_2$ (DMAD) in the presence of 1 equiv of $AgPF_6$ in CH_2Cl_2 led to the replacement of the chloride by the alkyne and gave the

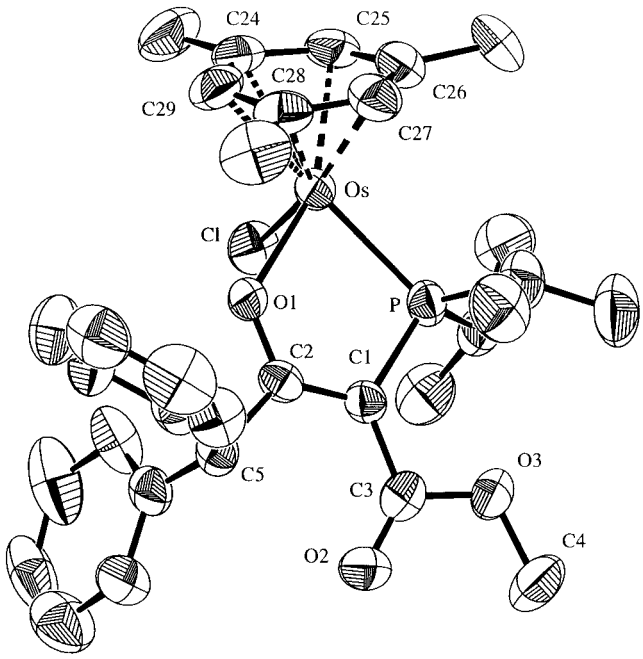


Figure 3. ORTEP drawing of **22**.

Table 3. Selected Bond Distances and Angles with Esd's for Compound 22

Bond Distances (Å)			
Os−Cl	2.389(3)	Os−C29	2.23(1)
Os−P	2.341(3)	O1−C2	1.28(1)
Os−O1	2.074(7)	C1−C2	1.36(1)
Os−C24	2.29(1)	C2−C5	1.55(1)
Os−C25	2.19(1)	P−C1	1.79(1)
Os−C26	2.21(1)	C1−C3	1.47(2)
Os−C27	2.17(1)	C3−O2	1.21(1)
Os−C28	2.15(1)	C3−O3	1.36(1)
Bond Angles (deg)			
Cl−Os−P	88.6(1)	C2−C1−C3	123.0(9)
Cl−Os−O1	83.8(2)	P−C1−C2	113.7(8)
P−Os−O1	79.6(2)	P−C1−C3	123.3(8)
Os−O1−C2	122.8(6)	C1−C3−O2	129(1)
Os−P−C1	100.7(3)	C1−C3−O3	110(1)
O1−C2−C1	122.8(9)	O2−C3−O3	121(1)
O1−C2−C5	113.3(9)	C3−O3−C4	116(1)
C1−C2−C5	123.9(9)		

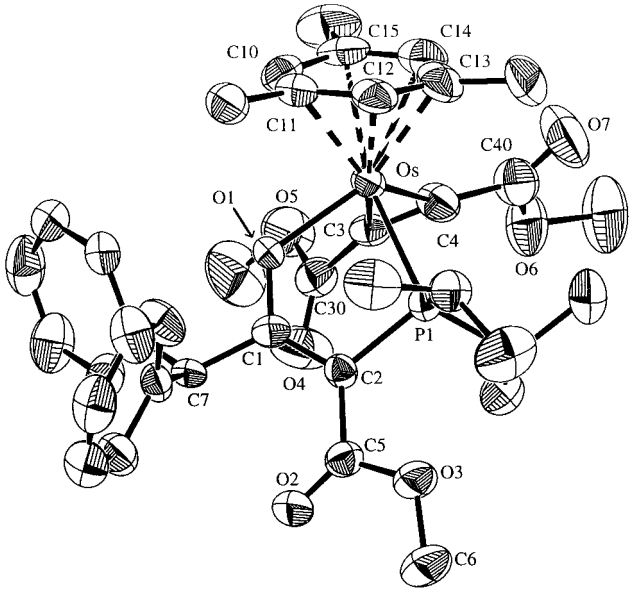


Figure 4. ORTEP drawing of **23**.

cationic complex **23** as an orange solid in almost quantitative yield. The aim of this experiment was to find out whether compound **22** behaves similarly to phosphanyl *keto* enolates of nickel, palladium, and platinum, which react with DMAD by insertion to form a new C−C bond.[4b] However, with **22** as the starting material such a coupling process does not occur.

The coordination of the acetylene derivative in **23** via the triple bond, as indicated by the appearance of the ν(C≡C) stretching vibration at 1863 cm^{-1} in the IR and the two signals for the alkyne carbon atoms at δ 95.9 and 95.4 in the ^{13}C NMR spectrum, was confirmed by an X-ray structure analysis. As the ORTEP plot (Figure 4) reveals, the steric requirements around the osmium are quite severe, and this may explain why the DMAD ligand is not symmetrically coordinated to the metal center. The difference in the bond lengths Os−C3 and Os−C4 is ca. 0.05 Å (Table 4). The DMAD backbone C30−C3−C4−C40 is not linear, possessing C−C−C

Table 4. Selected Bond Distances and Angles with Esd's for Compound 23

Bond Distances (Å)			
Os−O1	2.052(4)	O1−C1	1.304(7)
Os−P1	2.374(2)	C1−C2	1.372(9)
Os−C3	2.095(7)	C1−C7	1.542(8)
Os−C4	2.147(7)	C2−C5	1.465(9)
Os−C10	2.274(7)	O2−C5	1.188(8)
Os−C11	2.350(7)	O3−C5	1.341(8)
Os−C12	2.316(7)	O3−C6	1.438(9)
Os−C13	2.246(7)	C3−C4	1.243(9)
Os−C14	2.253(8)	C3−C30	1.48(1)
Os−C15	2.324(8)	C4−C40	1.47(1)
P1−C2	1.803(6)		
Bond Angles (deg)			
P1−Os−O1	79.0(1)	P1−C2−C5	124.3(5)
P1−Os−C3	92.6(2)	O1−C1−C2	122.0(6)
P1−Os−C4	88.8(2)	O1−C1−C7	113.8(5)
O1−Os−C3	84.7(2)	C2−C1−C7	124.1(6)
O1−Os−C4	117.1(2)	C1−C2−C5	122.5(6)
C3−Os−C4	34.1(2)	O2−C5−C2	127.6(7)
Os−C3−C4	75.3(5)	O2−C5−O3	121.5(7)
Os−C4−C3	70.6(5)	C2−C5−O3	110.9(6)
Os−O1−C1	123.5(4)	C5−O3−C6	116.1(6)
Os−P1−C2	100.1(2)	C3−C4−C40	147.7(8)
P1−C2−C1	113.1(5)	C4−C3−C30	146.2(7)

bond angles of 146.2(7) and 147.7(8)°, respectively. A similar degree of bending has also been found in other (alkyne)osmium complexes.[15] The distances from the metal to the mesitylene ring carbon atoms in **23** are approximately 0.08 Å longer than in **22**, which could be due to the decrease in back-donation by increasing the positive charge at the metal center.

In the presence of water in acetone solution, hydrolysis of the enolate function of compound **20** takes place and the phosphanyl acetate complex **24** (see Scheme 6) is formed in 92% yield. A related metal-assisted transformation of a phosphanyl enolate to a corresponding acetate was recently observed by us[16] as well as by Braunstein et al.[17] in the case of square-planar iridium and palladium derivatives. The IR and NMR data of **23** (a pale yellow, almost air-stable solid) are similar to those of [(mes)RuCl(κ^2(*P,O*)-$Ph_2PCH_2CO_2$)], which was obtained by acid hydrolysis of [(mes)$RuCl_2$(κ^1(*P*)-$Ph_2PCH_2CO_2Me$)].[18] It should be mentioned that upon treatment of **20** with HCl, instead of cleavage of the O−CH_3 bond of the enolate moiety protonation of the PCH═ carbon atom occurs and the dichloroosmium(II) complex **14** is generated quantitatively.

Conclusions

The work presented in this paper has shown that bulky, functionalized phosphines of the general composition $i$$Pr_2P(CH_2)_nY$ with n = 1−3 and Y = OMe, NMe_2, CO_2Me behave in half-sandwich-type (arene)osmium(II) complexes as monodentate (P-bonded) as well as bidentate ligands. In contrast to ruthenium for which numerous compounds with coordinated phosphanyl derivatives $R_2P(CH_2)_nY$ (R mainly phenyl) are known,[3,18] related osmium complexes are quite rare and up to now have been mainly described from our laboratory.[7,11] Not

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unexpectedly, the state of the art is that the functional group Y of the substituted phosphines $i\mathrm{Pr_2P(CH_2)}_n\mathrm{Y}$ form stronger bonds to Os than to Ru with the consequence that these phosphines are not typical hemilabile chelating systems if bonded to osmium. The advantage of forming stronger chelate bonds is that it is easier to transform the original phosphanyl compounds into phosphanyl enolate or phosphanylmethanide derivatives and these, as it was illustrated by several examples reported here, are useful starting materials for further synthesis.

Experimental Section

General Considerations. All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**,[19] **8**,[7] **17**,[7] and **18**,[7] as well as the functionalized phosphine ligands $i\mathrm{Pr_2P(CH_2)}_n\mathrm{NMe_2}$,[20] were prepared as described in the literature.

Physical Measurements. NMR spectra were recorded at room temperature or at the temperature mentioned in the appropriate procedure on Bruker AC 200 and Bruker AMX 400 instruments. Chemical shifts are expressed in ppm downfield from $SiMe_4$ (^{1}H and ^{13}C) and (85%) H_3PO_4 (^{31}P). Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal. Coupling constants *J* are given in hertz. The conductivity Λ was measured in nitromethane with a Schott Konduktometer CG 851 instrument, and melting and decomposition points were determined by DTA.

Preparation of [(mes)OsCl$_2$(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$)] (2). A suspension of **1** (242 mg, 0.32 mmol for $n = 2$) in 30 mL of CH_2Cl_2 was treated dropwise with $i\mathrm{Pr_2PCH_2CH_2NMe_2}$ (310 μL, 1.47 mmol) and stirred for 2.5 h at room temperature. The solution was filtered, the solid residue on the filter disk was washed three times with 10 mL portions of CH_2Cl_2, and the combined filtrates were concentrated to ca. 6−8 mL in vacuo. Upon addition of 30 mL of hexane an orange solid precipitated, which was separated from the mother liquor, washed with 5 mL of hexane, and dried: yield 317 mg (87%); mp 136 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ 4.85 (s, 3H, $C_6H_3Me_3$), 2.73 (m, 2H, CH_2NMe_2), 2.58 (m, 2H, PCH_2), 2.31 (m, 2H, $PCHCH_3$), 2.14 (s, 6H, NMe_2), 1.94 (s, 9H, $C_6H_3Me_3$), 1.14 [dd, *J*(PH) = 13.2, *J*(HH) = 7.0 Hz, 6H, $PCHCH_3$], 1.08 [dd, *J*(PH) = 14.4, *J*(HH) = 7.0 Hz, 6H, $PCHCH_3$]. ^{31}P NMR (162.0 MHz, C_6D_6): δ −9.5 [s, $J(^{187}Os^{31}P)$ = 278.0 Hz]. Anal. Calcd for $C_{19}H_{36}Cl_2NOsP$ (570.6): C, 40.00; H, 6.36; N, 2.45. Found: C, 40.32; H, 6.59; N, 2.34.

Preparation of [(mes)OsCl$_2$(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$CH$_2$NMe$_2$)] (3). This compound was prepared as described for **2**, using **1** (340 mg, 0.45 mmol for $n = 2$) and $i\mathrm{Pr_2PCH_2CH_2CH_2NMe_2}$ (400 μL, 1.58 mmol) as starting materials: orange solid; yield 493 mg (94%); mp 144 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ 4.90 (s, 3H, $C_6H_3Me_3$), 2.40 (m, 2H, PCH_2), 2.27 (m, 2H, $PCHCH_3$), 2.15 [t, *J*(HH) = 7.0 Hz, 2H, CH_2NMe_2], 2.08 (s, 6H, NMe_2), 1.97 (s, 9H, $C_6H_3Me_3$), 1.86 (m, 2H, $CH_2CH_2NMe_2$), 1.11 [dd, *J*(PH) = 12.6, *J*(HH) = 6.9 Hz, 6H, $PCHCH_3$], 1.10 [dd, *J*(PH) = 14.1, *J*(HH) = 7.2 Hz, 6H, $PCHCH_3$]. ^{31}P NMR (162.0 MHz, C_6D_6): δ −9.4 [s, $J(^{187}Os^{31}P)$ = 277.3 Hz]. Anal. Calcd for $C_{20}H_{38}Cl_2NOsP$ (584.6): C, 41.09; H, 6.55; N, 2.40. Found: C, 41.51; H, 6.83; N, 2.18.

Preparation of [(mes)OsHCl(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$)] (4) and [(mes)OsH$_2$(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$)] (6). A solution of **2** (92 mg, 0.16 mmol) in 7 mL of THF was added to a mixture of magnesium amalgam (30 mg of Mg, 1.23 mmol; 2.0 g of Hg, 9.97 mmol) in 5 mL of THF and 0.2 mL of ethanol. The reaction mixture was rigorously stirred for 2 h at room temperature. After the solution and the solid material became separated, the solution was decanted and the solid was washed twice with 10 mL portions of THF. The combined liquid phases were brought to dryness in vacuo, and the residue was extracted with 30 mL of benzene. The solvent was removed from the extract, and the residue was recrystallized from CH_2Cl_2/hexane to give a yellow solid. The ^{1}H and ^{31}P NMR spectra confirmed that the solid consists of a 2:1 mixture of compounds **4** and **6**, which could not be separated either by column chromatography or by fractional crystallization. **4**: ^{1}H NMR (400 MHz, C_6D_6) δ 4.64 (s, 3H, $C_6H_3Me_3$), 2.83, 2.55 (both m, 2H, CH_2NMe_2), 2.38 (m, 1H, $PCHCH_3$), 2.26 (m, 1H, PCH_2), 2.17 (s, 6H, NMe_2), 2.09 (s, 9H, $C_6H_3Me_3$), 1.95 (m, 1H, $PCHCH_3$), 1.86 (m, 1H, PCH_2), 1.19 [dd, *J*(PH) = 14.1, *J*(HH) = 7.2 Hz, 3H, $PCHCH_3$], 1.06 [dd, *J*(PH) = 12.7, *J*(HH) = 7.4 Hz, 3H, $PCHCH_3$], 1.04 [dd, *J*(PH) = 14.9, *J*(HH) = 7.4 Hz, 3H, $PCHCH_3$], 1.01 [dd, *J*(PH) = 12.7, *J*(HH) = 7.1 Hz, 3H, $PCHCH_3$], −9.08 [d, *J*(PH) = 44.2 Hz, 1H, OsH]; ^{31}P NMR (162.0 MHz, C_6D_6) δ 13.1 [s; d in off-resonance, $J(^{187}Os^{31}P)$ = 266.2 Hz]. **6**: ^{1}H NMR (400 MHz, C_6D_6) δ 4.83 (s, 3H, $C_6H_3Me_3$), 2.63 (m, 2H, CH_2NMe_2), 2.34 (s, 6H, NMe_2), 2.14 (s, 9H, $C_6H_3Me_3$), 1.83 (m, 2H, PCH_2), 1.64 (m, 2H, $PCHCH_3$), 1.00, 0.99 (both m, 12H, $PCHCH_3$), −12.15 [d, *J*(PH) = 37.9 Hz, 2H, OsH_2]; ^{31}P NMR (162.0 MHz, C_6D_6) δ 30.3 [s; t in off-resonance, $J(^{187}Os^{31}P)$ = 267.9 Hz].

Preparation of [(mes)OsHCl(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$CH$_2$NMe$_2$)] (5) and [(mes)OsH$_2${κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$CH$_2$NMe$_2$)] (7). This was carried out as described for **4**/**6**, from **3** (103 mg, 0.18 mmol) and magnesium amalgam (30 mg of Mg, 1.23 mmol; 2.0 g of Hg, 9.97 mmol) in THF/ethanol. A yellow solid was obtained, the NMR spectra of which revealed that it is a 10:1 mixture of compounds **5** and **7**. After column chromatography (basic Al_2O_3, activity grade III, height of column 5 cm) a product was isolated which still contained small amounts of **7**. **5**: ^{1}H NMR (400 MHz, C_6D_6) δ 4.64 (s, 3H, $C_6H_3Me_3$), 2.37, 2.29, 2.25, 2.23, 1.95 (all m, 6H, PCH_2, CH_2NMe_2 and $PCHCH_3$), 2.12 (s, 6H, NMe_2), 2.09 (s, 9H, $C_6H_3Me_3$), 1.76, 1.64 (both m, 2H, PCH_2CH_2), 1.20 [dd, *J*(PH) = 14.0, *J*(HH) = 7.1 Hz, 3H, $PCHCH_3$], 1.06 [dd, *J*(PH) = 12.7, *J*(HH) = 7.1 Hz, 3H, $PCHCH_3$], 1.01, 0.99 (both m, 6H, $PCHCH_3$), −9.01 [d, *J*(PH) = 43.2 Hz, 1H, OsH]; ^{31}P NMR (C_6D_6, 162.0 MHz) δ 14.7 [s; d in off-resonance, $J(^{187}Os^{31}P)$ = 266.2 Hz]. Typical data for **7**: ^{1}H NMR (400 MHz, C_6D_6) δ 4.84 (s, 3H, $C_6H_3Me_3$), 2.34 (s, 6H, NMe_2), 2.11 (s, 9H, $C_6H_3Me_3$), −12.11 [d, *J*(PH) = 38.2 Hz, 2H, OsH_2]; ^{31}P NMR (162.0 MHz, C_6D_6) δ 31.9 [s; t in off-resonance].

Preparation of [(mes)OsHCl(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$OMe)] (9). This compound was prepared as described for the mixture of **4**/**6**, from **8** (141 mg, 0.25 mmol) and magnesium amalgam (30 mg of Mg, 1.23 mmol; 2.0 g of Hg, 9.97 mmol) in THF/ethanol: yellow solid; yield 117 mg (88%); mp 132 °C dec; MS (70 eV) *m*/*z* 524 (M^+). IR (KBr): ν(OsH) 2040, ν(C−O) 1103 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 4.62 (s, 3H, $C_6H_3Me_3$), 3.90, 3.72 (both m, 2H, CH_2OMe), 3.18 (s, 3H, OCH_3), 2.49 (m, 1H, PCH_2), 2.26 (m, 1H, $PCHCH_3$), 2.07 (s, 9H, $C_6H_3Me_3$), 1.98 (m, 1H, PCH_2), 1.91 (m, 1H, $PCHCH_3$), 1.17 [dd, *J*(PH) = 14.3, *J*(HH) = 7.0 Hz, 3H, $PCHCH_3$], 1.02 [dd, *J*(PH) = 13.2, *J*(HH) = 7.0 Hz, 3H, $PCHCH_3$], 0.96 [dd, *J*(PH) = 14.4, *J*(HH) = 7.0 Hz, 3H, $PCHCH_3$], 0.95 [dd, *J*(PH) = 13.1, *J*(HH) = 7.0 Hz, 3H, $PCHCH_3$], −9.18 [d, *J*(PH) = 44.4 Hz, 1H, OsH]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 12.7 [s; d in off-resonance, $J(^{187}Os^{31}P)$ = 267.0 Hz]. Anal. Calcd for $C_{18}H_{34}ClOOsP$ (523.1): C, 41.33; H, 6.55. Found: C, 41.74; H, 6.71.

Preparation of [(mes)OsH$_2$(κ^1(*P*)-*i*Pr$_2$PCH$_2$CH$_2$OMe)] (10). A solution of **9** (110 mg, 0.21 mmol) in 7 mL of THF was added to a mixture of magnesium amalgam (100 mg of Mg, 4.11 mmol; 2.0 g of Hg, 9.97 mmol) in 5 mL of THF and 0.5 mL of ethanol. After the reaction mixture was rigorously stirred for 2 h at room temperature, it was worked up as

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described for **4**/**6**. The crude product (yellow solid) was dissolved in 3 mL of benzene, and the solution was chromatographed on Al_2O_3 (basic, activity grade III, column length 5 cm). With benzene, a yellow fraction was eluted which contained unreacted **9** (32 mg; 29%). A second fraction was eluted with CH_2Cl_2, from which the white solid **10** was isolated: yield 60 mg (58%); mp 74 °C; MS (70 eV) *m*/*z* 488 (M^+). IR (KBr): ν(OsH) 2042 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 4.82 (s, 3H, $C_6H_3Me_3$), 3.77 (m, 2H, CH_2OMe), 3.16 (s, 3H, OCH_3), 2.32 (s, 9H, $C_6H_3Me_3$), 2.03 (m, 2H, PCH_2), 1.61 (m, 2H, $PCHCH_3$), 0.98 [dd, J(PH) = 14.8, J(HH) = 7.0 Hz, 6H, $PCHCH_3$], 0.95 [dd, J(PH) = 13.6, J(HH) = 7.0 Hz, 6H, $PCHCH_3$], −12.20 [d, J(PH) = 36.0 Hz, 2H, OsH_2]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 27.5 [s; t in off-resonance]. Anal. Calcd for $C_{18}H_{35}OOsP$ (488.7): C, 44.24; H, 7.22. Found: C, 44.28; H, 8.07.

Reaction of Compound 8 with $NaBH_4$. A suspension of **8** (200 mg, 0.36 mmol) in 10 mL of benzene was treated first with an excess of $NaBH_4$ (ca. 200 mg) and then dropwise with 1 mL of methanol. After the reaction mixture was stirred for 1 h at room temperature, the solvent was removed and the residue was extracted with 20 mL of benzene. The extract was worked up as described for **10**. The chromatographic separation afforded both **9** (84 mg) and **10** (82 mg) in, respectively, 45% and 47% yield.

Preparation of [(mes)OsCl(κ^2(*P,N*)-*i*$Pr_2PCH_2CH_2NMe_2$)]PF_6 (11). A solution of **2** (178 mg, 0.31 mmol) in 15 mL of CH_2Cl_2 was treated with a solution of $AgPF_6$ (79 mg, 0.31 mmol) in 10 mL of CH_2Cl_2 and stirred for 45 min at room temperature. The reaction mixture was filtered with Celite, and the filtrate was brought to dryness in vacuo. The residue was repeatedly washed with ether and then dissolved in 2 mL of CH_2Cl_2, and the solution was layered with 10 mL of hexane. Orange crystals slowly precipitated which (after 5 days) were filtered, washed twice with ether, and dried: yield 158 mg (52%); mp 157 °C dec; Λ = 75 cm^2 Ω^{-1} mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.97 (s, 3H, $C_6H_3Me_3$), 3.09 (m, 2H, CH_2NMe_2), 3.05 (s, 6H, NMe_2), 2.73, 2.57 (both m, 2H, $PCHCH_3$), 2.38 (s, 9H, $C_6H_3Me_3$), 1.97, 1.87 (both m, 2H, PCH_2), 1.44 [dd, J(PH) = 15.0, J(HH) = 7.2 Hz, 3H, $PCHCH_3$], 1.35, 1.33, 1.31 (all m, 9H, $PCHCH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 93.2 [d, J(PC) = 2.1 Hz, *C*Me of mes], 78.6 [d, J(PC) = 1.9 Hz, CH of mes], 65.2 [d, J(PC) = 2.3 Hz, CH_2NMe_2], 59.6, 57.3 (both s, NMe_2), 26.4 [d, J(PC) = 29.5 Hz, $PCHCH_3$], 24.1 [d, J(PC) = 30.5 Hz, $PCHCH_3$], 22.1 [d, J(PC) = 27.1 Hz, PCH_2], 19.5, 19.0, 18.5, 18.3 (all s, $PCHCH_3$), 18.4 (s, CH_3 of mes). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 27.3 (s, P*i*Pr_2), −144.2 [sept, J(PF) = 712.7 Hz, PF_6^-]. Anal. Calcd for $C_{19}H_{36}ClF_6NOsP_2$ (680.1): C, 33.56; H, 5.34; N, 2.06; Os, 27.97. Found: C, 33.43; H, 5.32; N, 2.00; Os, 27.80.

Preparation of[(mes)OsCl(κ^2(*P,O*)-*i*$Pr_2PCH_2CH_2OMe$)]PF_6 (12). This compound was prepared as described for **11**, from **8** (524 mg, 0.94 mmol) and $AgPF_6$ (237 mg, 0.94 mmol) as starting materials: pale yellow solid; yield 596 mg (95%); mp 134 °C dec; Λ = 68 cm^2 Ω^{-1} mol^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.75 (s, 3H, $C_6H_3Me_3$), 4.01 (s, 3H, OCH_3), 3.57, 3.28 (both m, 2H, CH_2OMe), 2.81, 2.64 (both m, 2H, PCH_2), 2.28 (s, 9H, $C_6H_3Me_3$), 1.74, 1.70 (both m, 2H, $PCHCH_3$), 1.33, 1.25 (both m, 12H, $PCHCH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 92.9 [d, J(PC) = 2.0 Hz, *C*Me of mes], 78.0 [d, J(PC) = 2.0 Hz, CH of mes], 77.1 [d, J(PC) = 3.0 Hz, CH_2OMe], 71.5 (s, OCH_3), 26.7 [d, J(PC) = 30.5 Hz, $PCHCH_3$], 24.4 [d, J(PC) = 31.5 Hz, $PCHCH_3$], 22.4 [d, J(PC) = 27.5 Hz, PCH_2], 19.3, 18.8, 18.5, 18.3 (all s, $PCHCH_3$), 18.7 (s, CH_3 of mes). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 34.5 [s, $J(^{187}Os^{31}P)$ = 287.7 Hz, P*i*Pr_2], −144.2 [sept, J(PF) = 712.8 Hz, PF_6^-]. Anal. Calcd for $C_{18}H_{33}ClF_6OOsP_2$ (667.0): C, 32.41; H, 4.99. Found: C, 32.32; H, 4.77.

Preparation of [(mes)OsH(κ^2(*P,O*)-*i*$Pr_2PCH_2CH_2OMe$)]PF_6 (13). This compound was prepared as described for **11**, from **9** (65 mg, 0.12 mmol) and $AgPF_6$ (30 mg, 0.12 mmol) as starting materials: pale yellow solid; yield 70 mg (92%); mp 144 °C dec; Λ = 69 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(OsH) 2061, ν(C−O) 1037 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.26 (s, 3H, $C_6H_3Me_3$), 3.85 (s, 3H, OCH_3), 3.67, 3.26 (both m, 2H, CH_2OMe), 2.40 (s, 9H, $C_6H_3Me_3$), 2.28 (m, 2H, PCH_2 and $PCHCH_3$), 1.66 (m, 1H, $PCHCH_3$), 1.43 (m, 1H, PCH_2), 1.34 [dd, J(PH) = 15.5, J(HH) = 6.4 Hz, 3H, $PCHCH_3$], 1.29 [dd, J(PH) = 11.4, J(HH) = 7.6 Hz, 3H, $PCHCH_3$], 1.00 [dd, J(PH) = 15.3, J(HH) = 7.6 Hz, 3H, $PCHCH_3$], 0.90 [dd, J(PH) = 17.8, J(HH) = 7.6 Hz, 3H, $PCHCH_3$], −8.29 [d, J(PH) = 36.9 Hz, 1H, OsH]. ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 55.4 [s; d in off-resonance, $J(^{187}Os^{31}P)$ = 274.7 Hz, P*i*Pr_2], −144.4 [sept, J(PF) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{18}H_{34}F_6OOsP_2$: C, 34.18; H, 5.42. Found: C, 33.93; H, 5.34.

Reaction of [(mes)OsCl(κ^2(*P,O*)-*i*$Pr_2PCH_2CH_2OMe$)]PF_6 (12) with CO. A stream of CO was passed through a solution of **12** (73 mg, 0.11 mmol) in 2 mL of CH_2Cl_2 for 1 min at room temperature. This was repeated four times in 1 h. The solvent was removed, and the remaining yellow solid was washed repeatedly with 5 mL portions of ether and dried. The ^1H and ^{31}P NMR spectra revealed that besides [(mes)OsCl(CO)(κ^1(*P*)-*i*$Pr_2PCH_2CH_2OMe$)]PF_6 (**14**) small amounts of **12** were still present, which could not removed by fractional crystallization or other separation techniques. Data for **14**: IR (CH_2Cl_2) ν(CO) 1990; ^1H NMR (200 MHz, CD_2Cl_2) δ 6.02 (s, 3H, $C_6H_3Me_3$), 3.65 (m, 2H, CH_2OMe), 3.37 (s, 3H, OCH_3), 2.61 (s, 9H, $C_6H_3Me_3$), 2.49 (m, 4H, PCH_2 and $PCHCH_3$), 1.53 (m, 3H, $PCHCH_3$), 1.38 (m, 6H, $PCHCH_3$), 1.27 (m, 3H, $PCHCH_3$); ^{13}C NMR (50.3 MHz, CD_2Cl_2) δ 189.2 [d, J(PC) = 22.0 Hz, CO], 105.9 [d, J(PC) = 1.2 Hz, *C*Me of mes], 82.2 (s, CH of mes), 67.8 (s, CH_2OMe), 59.0 (s, OCH_3), 26.2 [d, J(PC) = 29.8 Hz, $PCHCH_3$], 25.8 [d, J(PC) = 31.5 Hz, $PCHCH_3$], 22.0 [d, J(PC) = 31.0 Hz, PCH_2], 19.4, 19.0, 18.8 (all s, $PCHCH_3$), 18.6 (s, CH_3 of mes), 18.4 [d, J(PC) = 2.2 Hz, $PCHCH_3$]; ^{31}P NMR (81.0 MHz, CD_2Cl_2) δ 10.9 (s, P*i*Pr_2), −143.9 [sept, J(PF) = 710.7 Hz, PF_6^-].

Preparation of [(mes)OsCl(CNMe)(κ^1(*P*)-*i*$Pr_2PCH_2CH_2OMe$)]PF_6 (15). A solution of **12** (180 mg, 0.27 mmol) in 10 mL of CH_2Cl_2 was treated with methyl isocyanide (15 mg, 0.37 mmol) and stirred for 30 min at room temperature. After removal of the solvent in vacuo, a pale yellow solid was isolated, which was washed repeatedly with 5 mL portions of ether and dried: yield 184 mg (96%); mp 144 °C dec; Λ = 74 cm^2 Ω^{-1} mol^{-1}. IR (CH_2Cl_2): ν(C≡N) 2183, ν(C−O) 1101 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 5.62 (s, 3H, $C_6H_3Me_3$), 3.85 [d, J(PH) = 1.2 Hz, 3H, $CNCH_3$], 3.60 (m, 2H, CH_2OMe), 3.32 (s, 3H, OCH_3), 2.49 (m, 2H, PCH_2), 2.42 (s, 9H, $C_6H_3Me_3$), 2.31 (m, 2H, $PCHCH_3$), 1.26 (m, 3H, $PCHCH_3$), 1.24 (m, 6H, $PCHCH_3$), 1.19 (m, 3H, $PCHCH_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 171.2 (s, *C*NMe), 107.0 [d, J(PC) = 1.5 Hz, *C*Me of mes], 84.6 (s, CH of mes), 68.4 (s, CH_2OMe), 58.7 (s, OCH_3), 31.0 (s, $CNCH_3$), 27.4 [d, J(PC) = 30.2 Hz, $PCHCH_3$], 26.6 [d, J(PC) = 32.0 Hz, $PCHCH_3$], 22.5 [d, J(PC) = 31.4 Hz, PCH_2], 19.5, 19.0 (both s, $PCHCH_3$), 19.1 (s, CH_3 of mes), 18.6 [d, J(PC) = 2.4 Hz, $PCHCH_3$]. ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 3.4 (s, P*i*Pr_2), −144.3 [sept, J(PF) = 710.6 Hz, PF_6^-]. Anal. Calcd for $C_{20}H_{36}ClF_6NOOsP_2$ (708.1): C, 33.92; H, 5.12; N, 1.98; Os, 26.86. Found: C, 33.93; H, 5.16; N, 1.92; Os, 26.65.

Preparation of [(mes)OsH(OMe)(*i*$Pr_2PCH{=}CH_2$)] (16). A solution of **13** (70 mg, 0.11 mmol) in 15 mL of THF was treated with KO*t*Bu (120 mg, 1.07 mmol) and stirred for 2 h at room temperature. The solvent was removed, and the remaining oily residue was extracted with 20 mL of hexane/benzene (2:1). The extract was brought to dryness in vacuo, and the remaining pale yellow oil was washed twice with 2 mL portions of hexane (0 °C): yield 39 mg (72%). IR (hexane): ν(OsH) 2048, ν(C=C) 1567 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 6.32 [m; in $^1H\{^{31}P\}$ dd, $J(H^1H^3)$ = 18.9, $J(H^1H^2)$ = 12.8 Hz, 1H, $PCH^1{=}CH_2$], 5.59 [m; dd in $^1H\{^{31}P\}$, $J(H^1H^2)$ = 12.8, $J(H^2H^3)$ = 2.0 Hz, 1H, H^2], 5.44 [m; dd in $^1H\{^{31}P\}$, $J(H^1H^3)$ = 18.9, $J(H^2H^3)$ = 2.0 Hz, 1H, H^3], 4.69 (s, 3H, $C_6H_3Me_3$), 4.05 (s, 3H, OCH_3), 2.36, 1.94 (both m, 2H, $PCHCH_3$), 2.08 (s, 9H,

$C_6H_3Me_3$), 1.22, 1.09 [both dd, J(PH) = 14.9, J(HH) = 7.0 Hz, 6H, PCHCH_3], 1.00, 0.91 [both dd, J(PH) = 13.5, J(HH) = 6.8 Hz, 6H, PCHCH_3], −8.55 [d, J(PH) = 43.2 Hz, 1H, OsH]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 133.0 [d, J(PC) = 37.6 Hz, PCH=CH_2], 127.0 [d, J(PC) = 2.0 Hz, PCH=CH_2], 93.6 [d, J(PC) = 3.0 Hz, CMe of mes], 74.1 [d, J(PC) = 3.1 Hz, CH of mes], 71.6 [d, J(PC) = 3.1 Hz, OCH_3], 24.7 [d, J(PC) = 32.6 Hz, PCHCH$_3$], 21.4 [d, J(PC) = 30.5 Hz, PCHCH$_3$], 20.1 (s, CH_3 of mes), 18.6, 18.4 [both d, J(PC) = 2.3 Hz, PCHCH$_3$], 18.2, 18.1 (both s, PCHCH$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 18.3 [s, d in off-resonance, J(^{187}Os^{31}P) = 286.5 Hz]. Anal. Calcd for $C_{18}H_{33}OOsP$ (486.6): C, 44.43; H, 6.83. Found: C, 44.65; H, 7.10.

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PCH$_2$C(OMe)*O*}]PF$_6$ (19a). This compound was prepared as described for **11**, from **17** (270 mg, 0.47 mmol) and $AgPF_6$ (119 mg, 0.47 mmol) as starting materials: pale yellow solid; yield 272 mg (85%); mp 162 °C dec; Λ = 82 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=O) 1595 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62 (s, 3H, $C_6H_3Me_3$), 4.03 (s, 3H, OCH_3), 3.14 [d, J(PH) = 9.2 Hz, 2H, PCH_2], 2.76, 2.65 (both m, 2H, PCHCH$_3$), 2.34 (s, 9H, $C_6H_3Me_3$), 1.33, 1.31 (both m, 6H, PCHCH_3), 1.24 [dd, J(PH) = 14.0, J(HH) = 7.2 Hz, 3H, PCHCH_3], 1.15 [dd, J(PH) = 17.2, J(HH) = 7.2 Hz, 3H, PCHCH_3]. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 191.1 [d, J(PC) = 8.3 Hz, CO_2], 98.5 (s, CMe of mes), 72.7 [d, J(PC) = 3.7 Hz, CH of mes], 57.7 (s, OCH_3), 29.5 [d, J(PC) = 32.3 Hz, PCH_2], 25.3 [d, J(PC) = 26.8 Hz, PCHCH$_3$], 24.3 [d, J(PC) = 30.5 Hz, PCHCH$_3$], 19.2 (s, CH_3 of mes), 18.8, 18.2, 16.9, 16.8 (all s, PCHCH$_3$).^{31}P NMR (162.0 MHz, $CDCl_3$): δ 33.9 [s, J(^{187}Os^{31}P) = 265.9 Hz, PiPr$_2$], −144.2 [sept, J(PF) = 712.8 Hz, PF_6^-]. Anal. Calcd for $C_{18}H_{31}ClF_6O_2OsP_2$ (681.0): C, 31.75; H, 4.59. Found: C, 31.60; H, 4.26.

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PCH$_2$C(OMe)*O*}]BF$_4$ (19b). A solution of **18** (85 mg, 0.16 mmol) in 10 mL of ether was treated dropwise with a 0.1 M solution of HBF_4 in ether (1.6 mL, 0.16 mmol) at room temperature. A yellow solid slowly precipitated. After the reaction mixture was stirred for 5 min, the solution was decanted, and the residue was washed twice with 10 mL portions of ether and dried: pale yellow microcrystalline solid; yield 95 mg (96%); mp 182 °C dec; Λ = 78 cm^2 Ω^{-1} mol^{-1}. The IR and NMR data of **19b**−**d** are almost identical with those of **19a**. However, in the ^{1}H NMR spectrum of **19b** (and similarly in the spectra of **19c** and **19d**) the signals for the PCH_2 protons appear as AB parts of an ABX spectrum with δ(H_A) 3.23, δ(H_B) 3.18, J(PH_A) = 9.5, J(PH_B) = 8.7, and ^2J(H_AH_B) = 17.5 Hz. Anal. Calcd for $C_{18}H_{31}BClF_4O_2OsP$ (622.9): C, 34.71; H, 5.02. Found: C, 34.18; H, 4.87.

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PCH$_2$C(OMe)*O*}]CF$_3$CO$_2$ (19c). A solution of **18** (73 mg, 0.14 mmol) in 10 mL of methanol was treated with CF_3CO_2H (23 mg, 0.20 mmol) and stirred for 20 min at room temperature. The solvent was removed, and the residue was washed three times with 5 mL portions of ether and dried: pale yellow solid; yield 84 mg (95%); mp 166 °C dec; Λ = 79 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{20}H_{31}ClF_3O_4OsP$ (649.1): C, 37.01; H, 4.81. Found: C, 36.87; H, 4.78.

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PCH$_2$C(OMe)*O*}]CF$_3$SO$_3$ (19d). A solution of **18** (154 mg, 0.29 mmol) in 10 mL of benzene was treated with CF_3SO_3H (100 μL, 0.88 mmol) and stirred for 1 h at room temperature. After the solvent was removed, a pale yellow oil was obtained, which was washed twice with 5 mL portions of hexane and dried in vacuo: yield 177 mg (94%); Λ = 72 cm^2 Ω^{-1} mol^{-1}. Anal. Calcd for $C_{19}H_{31}ClF_3O_5OsPS$ (685.2): C, 33.31; H, 4.56; S, 4.68. Found: C, 33.24; H, 4.70; S, 4.72.

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PCH=C(OMe)*O*}] (20). A suspension of **16a** (115 mg, 0.17 mmol) in 5 mL of THF was treated with a suspension of KO*t*Bu (19 mg, 0.17 mmol) in 5 mL of THF and stirred for 30 min at room temperature. The solvent was removed, and the residue was extracted with 30 mL of hexane/CH_2Cl_2 (2:1). After the extract was brought to dryness in vacuo, a pale yellow microcrystalline solid was obtained: yield 73 mg (80%); mp 90 °C dec; MS (70 eV) m/z 536 (M^+). IR (CH_2Cl_2): ν(C=O + C=C) 1536 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 4.69 (s, 3H, $C_6H_3Me_3$), 3.57 (s, 3H, OMe), 3.48 [d, J(PH) = 1.4 Hz, 1H, PCHCO$_2$], 2.51, 2.02 (both m, 2H, PCHCH$_3$), 1.91 (s, 9H, $C_6H_3Me_3$), 1.32, 1.24, 1.11, 0.92 (all m, 12H, PCHCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 184.4 [d, J(PC) = 27.0 Hz, CO_2], 93.3 [d, J(PC) = 2.3 Hz, CMe of mes], 72.6 [d, J(PC) = 3.5 Hz, CH of mes], 53.7 [d, J(PC) = 1.7 Hz, OCH_3], 45.6 [d, J(PC) = 73.9 Hz, PCHCO$_2$], 26.1 [d, J(PC) = 30.5 Hz, PCHCH$_3$], 25.6 [d, J(PC) = 27.0 Hz, PCHCH$_3$], 20.2 [d, J(PC) = 2.3 Hz, PCHCH$_3$], 19.9 [d, J(PC) = 3.5 Hz, PCHCH$_3$], 19.4 [d, J(PC) = 2.3 Hz, PCHCH$_3$], 19.1 [d, J(PC) = 1.2 Hz, PCHCH$_3$], 18.8 (s, CH_3 of mes). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 20.8 (s). Anal. Calcd for $C_{18}H_{30}ClO_2OsP$ (535.1): C, 40.41; H, 5.64. Found: C, 40.64; H, 5.64.

Reaction of Compound 20 with PhNCO. A solution of **20** (82 mg, 0.15 mmol) in 10 mL of benzene was treated with PhNCO (24 mg, 0.20 mmol) and stirred for 2 h at room temperature. A gradual change of color from yellow to brownish occurred. The solvent was removed, and the residue was washed repeatedly with 5 mL portions of hexane. The ^{1}H and ^{31}P NMR spectra of the yellow solid revealed that the crude product consisted mainly (ca. 85%) of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PC(CONHPh)=C(OMe)*O*}] (**21**) and at least one other byproduct which could not be separated by column chromatography or fractional crystallization. Data for **21**: IR (KBr) ν(NH) 3405, ν(C=O) 1625, ν(C=O + C=C) 1590 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 9.13 (s, 1H, NH), 8.06−6.79 (m, 5H, C_6H_5), 4.64 (s, 3H, $C_6H_3Me_3$), 3.54 (s, 3H, OMe), 2.35, 2.20 (both m, 2H, PCHCH$_3$), 1.82 (s, 9H, $C_6H_3Me_3$), 1.22 [dd, J(PH) = 14.1, J(HH) = 7.0 Hz, 3H, PCHCH_3], 0.90 (m, 6H, PCHCH_3), 0.85 (m, 3H, PCHCH_3); ^{31}P NMR (162.0 MHz, C_6D_6) δ 28.8 (s).

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*Pr$_2$PC(CO$_2$Me)=C(CHPh$_2$)*O*}] (22). A solution of **20** (154 mg, 0.29 mmol) in 10 mL of hexane/CH_2Cl_2 (3:1) was treated with diphenylketene (112 mg, 0.58 mmol) and stirred for 1 h at room temperature. The solvent was removed, and the residue was washed twice with 5 mL portions of hexane and then dissolved in 1 mL of benzene. The solution was chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm). With benzene, a yellow fraction was eluted which was brought to dryness in vacuo. The residue was recrystallized from toluene/hexane (1:5) to give a pale yellow crystalline solid: yield 132 mg (63%); mp 107 °C dec; MS (70 eV) m/z 730 (M^+). IR (KBr): ν(C=O) 1671, ν(C=O +C=C) 1597 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.66, 7.51, 7.22, 7.12, 7.04 (all m, 10H, C_6H_5), 4.52 (s, 3H, $C_6H_3Me_3$), 3.57 (m, 1H, PCHCH$_3$), 3.45 (s, 3H, OCH_3), 2.25 (m, 1H, PCHCH$_3$), 2.10 (s, 1H, CHPh$_2$), 1.70 (s, 9H, $C_6H_3Me_3$), 1.62 [dd, J(PH) = 12.8, J(HH) = 7.1 Hz, 3H, PCHCH_3], 1.56 [dd, J(PH) = 15.3, J(HH) = 7.0 Hz, 3H, PCHCH_3], 1.12 [dd, J(PH) = 19.8, J(HH) = 7.2 Hz, 3H, PCHCH_3], 0.86 [dd, J(PH) = 16.4, J(HH) = 7.0 Hz, 3H, PCHCH_3]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 194.6 (s, CO_2), 182.3 [d, J(PC) = 28.5 Hz, CO], 143.2, 142.8, 130.2, 130.0, 129.3, 128.5, 126.2, 126.0 (all s, C_6H_5), 93.2 [d, J(PC) = 2.4 Hz, CMe of mes], 82.6 [d, J(PC) = 62.1 Hz, PC=C], 74.3 [d, J(PC) = 2.9 Hz, CH of mes], 59.8 [d, J(PC) = 4.4 Hz, CHPh$_2$], 52.8 (s, OCH_3), 30.1 [d, J(PC) = 32.3 Hz, PCHCH$_3$], 24.2 [d, J(PC) = 38.3 Hz, PCHCH$_3$], 20.9 [d, J(PC) = 2.0 Hz, PCHCH$_3$], 20.4 [d, J(PC) = 7.0 Hz, PCHCH$_3$], 19.8 [d, J(PC) = 5.0 Hz, PCHCH$_3$], 18.7 (s, PCHCH$_3$), 18.2 (s, CH_3 of mes). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 29.5 (s). Anal. Calcd for $C_{32}H_{40}ClO_3OsP$: C, 52.70; H, 5.53. Found: C, 52.17; H, 5.50

Preparation of [(mes)Os{κ^2(*P,O*)-*i*Pr$_2$PC(CO$_2$Me)=C(CHPh$_2$)*O*}{C$_2$(CO$_2$Me)$_2$}]PF$_6$ (23). A solution of **22** (137 mg, 0.19 mmol) in 10 mL of CH_2Cl_2 was treated with $C_2(CO_2Me)_2$ (57 mg, 0.40 mmol) and then dropwise with a solution of $AgPF_6$ (48 mg, 0.19 mmol) in 15 mL of CH_2Cl_2. After the reaction mixture was stirred for 15 min at room temperature, the solution was filtered and the filtrate was brought to dryness in vacuo. The oily residue was treated with 10 mL of ether, and when the mixture was stirred for 12 h, a solid was

Table 5. Crystallographic Data for 9, 11, 22, and 23

	$C_{18}H_{34}ClOOsP$ (**9**)	$C_{19}H_{36}ClF_6NOsP_2$ (**11**)	$C_{32}H_{40}ClO_3OsP$ (**22**)	$C_{38}H_{46}F_6O_7OsP_2$ (**23**)
fw	523.07	680.08	729.26	980.89
cryst size, mm^3	0.1 × 0.25 × 0.5	0.40 × 0.40 × 0.20	0.05 × 0.13 × 0.15	0.08 × 0.20 × 0.35
cryst syst	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
cell dimens determn	23 rflns, 10° < θ < 14°	8192 rflns, 2° < θ < 25°	23 rflns, 10° < θ < 14°	24 rflns, 5° < θ < 18°
a, Å	8.060(4)	16.144(2)	11.455(4)	10.550(3)
b, Å	8.481(4)	16.481(1)	12.731(4)	13.840(3)
c, Å	15.46(1)	18.289(3)	23.013(2)	28.130(3)
α, deg	79.67(4)			
β, deg	89.56(4)		92.04(2)	99.820(5)
γ, deg	78.05(4)			
V, $Å^3$	1017(1)	4866(1)	3354(2)	4047(2)
Z	2	8	4	4
d_{calcd}, g cm^{-3}	1.709	1.857	1.444	1.610
temp, K	293(2)	193(2)	293(2)	293(2)
μ, mm^{-1}	6.494	5.535	3.964	3.309
scan method	ω/θ	φ/ω	ω/θ	ω/θ
2θ(max), deg	48	50.12	48	48
tot. no. of rflns	3446	37 863	5535	5562
no. of unique rflns	3186 (R(int) = 0.0106)	42854 (R(int) = 0.0452)	5240 (R(int) = 0.0202)	5178 (R(int) = 0.0213)
no. of obsd rflns ($I > 2\sigma(I)$)	3085	3800	4027	3846
no. of rflns used for refinement	3186	4284	5239	5177
no. of params refined	210	314	351	487
final R indices ($I > 2\sigma(I)$)	R1 = 0.0219, wR2 = 0.0590[a]	R1 = 0.0262, wR2 = 0.0633[a]	R1 = 0.0439, wR2 = 0.1294[a]	R1 = 0.0331, wR2 = 0.0687[a]
R indices (all data)	R1 = 0.0232, wR2 = 0.0599[a]	R1 = 0.0320, wR2 = 0.0661	R1 = 0.0753, wR2 = 0.1439[a]	R1 = 0.0668, wR2 = 0.0812[a]
resid electron density, e $Å^{-3}$	1.055/−0.889	2.561/−0.760	2.556/−0.479	0.655/−0.430

[a] $w^{-1} = [\sigma^2F_o^2 + (0.040P)^2 + 1.2636P]$ (**9**), $w^{-1} = [\sigma^2F_o^2 + (0.0325^2 + 11.6154P]$ (**11**), $w^{-1} = [\sigma^2F_o^2 + (0.0346P)^2 + 13.7168P]$ (**22**), and $w^{-1} = [\sigma^2F_o^2 + (0.0271P)^2 + 10.3744P]$ (**23**), where $P = (F_o^2 + 2F_c^2)/3$.

obtained. The orange solid was separated from the mother liquor, washed with small amounts of ether, and dried: yield 164 mg (89%); mp 142 °C dec; Λ = 68 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C≡C) 1863, ν(C═O) 1725, 1715, 1700, ν(C═O +C═C), 1505 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31, 7.22, 7.13 (all m, 10H, C_6H_5), 6.40 (s, 3H, $C_6H_3Me_3$), 3.92, 3.68 (both s, 6H, OCH_3), 3.32 (m, 1H, PC*H*CH_3), 3.14 (s, 3H, OMe), 2.50 (m, 1H, PC*H*CH_3), 2.11 (s, 1H, C*H*Ph_2), 1.97 (s, 9H, C_6H_3*Me*$_3$), 1.41 [dd, J(PH) = 14.6, J(HH) = 6.8 Hz, 3H, PCHC*H*$_3$], 1.05 [dd, J(PH) = 18.8, J(HH) = 7.3 Hz, 3H, PCHC*H*$_3$], 0.92 [dd, J(PH) = 16.4, J(HH) = 7.2 Hz, 3H, PCHC*H*$_3$], 0.85 [dd, J(PH) = 17.8, J(HH) = 6.8 Hz, 3H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 201.0 [d, J(PC) = 11.1 Hz, CO], 167.9 [d, J(PC) = 4.0 Hz, PC*C*O_2], 160.6, 159.7 (both s, C*C*O_2), 143.4, 141.3, 131.1, 131.0, 129.9, 128.4, 128.1 (all s, C_6H_5), 116.7 (s, *C*Me of mes), 101.6 (s, CH of mes), 95.9, 95.4 (both s, C═C), 67.0 [d, J(PC) = 59.4 Hz, P*C*═C], 56.6 [d, J(PC) = 6.1 Hz, *C*HPh_2], 55.2, 54.0, 51.9 (all s, OCH_3), 36.1 [d, J(PC) = 33.2 Hz, PCHCH_3], 25.2 [d, J(PC) = 34.2 Hz, P*C*HCH_3], 19.8 (s, PCH*C*H_3), 19.0 [d, J(PC) = 5.1 Hz, PCH*C*H_3], 18.5 (s, CH_3 of mes), 18.3 [d, J(PC) = 2.0 Hz, PCH*C*H_3], 17.5 [d, J(PC) = 3.1 Hz, PCH*C*H_3]. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 55.7 (s, P*i*Pr_2), −144.3 [sept, J(PF) = 712.1 Hz, PF_6^-]. Anal. Calcd for $C_{38}H_{46}F_6O_7OsP_2$ (980.9): C, 46.53; H, 4.73. Found: C, 46.27; H, 4.62.

Reaction of Compound 20 with HCl. A slow stream of dry HCl was passed for 20 s through a solution of **20** (65 mg, 0.12 mmol) in 10 mL of benzene at room temperature. After the reaction mixture was stirred for 10 min, the solvent was removed and the orange residue dried in vacuo. It was identified by comparison of the ^{1}H and ^{31}P NMR spectra with those of an authentic sample as [(mes)$OsCl_2${κ^1(*P*)-*i*$Pr_2$$PCH_2$-$CO_2$Me}] (**14**).[7] The yield was quantitative.

Preparation of [(mes)OsCl{κ^2(*P,O*)-*i*$Pr_2$$PCH_2C(O)O$}] (24). A solution of **20** (135 mg, 0.25 mmol) in 5 mL of acetone was treated with excess water (ca. 100 μL) and stirred for 10 min at room temperature. The solvent was removed, and the yellow residue was washed three times with 5 mL portions of ether and dried: yield 121 mg (92%); mp 196 °C dec; MS (70 eV) m/z 521 (M^+). IR (CH_2Cl_2): ν(C═O) 1644 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 4.69 (s, 3H, $C_6H_3Me_3$), 3.13 [dd, J(PH) = 10.2, J(HH) = 16.0 Hz, 1H, one H of PCH_2], 2.55 [dd, J(PH) = 9.1, J(HH) = 16.0 Hz, 1H, one H of PCH_2], 2.44 (m, 1H, PC*H*CH_3), 1.91 (s, 9H, C_6H_3*Me*$_3$), 1.77 (m, 1H, PC*H*CH_3), 0.95 [dd, J(PH) = 15.7, J(HH) = 7.4 Hz, 3H, PCHC*H*$_3$], 0.87, 0.85 (both m, 6H, PCHC*H*$_3$), 0.76 [dd, J(PH) = 13.1, J(HH) = 6.9 Hz, 3H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 182.6 [d, J(PC) = 7.6 Hz, CO_2], 95.7 [d, J(PC) = 1.9 Hz, *C*Me of mes], 72.7 [d, J(PC) = 3.8 Hz, CH of mes], 27.3 [d, J(PC) = 33.4 Hz, PCH_2], 25.4 [d, J(PC) = 29.5 Hz, P*C*HCH_3], 24.0 [d, J(PC) = 30.5 Hz, P*C*HCH_3], 19.2 (s, PCH*C*H_3), 19.1 (s, CH_3 of mes), 18.8 [d, J(PC) = 1.6 Hz, PCH*C*H_3], 17.5 [d, J(PC) = 4.2 Hz, PCH*C*H_3]. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 13.4 [s, J(^{187}Os^{31}P) = 257.7 Hz]. Anal. Calcd for $C_{17}H_{28}ClO_2OsP$: C, 39.19; H, 5.42. Found: C, 39.01; H, 5.69.

X-ray Structural Determination of Compounds 9, 11, 22, and 23. Single crystals of **9** were grown from hexane at 0 °C, those of **11** and **23** from hexane/CH_2Cl_2 (6:1) at 10 °C, and those of **22** from hexane/toluene (5:1) at room temperature. Crystal data collection parameters are summarized in Table 5. Intensity data were corrected by Lorentz and polarization effects, and a semiempirical absorption correction was applied in each case (minimum transmission 44.55% (**9**), 21.56% (**11**), 73.37% (**22**), and 59.72% (**23**); maximum transmission 40.40% (**11**), near 100% (**9**, **22**, and **23**). The structures of **11**, **22,** and **23** were solved by direct methods (SHELXS-86 and SHELXS-97),[21] and that of **9** was solved by the Patterson method (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93 and SHELXL-97).[22] In **11** there are two PF_6 anions in the asymmetric unit lying on 2-fold axes. One of them is disordered and was refined with distance restraints. Both anions were refined with restraints for the anisotropic displacement parameters. For **11** an extinction

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correction with an coefficient of 0.000 49(5) was applied. The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by using the riding method, except for all hydrogen atoms of **9**, which were found and refined isotropically.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant No. SFB 347) and the Fonds der Chemischen Industrie for financial support. Moreover, we gratefully acknowledge support by R. Schedl and C. P. Kneis (DTA and elemental analysis), M.-L. Schäfer and Dr. W. Buchner (NMR spectra), Prof. Dr. D. Stalke and B. Weberndörfer (X-ray structure analysis), and Degussa AG (gifts of chemicals). G.H. is particularly grateful to the Alexander von Humboldt Foundation for supporting a 3 month visit to the Australian National University.

Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **9**, **11**, **22**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980909E