Halfsandwich-Type Osmium Complexes Containing Phosphanylmethanide and Phosphanyl Alcoholate Anions as Bidentate Ligands☆

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The mononuclear dichloroosmium(II) complexes [(mes)Os(L)Cl_2] (**2**–**5**) with the phosphanyl ether L = $iPr_2PCH_2CH_2OMe$ and phosphanyl esters L = $iPr_2P(CH_2)_nCO_2R$ as ligands are obtained from $[(mes)OsCl_2]_n$ and L in almost quantitative yield. While compound **3** (L = $iPr_2PCH_2CH_2CO_2Me$) reacts with Mg/Hg in THF in the presence of ethanol to give the monohydrido derivative **6**, treatment of **4** (L = $iPr_2PCH_2CO_2Me$) or **5** (L = $iPr_2PCH_2CO_2Et$) with Al_2O_3/NaH in THF yields the phosphanylmethanide complexes [(mes)Os{κ²(*P*,*C*)-iPr_2PCHCO_2R}Cl] (**7**, **8**). In contrast to the reaction of **4** with Mg/Hg in THF/EtOH which yields the dihydrido compound [(mes)OsH_2{κ(*P*)-$iPr_2PCH_2CO_2Me$}] (**10**), the corresponding reaction of **4** with excess PhMgBr does not lead to an $OsPh_2$ species but instead gives the new chelate complex [(mes)OsPh{κ²(*P*,*O*)-$iPr_2PCH_2CPh_2O$}] (**11**). The crystal and molecular structures of **7** and **11** were determined.

In a series of papers[1–4], we have reported on the reactivity of (mesitylene)osmium complexes of general composition [(mes)Os(L)Cl_2] (mes = 1,3,5-$C_6H_3Me_3$), where L is CO or CNR, toward organolithium and Grignard reagents. We found that while the reaction of [(mes)Os(CO)Cl_2] with PhLi in benzene leads to the formation of the diphenylosmium compound [(mes)$OsPh_2$(CO)], on treatment of [(mes)Os(CO)Cl_2] with PhMgBr the monoaryl complex [(mes)OsPh(CO)Br] is obtained[2]. Moreover, the methyl isocyanide derivative [(mes)Os(CNMe)Cl_2] reacts with PhMgI to yield [(mes)OsPh(CNMe)I] and [(mes)Os(CNMe)I_2] but with PhMgBr to give, besides [(mes)OsPh(CNMe)Br], the aminocarbene complex [(mes)Os(=C(NHMe)Ph)Ph_2] as the main product[3].

In the context of our work on the behaviour of $[(mes)OsCl_2]_n$ (**1**) toward nucleophiles including trialkylphosphanes[5] we also prepared the corresponding compound with the phosphanyl ester $iPr_2PCH_2CO_2Me$ as ligand. We were therefore interested in finding out how this complex [(mes)Os{κ(*P*)-($iPr_2PCH_2CO_2Me$)Cl_2}] (**4**) would react with phenylmagnesium halides. Besides a substitution of one or both of the chloride atoms by phenyl groups, an attack of the Grignard reagent at the ester unit seemed to be feasible. However, we obtained as the only isolated product a (mesitylene)osmium complex of unusual composition which contains the anion of the unknown phosphanyl alcohol $iPr_2PCH_2CPh_2OH$ as bidentate ligand[6]. In this paper we describe the synthesis and the structure of this compound together with the preparation of a series of related (mesitylene)osmium complexes in which different functionalized diisopropylphosphane derivatives are linked to the metal centre.

Results

Phosphane and Phosphanylmethanide Osmium Complexes

The bridging chloro complex $[(mes)OsCl_2]_n$ (**1**), which is either a dimer[7] or a polymer[1], reacts with the phosphanyl ether $iPr_2PCH_2CH_2OMe$ or the phosphanyl esters $iPr_2P(CH_2)_nCO_2R$ (n = 1: R = Me, Et; n = 2: R = Me) at 20°C in CH_2Cl_2, i.e. under similar conditions as with CO, CNR, and $PiPr_3$, to give the mononuclear compounds **2**–**5** in almost quantitative yield (Scheme 1). They are orange solids which are air-stable and moderately soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, or acetone. The IR spectra of the phosphanyl ester derivatives **3**–**5** display a C=O stretching frequency at 1710–1730 cm^{-1} which is characteristic for a non-coordinated ester unit. Although the ^1H-, ^{13}C-, and ^{31}P-NMR data of **2**–**5** deserve no further comment, it should be mentioned that the expected singlet in the ^{31}P-NMR spectra is associated with two satellites which arise from $^1J(^{187}Os^{31}P)$ coupling in the range of 277–280 Hz.

The experiments aimed at substituting the chloro ligands in **3**–**5** by hydride ions led to some puzzling results. When we attempted to prepare the complex [(mes)OsH_2{κ(*P*)-$iPr_2PCH_2CH_2CO_2Me$}] from **3** and Mg/Hg in THF in the presence of EtOH, i.e. by the same method which we have already applied to the synthesis of [(mes)OsH_2(CO)] and [(mes)OsH_2(CNMe)] from [(mes)$OsCl_2$(L)] (L = CO, CNMe)[8], we obtained the monohydridoosmium derivative **6** (see Scheme 2) instead of the dihydride. Obviously, a transesterification caused by formation of the OEt^- anion from the alcohol and magnesium amalgam had taken place. Compound **6** forms yellow air-sensitive crystals which were characterized by elemental analysis, mass spectrometry, and

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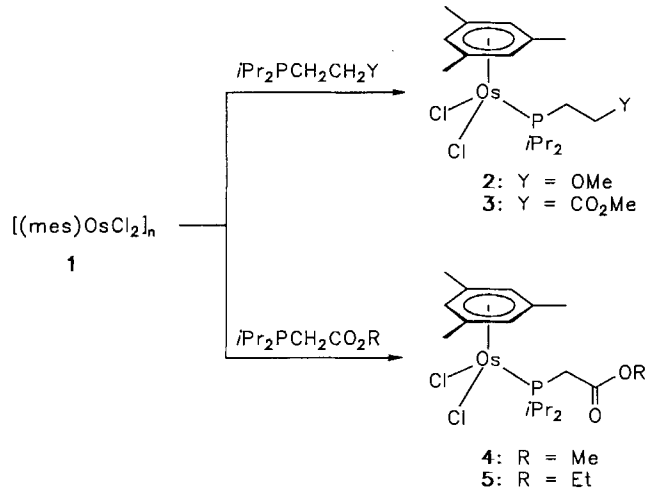
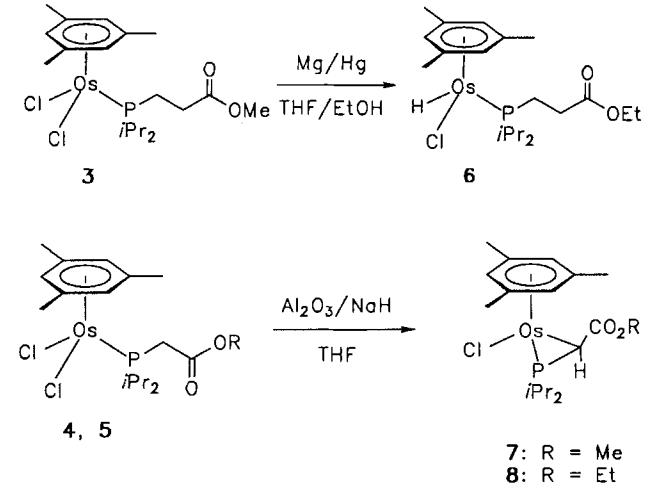
Scheme 1



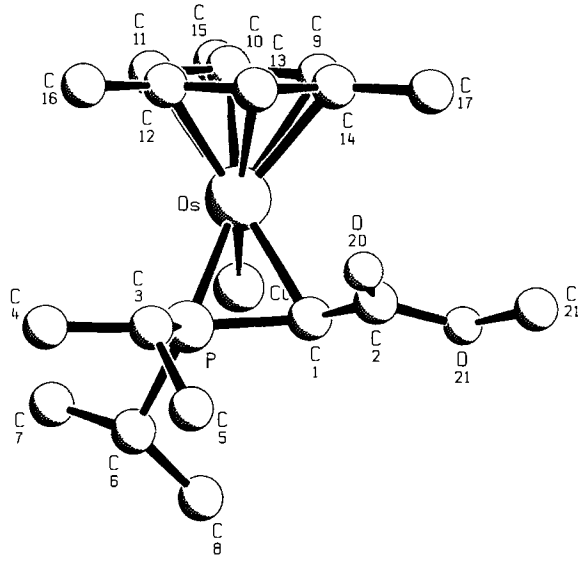
IR and NMR-spectroscopic data. The ^{1}H-NMR spectrum displays a hydride signal at high field ($\delta = -9.14$) with a large P–H coupling of 44 Hz and the ^{31}P-NMR spectrum a singlet resonance which under off-resonance conditions splits into a doublet.

Scheme 2



Attempts to prepare complexes [(mes)OsH{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$R}Cl] (R = Me, Et), which should be structurally similar to **6**, from **4** or **5** and NaH led to the isolation of the new phosphanylmethanide osmium(II) compounds **7** and **8** (pale yellow solids) in 75–80% yield. The reaction is probably initiated by deprotonation of the CH_2 group of the phosphanyl ester ligand. As far as the spectroscopic data of **7** and **8** are concerned, the most typical features are the lowering of the C=O stretching frequency in the IR spectra from 1722 (**4**) and 1712 (**5**) to 1676 (**7**) and 1673 (**8**) cm^{-1} and the appearance of a high-field resonance at $\delta = -0.22$ (**7**) and 0.05 (**8**) in the ^{13}C-NMR spectra assigned to the metal-bonded carbon of the *i*Pr$_2$PCHCO$_2$R unit. We note that phosphanylmethanide complexes with an Os{κ^2(*P,C*)-Me$_2$PCH$_2$} moiety but without an arene ligand are well known[9] and have been recently used by Flood et al. for the activation of C–H bonds in aliphatic and aromatic hydrocarbons[10].

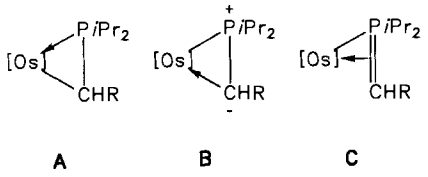
Figure 1. Molecular structure of **7**[a]



[a] Selected bond lengths [Å] and angles [°]: Os–P 2.287(2), Os–Cl 2.407(2), Os–C1 2.205(6), Os–C9 2.240(6), Os–C10 2.267(6), Os–C11 2.238(7), Os–C12 2.172(6), Os–C13 2.182(6), Os–C14 2.211(6), P–C1 1.785(5), P–C3 1.850(6), P–C6 1.849(7), C1–C2 1.448(8), C2–O20 1.210(7), C2–O21 1.373(7); P–Os–Cl 88.5(1), P–Os–C1 46.8(1), Cl–Os–C1 84.6(1), Os–P–C1 64.2(2), Os–P–C3 124.0(2), Os–P–C6 128.0(2), Os–C1–C2 118.1(4), Os–C1–P 69.0(2), C1–P–C3 114.1(3), C1–P–C6 115.0(3), C3–P–C6 104.3(3), P–C1–C2 124.6(4), C1–C2–O20 129.1(5), C1–C2–O21 109.8(5), O20–C2–O21 121.0(5), C2–O21–C21 116.5(5).

The structure of **7** was confirmed by a single-crystal X-ray structure analysis. The SCHAKAL structure plot (Figure 1) reveals that osmium is coordinated by the mesitylene ring, one chloride, and the κ^2(*P,C*)-bonded phosphanylmethanide ligand, the CO_2Me substituent of which is directed away from the Os–Cl axis. The bond angles of the OsPC fragment are comparable to those found in [Mn(CO)$_4${κ^2(*P,C*)-Ph$_2$PCH$_2$}][11], [C$_5$H$_5$Mo(CO)$_2${κ^2(*P,C*)-Ph$_2$PCH$_2$}][12] and in the novel chelating ruthenium complex [(mes)Ru{κ^3(*P,C,O*)-*i*PrP(*C*HCO$_2$Me)(CH=C(OMe)*O*)}] containing both a five-membered phosphanyl enolate and a three-membered phosphanylmethanide ring system[13]. The Os–C bond length [2.205(6) Å] is similar to that of Os–CH$_3$ [2.197(17) Å] in [OsH(CH$_3$)(CO)$_2$(P*i*Pr$_3$)$_2$][14] but significantly longer than that of Os–CH=CHPh [2.090(7) Å] in [C$_6$H$_6$Os(CH=CHPh)(P*i*Pr$_3$)I][15]. The distance P–C1 is shorter by 0.065 Å than the other distances P–C3 and P–C6 which indicates a substantial double-bond character of the phosphorus-carbon bond in the three-membered ring. Thus, for a description of the bonding situation the resonance form **C** should be taken into consideration besides **A** and **B**.

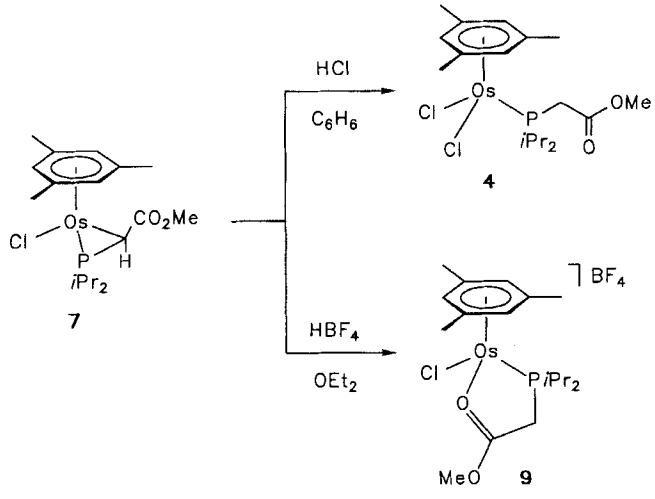
Some preliminary results regarding the reactivity of **7** are summarized in Scheme 3. While all attempts to insert CO_2 or ketones into the Os–C bond of the OsPC fragment failed and the starting material also proved to be inert toward CH_3I, the reactions of **7** with HCl or HBF_4 lead to



A B C

protonation of the methanide carbon and regeneration of the iPr$_2$PCH$_2$CO$_2$Me ligand. In the cationic complex **9**, the phosphanyl ester is coordinated via phosphorus and the C=O oxygen of the ester unit which is supported by the decrease of the C=O stretching frequency from 1722 cm^{-1} in **4** to 1604 cm^{-1} in **9**. A ruthenium compound of composition [C$_5$Me$_5$Ru{κ^2(*P,O*)-iPr$_2$PCH$_2$C(OMe)*O*}Cl] which is structurally related to **9** was recently prepared in our laboratory and characterized by X-ray analysis[16].

Scheme 3

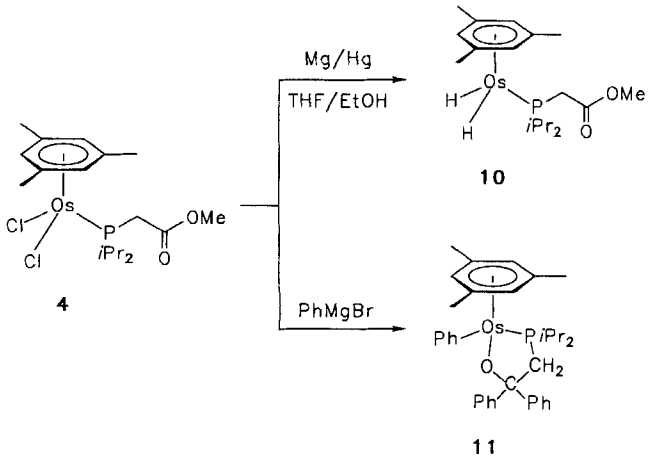


Osmium-Mediated Conversion of a Phosphanyl Ester to a Phosphanyl Alcoholate Unit

In contrast to **3**, the dichloro complex **4** reacts with magnesium amalgam in THF in the presence of ethanol to give the dihydridoosmium(II) compound **10** in nearly quantitative yield (Scheme 4). The possible formation of a monohydridometal derivative such as [(mes)OsHCl{κ(*P*)-iPr$_2$PCH$_2$CO$_2$Me}] or [(mes)OsH{κ^2(*P,C*)-iPr$_2$PCHCO$_2$Me}] was not observed. The ^{1}H-NMR spectrum of **10** displays a characteristic doublet for the Os–H protons, the chemical shift and the coupling constant of which are very similar to those of [(mes)OsH$_2$(PiPr$_3$)][5] and [C$_6$H$_6$OsH$_2$(PiPr$_3$)][17].

The reaction of **4** with PhMgBr does not lead to the formation of [(mes)OsPh$_2${κ(*P*)-iPr$_2$PCH$_2$CO$_2$Me}] as expected in analogy to the preparation of [(mes)OsPh$_2$(CO)] from [(mes)Os(CO)Cl$_2$][2], but instead gives the new chelate complex **11** in 41% yield. The composition of the orange-red air-sensitive crystalline solid was confirmed by elemental analysis, mass spectrometry and, finally, by X-ray analysis. The ^{1}H-NMR spectrum of **11** shows nine signals at δ = 7.7–6.8 for the C$_6$H$_5$ protons of which two (at δ = 7.31 and 6.77) are broadened. Since a similar broadening also appears in the ^{13}C-NMR spectrum for some of the phenyl carbon signals (at δ = 141.0, 140.4, 126.2, and 125.8), we assume a slightly hindered rotation around the Os–C$_6$H$_5$ bond.

Scheme 4

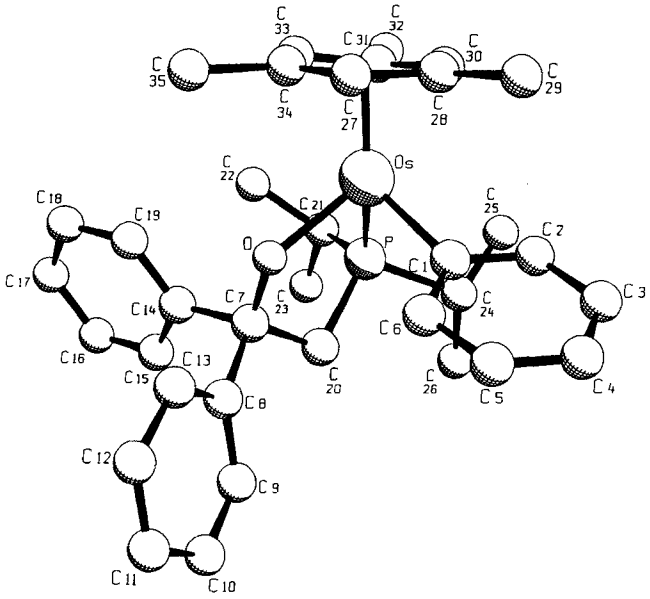


The molecular structure of **11** is shown in Figure 2. The configuration around osmium corresponds to that of a piano stool with bond angles P–Os–O, P–Os–Cl, and O–Os–Cl near to 90°. The Os–Cl distance [2.071(6) Å] is similar to the Os–C$_6$H$_5$ bond lengths in the (aminocarbene)osmium complex [(mes)OsPh$_2${=C(Ph)NHMe}] [2.100(4) and 2.092(5) Å][3], while the Os–O distance [2.147(4) Å] is significantly shorter than in the phosphanyl ether derivative [OsCl$_2${κ^2(*C,P*)-*C*HOCH$_2$CH$_2$PiPr$_2$}-{κ^2(*P,O*)-iPr$_2$PCH$_2$CH$_2$OMe}] [2.297(8) Å][18]. The Os–O bond length in **11**, however, is almost the same as in the phosphanyl acetate complex [OsCl$_2$(≡CCH=CPh$_2$){κ(*P*)-iPr$_2$PCH$_2$CO$_2$Me}{κ^2(*P,O*)-iPr$_2$PCH$_2$C(=O)*O*}] [2.119(6) Å][19]. We furthermore note that the distances in the chelate ring O–C7, C7–C20, and P–C20 correspond to those of O–C, C–C, and P–C single bonds, and the bond angles in the five-membered fragment are nearly identical to those of the platinum compound [Pt{κ^2(*P,O*)-Ph$_2$PCH$_2$-CMe$_2$O}$_2$][20].

Although the mesitylene ring is almost planar [maximum deviation 0.06(1) Å], the Os–C27 to Os–C34 bond lengths differ by 0.17 Å. The greatest distance Os–C33 [2.377(7) Å] is that to the ring carbon atom which is nearest to one of the isopropyl groups and *trans* to the η^1-phenyl ligand, and therefore we assume that both steric requirements and electronic effects are responsible for the differences in bond lengths. The second largest distance Os–C27 [2.348(7) Å] is found opposite to phosphorus[21], an observation probably reflecting the strong *trans* influence of the phosphanyl unit.

As far as the mechanism of formation of the chelate complex **11** from **4** is concerned, we suppose that in complete analogy to the reaction of [(mes)Os(CO)Cl$_2$] with PhMgBr[2] initially a Cl/Ph exchange takes place. The excess of the Grignard reagent presumably attacks the non-coordinated ester function of the assumed intermediate [(mes)OsPh{κ(*P*)-iPr$_2$PCH$_2$CO$_2$Me}Br] and yields the anionic species [(mes)OsPh{κ(*P*)-iPr$_2$PCH$_2$CPh$_2$O}Br]$^-$. Nucleophilic attack of the alcoholate oxygen at the metal

Figure 2. Molecular structure of **11**[a]



[a] Selected bond lengths [Å] and angles [°]: Os–P 2.271(2), Os–O 2.147(4), Os–C1 2.071(6), Os–C27 2.348(7), Os–C28 2.317(7), Os–C30 2.213(6), Os–C31 2.205(7), Os–C33 2.377(7), Os–C34 2.332(8), P–C20 1.838(6), P–C21 1.856(6), P–C24 1.863(7), O–C7 1.422(7), C7–C8 1.556(8), C7–C14 1.539(9), C7–C20 1.53(1); P–Os–O 81.3(1), P–Os–C1 88.8(2), O–Os–C1 87.2(2), Os–P–C20 101.4(2), Os–P–C21 121.6(2), Os–P–C24 114.0(2), Os–O–C7 121.3(4), O–C7–C8 106.3(5), O–C7–C14 110.6(5), O–C7–C20 112.0(5), P–C20–C7 108.8(4).

would then lead to bromide abstraction and closure of the chelate ring. In this context, it is worth mentioning that the preparation of tertiary alcohols RCR''_2OH from esters RCO_2R' and Grignard reagents R''MgX is a standard procedure in organic synthesis[22].

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Experimental

All operations were carried out under Ar with the Schlenk-tube technique. The starting materials **1**[1], $iPr_2PCH_2CH_2OMe$[23], $iPr_2PCH_2CH_2CO_2Me$[24], and $iPr_2PCH_2CO_2R$ (R = Me, Et)[24] were prepared by published procedures. – IR: Perkin-Elmer 1420. – NMR: Jeol FX 90 Q and Bruker AMX 400. – MS: Varian MAT CH7 and Finnigan 8200 MAT.

1. *[(mes)Os{κ(P)-iPr$_2$PCH$_2$CH$_2$OMe}Cl$_2$]* (**2**): A suspension of 300 mg (0.50 mmol for $n = 2$) of **1** in 30 ml of CH_2Cl_2 was treated with 350 µl (1.97 mmol) of $iPr_2PCH_2CH_2OMe$ and stirred for 2.5 h at room temp. The reaction mixture was filtered through Celite, the filter cake was washed three times with 10 ml of CH_2Cl_2 each, and the combined filtrates were concentrated to appr. 5 ml in vacuo. After 30 ml of hexane were added, an orange solid precipitated which was separated from the solution, washed with hexane and dried in vacuo; yield 502 mg (92%), m.p. 149°C (dec.). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.22 (s, 3H, $C_6H_3Me_3$), 3.50 [dt, ^3J(PH) = 8.0, ^3J(HH) = 7.5 Hz, 2H, CH_2OMe], 3.19 (s, 3H, OCH_3), 2.39 (m, 2H, $PCHCH_3$), 2.31 [dt, ^2J(PH) = 11.0, ^3J(HH) = 7.5 Hz, 2H, PCH_2], 2.15 (s, 9H, $C_6H_3Me_3$), 1.15 and 1.14 [both dd, ^3J(PH) = 14.5, ^3J(HH) = 7.2 Hz, 6H each, $PCHCH_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 92.72 (s, CCH_3 of mes), 77.18 (s, CH of mes), 69.00 (s, CH_2OMe), 58.04 (s, OCH_3), 26.23 [d, ^1J(PC) = 28.0 Hz, $PCHCH_3$], 19.80 [d, ^1J(PC) = 1.0 Hz, PCH_2], 19.50 [d, ^2J(PC) = 1.0 Hz, $PCHCH_3$], 18.82 [d, ^2J(PC) = 2.4 Hz, $PCHCH_3$], 18.43 (s, CCH_3 of mes). – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = −9.12 [s, $^1J(^{187}Os^{31}P)$ = 277.1 Hz]. – $C_{18}H_{33}Cl_2OOsP$ (557.5): calcd. C 38.79, H 5.97; found C 38.26, H 6.15.

2. *[(mes)Os{κ(P)-iPr$_2$PCH$_2$CH$_2$CO$_2$Me}Cl$_2$]* (**3**): Analogously as described for **2**, by using 540 mg (0.71 mmol for $n = 2$) of **1** and 500 µl (2.52 mmol) of $iPr_2PCH_2CH_2CO_2Me$ as starting materials; an orange microcrystalline solid was obtained; yield 727 mg (87%), m.p. 150°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1727 cm^{-1} [ν(C=O)$_{noncoord}$]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 4.77 (s, 3H, $C_6H_3Me_3$), 3.28 (s, 3H, CO_2Me), 3.06 (m, 2H, CH_2CO_2Me), 2.55 (m, 2H, PCH_2), 2.25 (m, 2H, $PCHCH_3$), 1.91 (s, 9H, $C_6H_3Me_3$), 1.07 [dd, ^3J(PH) = 13.1, ^3J(HH) = 7.1 Hz, 6H, $PCHCH_3$), 1.01 [dd, ^3J(PH) = 13.7, ^3J(HH) = 7.2 Hz, 6H, $PCHCH_3$]. – ^{31}P NMR (C_6D_6, 162.0 MHz): δ = −9.94 [s, $^1J(^{187}Os^{31}P)$ = 278.0 Hz]. – $C_{19}H_{33}Cl_2O_2OsP$ (585.6): calcd. C 38.97, H 5.68; found C 38.26, H 5.65.

3. *[(mes)Os{κ(P)-iPr$_2$PCH$_2$CO$_2$Me}Cl$_2$]* (**4**): Analogously as described for **2**, by using 900 mg (1.18 mmol for $n = 2$) of **1** and 400 µl (2.03 mmol) of $iPr_2PCH_2CO_2Me$ as starting materials; an orange microcrystalline solid was obtained; yield 1.23 g (91%), m.p. 172°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1} [ν(C=O)$_{noncoord}$]. – ^{1}H NMR ($CDCl_3$, 90 MHz): δ = 5.43 (s, 3H, $C_6H_3Me_3$), 3.56 (s, 3H, CO_2Me), 3.45 [d, ^2J(PH) = 10.9 Hz, 2H, PCH_2], 2.64 (m, 2H, $PCHCH_3$), 2.23 (s, 9H, $C_6H_3Me_3$), 1.23 [dd, ^3J(PH) = 15.6, ^3J(HH) = 7.2 Hz, 6H, $PCHCH_3$], 1.13 [dd, ^3J(PH) = 13.9, ^3J(HH) = 7.0 Hz, 6H, $PCHCH_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 171.5 [d, ^2J(PC) = 10.5 Hz, CO_2Me], 92.5 [d, ^2J(PC) = 2.9 Hz, CCH_3 of mes], 77.5 [d, ^2J(PC) = 2.9 Hz, CH of mes], 51.6 (s, OCH_3), 25.5 [d, ^1J(PC) = 27.7 Hz, $PCHCH_3$], 22.1 [d, ^1J(PC) = 21.0 Hz, PCH_2], 18.7 (s, CCH_3 of mes), 18.7 and 18.1 [both d, ^2J(PC) = 1.9 Hz, $PCHCH_3$]. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = −0.85 (s). – $C_{18}H_{31}Cl_2O_2OsP$ (571.5): calcd. C 37.83, H 5.47; found C 38.28, H 5.46. – Mol. mass 572 (MS).

4. *[(mes)Os{κ(P)-iPr$_2$PCH$_2$CO$_2$Et}Cl$_2$]* (**5**): Analogously as described for **2**, by using 625 mg (0.82 mmol for $n = 2$) of **1** and 500 µl (2.37 mmol) of $iPr_2PCH_2CO_2Et$ as starting materials; an orange microcrystalline solid was obtained; yield 901 mg (94%), m.p. 143°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1712 cm^{-1} [ν(C=O)$_{noncoord}$]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.48 (s, 3H, $C_6H_3Me_3$), 4.07 [q, ^3J(HH) = 7.0 Hz, 2H, CH_2CH_3], 3.52 [d, ^2J(PH) = 10.9 Hz, 2H, PCH_2], 2.72 (m, 2H, $PCHCH_3$), 2.28 (s, 9H, $C_6H_3Me_3$), 1.30 and 1.22 [both dd, ^3J(PH) = 15.0, ^3J(HH) = 7.0 Hz, 6H each, $PCHCH_3$], 1.23 [t, ^3J(HH) = 7.0 Hz, 3H, CH_2CH_3]. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = −1.16 [s, $^1J(^{187}Os^{31}P)$ = 280.0 Hz]. – $C_{19}H_{33}Cl_2O_2OsP$ (585.55): calcd. C 38.97, H 5.68; found C 38.48, H 5.70.

5. *[(mes)OsH{κ(P)-iPr$_2$PCH$_2$CH$_2$CO$_2$Et}Cl]* (**6**): A suspension of 227 mg (0.21 mmol) of **3** in 7 ml of THF was added slowly to magnesium amalgam (2.0 g Hg, 9.97 mmol; 100 mg Mg, 4.4 mmol) layered by a mixture of 5 ml of THF and 0.5 ml of EtOH. After the reaction mixture had vigorously been stirred for 2 h at room temp., the solution was separated and the residue extracted twice with 10 ml of THF each. The solution and the extracts were

combined, and the solvent was removed in vacuo. The residue was dissolved in 1 ml of benzene, and the solution was chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm). With CH_2Cl_2, a yellow fraction was eluted which was concentrated to appr. 1 ml in vacuo. After 5 ml of hexane had been added, a light yellow solid precipitated which was repeatedly washed with hexane and dried; yield 84 mg (71%), m.p. 110°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2053 cm^{-1} [ν(OsH)], 1731 [ν(C=O)$_{noncoord}$]. – ^1H NMR (C_6D_6, 400 MHz): δ = 4.60 (s, 3H, $C_6H_3Me_3$), 3.96 (m, 2H, $OCH_AH_{A'}CH_3$), 3.24 (m, 2H, CH_2CO_2Et), 2.66 and 2.45 (both m, 1H each, PCH_2), 2.25 and 1.86 (both m, 1H each, $PCHCH_3$), 2.06 (s, 9H, $C_6H_3Me_3$), 1.12 and 1.01 [both dd, ^3J(PH) = 13.7, ^3J(HH) = 6.3 Hz, 3H each, $PCHCH_3$], 0.95 [dd, $^3J(H_AH_M)$ = $^3J(H_{A'}H_M)$ = 7.4 Hz, 3H, $OCH_2C(H_M)_3$], 0.91 [dd, ^3J(PH) = 13.0, ^3J(HH) = 6.6 Hz, 3H, $PCHCH_3$], 0.88 [dd, ^3J(PH) = 14.1, ^3J(HH) = 6.8 Hz, 3H, $PCHCH_3$], −9.14 [d, ^2J(PH) = 44.2 Hz, 1H, OsH]. – ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 16.93 [s, d in off resonance, $^1J(^{187}Os^{31}P)$ = 267.9 Hz]. – $C_{20}H_{36}ClO_2OsP$ (565.1): calcd. C 42.51, H 6.42; found C 42.80, H 6.58. – Mol. mass 566 (MS).

6. *[(mes)Os{κ²(P,C)-iPr₂PCHCO₂Me}Cl]* (**7**): A solution of 130 mg (0.23 mmol) of **4** in 20 ml of THF was first treated with 200 mg of Al_2O_3 and then (in 20-mg portions) with 200 mg (8.33 mmol) of NaH. After the reaction mixture had been vigorously stirred for 1 h at room temp., the solvent was removed in vacuo, and the residue was extracted twice with 10 ml of benzene each. The combined extracts were concentrated to appr. 1 ml in vacuo, and the obtained solution was chromatographed on Al_2O_3 (basic, activity grade III, height of column 2 cm). With benzene, a pale yellow fraction was eluted which after removal of the solvent gave a pale yellow microcrystalline powder; yield 96 mg (78%), m.p. 142°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1676 cm^{-1} [ν(C=O)$_{noncoord}$]. – ^1H NMR (C_6D_6, 400 MHz): δ = 4.64 (s, 3H, $C_6H_3Me_3$), 3.55 (s, 3H, CO_2Me), 3.11 (s, 1H, $CHCO_2Me$), 2.70 and 2.38 (both m, 1H each, $PCHCH_3$), 2.09 (s, 9H, $C_6H_3Me_3$), 1.35 [dd, ^3J(PH) = 16.2, ^3J(HH) = 6.5 Hz, 3H, $PCHCH_3$], 1.34 [dd, ^3J(PH) = 17.9, ^3J(HH) = 6.6 Hz, 3H, $PCHCH_3$], 1.22 [dd, ^3J(PH) = 13.3, ^3J(HH) = 7.4 Hz, 3H, $PCHCH_3$], 1.11 [dd, ^3J(PH) = 18.2, ^3J(HH) = 7.6 Hz, 3H, $PCHCH_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 180.94 (s, CO_2Me), 92.30 (s, CCH_3 of mes), 72.35 [d, ^2J(PC) = 3.1 Hz, CH of mes), 50.26 (s, OCH_3), 25.56 [d, ^1J(PC) = 24.5 Hz, $PCHCH_3$], 22.02 [d, ^2J(PC) = 0.5 Hz, $PCHCH_3$], 20.83 [d, ^2J(PC) = 8.2 Hz, $PCHCH_3$], 20.66 [d, ^2J(PC) = 1.0 Hz, $PCHCH_3$], 19.40 (s, CCH_3 of mes), 18.81 [d, ^2J(PC) = 4.5 Hz, $PCHCH_3$], 18.41 [d, ^1J(PC) = 20.5 Hz, $PCHCH_3$], −0.22 (s, $CHCO_2Me$). – ^{31}P NMR (C_6D_6, 162.0 MHz): δ = −17.99 [s, $^1J(^{187}Os^{31}P)$ = 205.2 Hz]. – $C_{18}H_{30}ClO_2OsP$ (535.1): calcd. C 40.41, H 5.65; found C 40.70, H 5.26. – Mol. mass 536 (MS).

7. *[(mes)Os{κ²(P,C)-iPr₂PCHCO₂Et}Cl]* (**8**): Analogously as described for **7**, by using 143 mg (0.24 mmol) of **5** as starting material; a pale yellow solid was obtained; yield 102 mg (76%), m.p. 133°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1673 cm^{-1} [ν(C=O)$_{noncoord}$]. – ^1H NMR (C_6D_6, 400 MHz): δ = 4.67 (s, 3H, $C_6H_3Me_3$), 4.20 [dq, $^2J(H_AH_B)$ = 10.8, $^3J(H_AH_M)$ = 7.0 Hz, 1H, OCH_AH_B], 4.07 [dq, $^2J(H_AH_B)$ = 10.8, $^3J(H_BH_M)$ = 7.0 Hz, 1H, OCH_AH_B], 3.12 (s, 1H, $CHCO_2Et$), 2.71 and 2.40 (both m, 1H each, $PCHCH_3$), 2.11 (s, 9H, $C_6H_3Me_3$), 1.36 [dd, ^3J(PH) = 16.5, ^3J(HH) = 7.4 Hz, 3H, $PCHCH_3$], 1.35 [dd, ^3J(PH) = 17.7, ^3J(HH) = 7.2 Hz, 3H, $PCHCH_3$], 1.24 [dd, ^3J(PH) = 12.7, ^3J(HH) = 6.7 Hz, 3H, $PCHCH_3$], 1.16 [dd, $^3J(H_AH_M)$ = $^3J(H_BH_M)$ = 7.0 Hz, 3H, $OCH_2C(H_M)_3$], 1.10 [dd, ^3J(PH) = 17.9, ^3J(HH) = 7.6 Hz, 3H, $PCHCH_3$]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 180.61 (s, CO_2Et), 92.13 (s, CCH_3 of mes), 72.52 [d, ^2J(PC) = 3.1 Hz, CH of mes], 59.13 (s, OCH_2CH_3), 25.48 [d, ^1J(PC) = 24.5 Hz, $PCHCH_3$], 22.04 [d, ^2J(PC) = 0.5 Hz, $PCHCH_3$], 20.87 [d, ^2J(PC) = 8.4 Hz, $PCHCH_3$], 20.69 [d, ^2J(PC) = 0.5 Hz, $PCHCH_3$], 19.45 (s, CCH_3 of mes), 18.83 [d, ^2J(PC) = 4.2 Hz, $PCHCH_3$], 18.42 [d, ^1J(PC) = 20.6 Hz, $PCHCH_3$], 14.83 (s, OCH_2CH_3), 0.05 (s, $CHCO_2Et$). – ^{31}P NMR (C_6D_6, 162.0 MHz): δ = −17.74 [s, $^1J(^{187}Os^{31}P)$ = 205.1 Hz]. – $C_{19}H_{32}ClO_2OsP$ (549.1): calcd. C 41.56, H 5.87; found C 41.82, H 5.98. – Mol. mass 550 (MS). – Compound **8** has also been prepared by using **5** and $NaN(SiMe_3)_2$ or $LiNiPr_2$ (both in THF) as starting materials. The yield of **8** was 19 or 13%, respectively.

8. *Reaction of* **7** *with HCl:* A slow stream of gaseous HCl was passed through a solution of 45 mg (0.08 mmol) of **7** in 10 ml of benzene for 5 min at room temp. After the reaction mixture had been stirred for 10 min under HCl gas, the solvent was removed and the residue worked up as described for **4**. An orange solid was isolated which was shown by ^1H- and ^{31}P-NMR spectroscopy to be **4**; yield 45 mg (94%).

9. *[(mes)Os{κ²(P,O)-iPr₂PCH₂C(OMe)O}Cl]BF₄* (**9**): A solution of 85 mg (0.16 mmol) of **7** in 10 ml of diethyl ether was treated dropwise with a solution of 17 mg (0.20 mmol) of HBF_4 in 1 ml of OEt_2 at room temp. A light yellow precipitate was formed which was separated from the solution, washed twice with 10 ml of OEt_2 each, and dried in vacuo; yield 95 mg (95%), m.p. 182°C (dec.), conductivity (CH_3NO_2): Λ = 74 $cm^2\,\Omega^{-1}\,mol^{-1}$. – IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1} [ν(C=O)$_{coord}$], 1054 [ν(BF_4)]. – ^1H NMR (CD_2Cl_2, 400 MHz): δ = 5.66 (s, 3H, $C_6H_3Me_3$), 4.04 (s, 3H, OCH_3), 3.23 [dd, $^2J(PH_A)$ = 9.5, $^2J(H_AH_B)$ = 17.5 Hz, PCH_AH_B], 3.18 [dd, $^2J(PH_B)$ = 8.7, $^2J(H_AH_B)$ = 17.5 Hz, PCH_AH_B], 2.80 and 2.63 (both m, 1H each, $PCHCH_3$), 2.35 (s, 9H, $C_6H_3Me_3$), 1.35 [dd, ^3J(PH) = 17.1, ^3J(HH) = 7.3 Hz, 3H, $PCHCH_3$), 1.34 [dd, ^3J(PH) = 15.8, ^3J(HH) = 7.2 Hz, 3H, $PCHCH_3$], 1.26 [dd, ^3J(PH) = 14.7, ^3J(HH) = 7.4 Hz, 3H, $PCHCH_3$], 1.17 [dd, ^3J(PH) = 16.8, ^3J(HH) = 7.4 Hz, 3H, $PCHCH_3$]. – ^{31}P NMR (CD_2Cl_2, 162.0 MHz): δ = 33.96 [s, $^1J(^{187}Os^{31}P)$ = 269.6 Hz]. – $C_{18}H_{31}BClF_4O_2OsP$ (622.9): calcd. C 34.71, H 5.02; found C 34.18, H 4.87.

10. *[(mes)OsH₂{κ(P)-iPr₂PCH₂CO₂Me}]* (**10**): A suspension of 137 mg (0.24 mmol) of **4** in 5 ml of THF was added dropwise to magnesium amalgam (2.0 g Hg, 9.97 mmol; 25 mg Mg, 1.03 mmol) layered by a mixture of 5 ml of THF and 0.1 ml of EtOH. After the reaction mixture had been vigorously stirred for 1 h at room temp., the solution was separated and the residue extracted twice with 10 ml of THF each. The solution and the extracts were combined, and the solvent was removed in vacuo. The oily residue was extracted three times with 10 ml of benzene each, and the combined extracts were brought to dryness in vacuo. After sublimation of the residue at 60°C/5 · 10^{-5} mbar to a cooled trap, a colorless air-sensitive oil was obtained; yield 109 mg (90%), dec. temp. 100°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2035 cm^{-1} [ν(OsH)], 1720 [ν(C=O)$_{noncoord}$]. – ^1H NMR (C_6D_6, 400 MHz): δ = 4.82 (s, 3H, $C_6H_3Me_3$), 3.31 (s, 3H, OCH_3), 2.86 [d, ^2J(PH) = 8.6 Hz, 2H, PCH_2], 2.29 (s, 9H, $C_6H_3Me_3$), 1.99 (m, 2H, $PCHCH_3$), 1.10 [dd, ^3J(PH) = 14.0, ^3J(HH) = 7.0 Hz, 6H, $PCHCH_3$], 1.06 [dd, ^3J(PH) = 15.0, ^3J(HH) = 7.0 Hz, 6H, $PCHCH_3$], −12.17 [d, ^2J(PH) = 30.8 Hz, 2H, OsH_2]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 171.5 [d, ^2J(PC) = 6.1 Hz, CO_2Me], 91.9 [d, ^2J(PC) = 2.0 Hz, CCH_3 of mes], 74.1 [d, ^2J(PC) = 3.1 Hz, CH of mes], 50.9 (s, OCH_3), 39.8 [d, ^1J(PC) = 15.3 Hz, PCH_2], 28.3 [d, ^1J(PC) = 30.5 Hz, $PCHCH_3$], 22.0 (s, CCH_3 of mes), 19.1 and 19.0 (both s, $PCHCH_3$). – ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 33.37 (s). – $C_{18}H_{33}O_2OsP$ (502.6): calcd. C 43.01, H 6.62; found C 43.35, H 6.80. – Mol. mass 504 (MS).

11. *[(mes)OsPh{κ²(P,O)-iPr₂PCH₂CPh₂O}]* (**11**): A suspension of 150 mg (0.26 mmol) of **4** in 10 ml of benzene was treated at 5°C with 3.2 ml (0.80 mmol) of a 0.25 M solution of PhMgBr in diethyl ether. After the reaction mixture had been warmed to room temp., it was stirred for 30 min, and then appr. 100 mg of Al_2O_3 (basic) was added. The solvent was removed in vacuo, the residue was extracted with 2 ml of benzene, and the extract was chromatographed on Al_2O_3 (basic, activity grade III, height of column 3 cm). With benzene, an orange fraction was eluted which was brought to dryness in vacuo. The residue was recrystallized from hexane (−20°C) to give red-orange crystals; yield 75 mg (41%), m.p. 38°C (dec.). − ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.72 (m, 3H, C_6H_5), 7.56 (m, 2H, C_6H_5), 7.31 (m, 1H, C_6H_5), 7.22, 7.12, 7.06 (all m, 2H each, C_6H_5), 7.01, 6.90, 6.77 (all m, 1H each, C_6H_5), 4.63 (s, 3H, $C_6H_3Me_3$), 2.91 and 2.16 [both dd, ^2J(PH) = 10.7, ^2J(HH) = 13.0 Hz, 1H each, PCH_2], 2.35 and 1.67 (both m, 1H each, PC*H*CH₃), 1.92 (s, 9H, $C_6H_3Me_3$), 1.13 [dd, ^3J(PH) = 15.3, ^3J(HH) = 7.4 Hz, 3H, PCHC*H*₃], 0.91 [dd, ^3J(PH) = 11.1, ^3J(HH) = 7.4 Hz, 3H, PCHC*H*₃], 0.86 [dd, ^3J(PH) = 12.9, ^3J(HH) = 7.4 Hz, 3H, PCHC*H*₃], 0.51 [dd, ^3J(PH) = 13.9, ^3J(HH) = 7.4 Hz, 3H, PCHC*H*₃]. − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 154.7 (s, *ipso*-C of one C_6H_5), 154.4 [d, ^3J(PC) = 5.7 Hz, *ipso*-C of one C_6H_5], 150.0 [d, ^3J(PC) = 14.3 Hz, *ipso*-C of one C_6H_5], 141.0, 140.4, 127.6, 127.4, 127.3, 127.0, 126.2, 125.8, 125.3, 125.2, 121.9 (all s, C_6H_5), 93.4 [d, ^2J(PC) = 1.9 Hz, *C*CH₃ of mes], 84.7 [d, ^2J(PC) = 3.8 Hz, O*C*Ph₂], 79.1 [d, ^2J(PC) = 3.8 Hz, CH of mes], 44.2 [d, ^1J(PC) = 34.3 Hz, PCH_2], 27.3 [d, ^1J(PC) = 20.0 Hz, P*C*HCH₃], 24.1 [d, ^1J(PC) = 31.5 Hz, P*C*HCH₃], 21.3 (s, PCH*C*H₃), 20.9 [d, ^2J(PC) = 3.8 Hz, PCH*C*H₃], 20.5 [d, ^2J(PC) = 1.9 Hz, PCH*C*H₃], 19.0 [d, ^2J(PC) = 5.7 Hz, PCH*C*H₃], 18.9 (s, C*C*H₃ of mes). − ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 28.26 (s). − $C_{35}H_{43}OOsP$ (700.9): calcd. C 59.98, H 6.18; found C 60.53, H 6.51. − Mol. mass 702 (MS).

12. *X-ray Structure Determination of Compounds* **7** *and* **11**[25]: Single-crystals of **7** were grown from toluene/hexane (5:1) and by slow diffusion of hexane into a solution of **11** in CH_2Cl_2 at 15°C. Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86 and SHELXTL PLUS). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method. The positions of the hydrogen atoms were calculated according to ideal geometry (distance C−H = 0.95 Å) and were refined by the riding method with fixed isotropic *U* values. For other details see Table 1.

Table 1. Crystallographic data for **7** and **11**

	7	**11**
Formula	$C_{18}H_{30}ClO_2OsP$	$C_{35}H_{43}OOsP$
Mol. mass	535.07	700.90
Cryst. size [mm]	0.1 × 0.1 × 0.2	0.2 × 0.2 × 0.4
Cryst. system	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	$Pca2_1$ (No. 29)
a [Å]	14.214(7)	15.588(4)
b [Å]	15.442(8)	17.181(4)
c [Å]	9.221(6)	11.036(3)
α [°]	90	90
β [°]	94.64(5)	90
γ [°]	90	90
V [Å^3]	2017(2)	2995(1)
Z	4	4
$d_{calcd.}$ [g cm^{-1}]	1.726	1.575
Diffractometer	Siemens R3m/V	Enraf-Nonius CAD4
Radiation (graphite-monochromated)	Mo-K_α	Mo-K_α
T [K]	293	223
μ [cm^{-1}]	65.6	44.1
Transmission min./max.	0.064/0.112	0.7854/0.9995
h, *k*, *l*	18, 20, ± 11	20, 22, 14
Scan method	Wyckoff	ω/2θ
2θ(max) [°]	55	56
Absorption correction	Ψ scan	Ψ scan
Total no. of reflexions scanned	4957	3983
No. of unique reflexions	4608	3983
No. of observed reflexions [$F_o > 3\sigma(F_o)$]	3859	3319
No. of parameters refined	209	342
R	0.034	0.047
R_w	0.031	0.049
Reflexions/parameter ratio	18.46	9.70
Residual electron density [e Å^{-3}]	+1.59/-1.14	+2.52/-4.36[26]

☆ Dedicated to Professor *Herbert W. Roesky* on the occasion of his 60th birthday.

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[25] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59078, the names of the authors, and the journal citation.
[26] The six highest residual peaks of the final Fourier synthesis are within the range of 1.0 Å around the osmium atom.

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