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Osmium(II) and Osmium(IV) Complexes with Phosphane–Ethers, –Esters, and –Amines as Mono- and Bidentate Ligands

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Dedicated to Professor Max Herberhold on the occasion of his 70th birthday

Keywords: Osmium / Phosphane–Ethers / Phosphane–Esters / Phosphane–Amines / Vinylidene complexes

The six-coordinate dihydridoosmium(IV) complex $[OsH_2Cl_2(PiPr_3)_2]$ (**1**) reacted with the hemilabile chelating phosphanes $iPr_2PCH_2CH_2OMe$ and $iPr_2PCH_2CO_2R$ (R = Me, Et) at room temperature to give the substitution products $[OsH_2Cl_2(iPr_2PCH_2CH_2OMe)_2]$ (**2**) and $[OsH_2Cl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(=O)OR\}\{\kappa(P)\text{-}iPr_2PCH_2CO_2R\}]$ (**3**, **4**) in good to excellent yields. Treatment of **1** with $iPr_2PCH_2CH_2NMe_2$ led to the displacement of only one $PiPr_3$ ligand and gave $[OsH_2Cl_2(PiPr_3)(iPr_2PCH_2CH_2NMe_2)]$ (**5**). The reaction of **1** with $iPr_2PCH_2CH_2OMe$ and $iPr_2PCH_2CO_2R$ (R = Me, Et) at elevated temperature afforded the osmium(II) complexes $[OsCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}_2]$ (**6**) and $[OsCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(=O)OR\}_2]$ (**7**, **8**), which were also obtained on heating the osmium(IV) precursor **3** or the labile 1:1 adducts of **3** and **4** with ethene in benzene under reflux. The dihydrido compounds **2** and **3** reacted with CO at room temperature to give initially the octahedral all-*cis*-configured complexes $[OsCl_2(CO)_2\{\kappa(P)\text{-}iPr_2PCH_2CH_2OMe\}_2]$ (**11a**) and $[OsCl_2(CO)_2\{\kappa(P)\text{-}iPr_2PCH_2CO_2Me\}_2]$ (**12a**), which rearrange to the more stable *cis*,*cis*,*trans* isomers **11b** and **12b** in benzene under reflux. The all-*trans* isomer **11c** and the monocarbonyl complexes *trans*,*trans*-$[OsCl_2(CO)\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(=O)OR\}\{\kappa(P)\text{-}iPr_2PCH_2CO_2R\}]$ (**13**, **14**) were prepared by passing CO through a solution of **6**–**8** in benzene or toluene/dichloromethane at room temperature. While the osmium(IV) compounds **3**, **4** as well as the osmium(II) complexes **7**, **8** reacted with CN*t*Bu to give the neutral complexes *cis*,*cis*,*trans*-$[OsCl_2(CNtBu)_2\{\kappa(P)\text{-}iPr_2PCH_2CO_2R\}_2]$ (**15**, **16**), treatment of **5** with CN*t*Bu afforded the ionic product $[OsHCl(CNtBu)_2(PiPr_3)(iPr_2PCH_2CH_2NHMe_2)]Cl$ (**17**). The reaction of **7** with Ph_2CN_2 did not lead to the formation of a (carbene)osmium(II) compound but gave the dinitrogen complex *trans*,*trans*-$[OsCl_2(N_2)\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(=O)OMe\}(\kappa(P)\text{-}iPr_2PCH_2CO_2Me)]$ (**18**) instead. The structurally related vinylidene complexes *trans*,*trans*-$[OsCl_2(=C=CHPh)\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}\{\kappa(P)\text{-}iPr_2PCH_2CH_2OMe\}]$ (**19a**) and *trans*,*trans*-$[OsCl_2(=C=CHPh)\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(=O)OR\}\{\kappa(P)\text{-}iPr_2PCH_2CO_2R\}]$ (**20**, **21**) were prepared from **6**–**8** and PhC≡CH as starting materials. The *cis*,*cis*-configured compound $[OsCl_2(=C=CHPh)(PiPr_3)\{\kappa^2(P,N)\text{-}iPr_2PCH_2CH_2NMe_2\}]$ (**22**) was obtained analogously from **5** and phenylacetylene.

Introduction

In the context of our investigations to prepare highly reactive transition-metal complexes with coordinatively unsaturated metal centers, we reported the synthesis of the dichloridodihydridoosmium(IV) compounds $[OsH_2Cl_2(PR_3)_2]$ (PR_3 = $PiPr_3$, $PtBu_2Me$, PCy_3), in which the osmium atom, although six-coordinate, has only 16 instead of 18 electrons in its valence shell.[1,2] We as well as Esteruelas, Caulton and co-workers showed that these compounds have a diverse chemistry which opened the gate not only to (carbyne)- but also to (vinylidene)osmium complexes.[3,4]

The aim of the present work was to find out whether dichloridodihydridoosmium(IV) compounds containing hemilabile, potentially chelating phosphane ligands were also accessible and could be converted into the osmium(II) compounds $[OsCl_2(P\text{–}X)_2]$ (P–X = $iPr_2PCH_2CH_2OR$, $iPr_2PCH_2CO_2R$, $iPr_2PCH_2CH_2NMe_2$). Previous attempts in our laboratory to prepare the corresponding phosphane–ether complex $[OsCl_2(P\text{–}O)_2]$ (P–O = $iPr_2PCH_2CH_2OMe$) from $[OsCl_2(PPh_3)_3]$ and $iPr_2PCH_2CH_2OMe$ led unexpectedly to the formation of the (carbene)osmium complex $[OsCl_2\{\kappa^2(P,C)\text{-}(=CHOCH_2CH_2PiPr_2)\}\{\kappa^2(P,O)\text{-}iPr_2PCH_2CH_2OMe\}]$ by double metalation of the methoxy group of the phosphane.[5] The phosphane–amine $iPr_2PCH_2CH_2NMe_2$ behaves similarly.

In this paper we describe the synthesis of a series of osmium(II) and osmium(IV) compounds with hemilabile phosphane ligands which, as expected, are highly reactive and can serve as starting materials for the preparation of new carbonyl-, (isocyanide)- and (vinylidene)osmium(II) complexes.[6]

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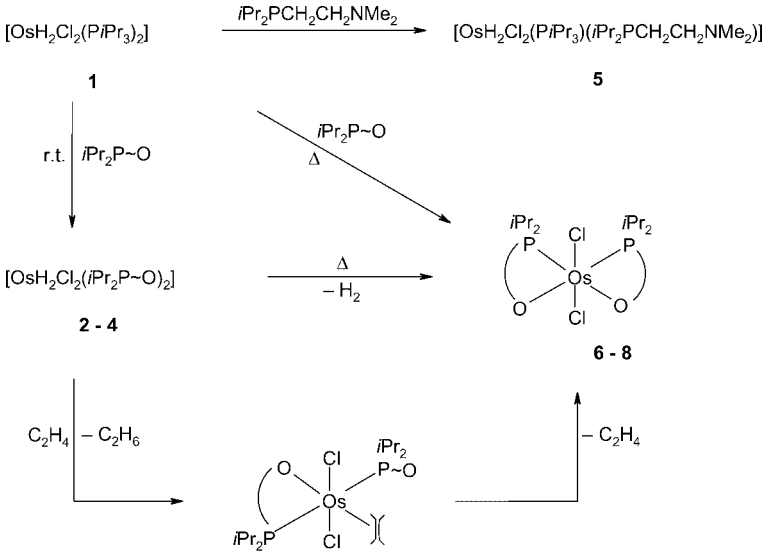
Results and Discussion

The reactions of the dichloridodihydridoosmium(IV) complex $[OsH_2Cl_2(PiPr_3)_2]$ (**1**) with the phosphane–ether $iPr_2PCH_2CH_2OMe$ and the phosphane–esters $iPr_2PCH_2CO_2R$ (R = Me, Et) in pentane or hexane at room temperature proceed smoothly and give the substitution products **2**–**4** in good to excellent yields (Scheme 1). These compounds are pale-yellow or colorless, only moderately air-sensitive solids, for which correct elemental analyses were obtained. The ^1H and ^{13}C NMR spectra of **2**–**4** in $CDCl_3$ or C_6D_6 display at room temperature only one set of signals for the protons and carbon atoms of the phosphane ligands, indicating that these are stereochemically equivalent under those conditions. The ^{31}P NMR spectra of **2**–**4** show in each case one singlet which, due to $^1H,^{31}P$ coupling, becomes a triplet in off-resonance.

The IR spectra of the phosphane–ester complexes **3** and **4** display two equally strong ν(C=O) stretching modes at 1720 and 1630 cm^{-1} (for **3**) and 1755 and 1665 cm^{-1} (for **4**), of which those at higher wavenumbers are assigned in analogy to the data of the phosphane–esters $iPr_2PCH_2CO_2R$ (R = Me, Et) to a free, noncoordinated C=O unit.[7] This indicates that in the ground state of compounds **3** and **4** one phosphane ligand is coordinated in a monodentate and the other in a bidentate fashion. In agreement with this proposal, the singlets observed in the room-temperature ^{31}P NMR spectra of **3** and **4** are split at –90 °C into two slightly broadened resonances at δ = 18.0 and 9.7 ppm (for **3**) and δ = 19.0 and 9.8 ppm (for **4**) of about equal intensity. The small $^{31}P,^{31}P$ coupling is consistent with a *cis* position of the $iPr_2PCH_2CO_2R$ ligands. The ^1H NMR spectrum of **3** at –90 °C in $[D_8]$toluene shows two singlets for the methoxy protons of the ester functionality, which supports the proposed different coordination mode of the phosphanes. It is conceivable that not only the phosphane–ester complexes **3** and **4** but also the phosphane–ether analogue **2** is fluxional on the NMR time scale in solution at room temperature.

In contrast to $iPr_2PCH_2CH_2OMe$ and $iPr_2PCH_2CO_2R$, the phosphane–amine $iPr_2PCH_2CH_2NMe_2$ reacts with the starting material **1** at room temperature to give compound **5**, which still contains one $PiPr_3$ ligand. Even with an excess of the phosphane–amine, the coordinated triisopropylphosphane could not be displaced. Treatment of **1** with $iPr_2PCH_2CH_2NMe_2$ in refluxing hexane or benzene did also not lead to the formation of $[OsH_2Cl_2(iPr_2PCH_2CH_2NMe_2)_2]$ or $[OsCl_2(iPr_2PCH_2CH_2NMe_2)_2]$, but afforded the aminocarbene complex $[OsCl_2\{\kappa^2(C,N)\text{-}(=CHN(Me)CH_2CH_2PiPr_2)\}\{\kappa^2(P,N)\text{-}iPr_2PCH_2CH_2NMe_2\}]$, probably via $[OsCl_2(iPr_2PCH_2CH_2NMe_2)_2]$ as the intermediate.[5] The ^{31}P NMR spectrum of **5** displays two broadened resonances at δ = 30.8 and 14.2 ppm, which indicates the coordination of two different phosphane ligands. The ^1H NMR spectrum of **5** shows a sharp triplet for the two hydrido ligands, the chemical shift of which (δ = –12.22 ppm) is nearly identical to that of the hydrido signal of **2** (δ = –12.39 ppm). Therefore, it is likely that the stereochemistry of compounds **2** and **5** is the same.

The reaction of **1** with $iPr_2PCH_2CH_2OMe$ and $iPr_2PCH_2CO_2R$ (R = Me, Et) in hexane at 110 °C in a closed vessel gave instead of the osmium(IV) compounds **2**–**4** the osmium(II) complexes **6**–**8** by elimination of dihydrogen. They are probably formed via the osmium(IV)



	P~O
2, 6	PCH_2CH_2OMe
3, 7, 9	PCH_2CO_2Me
4, 8, 10	PCH_2CO_2Et

Scheme 1.

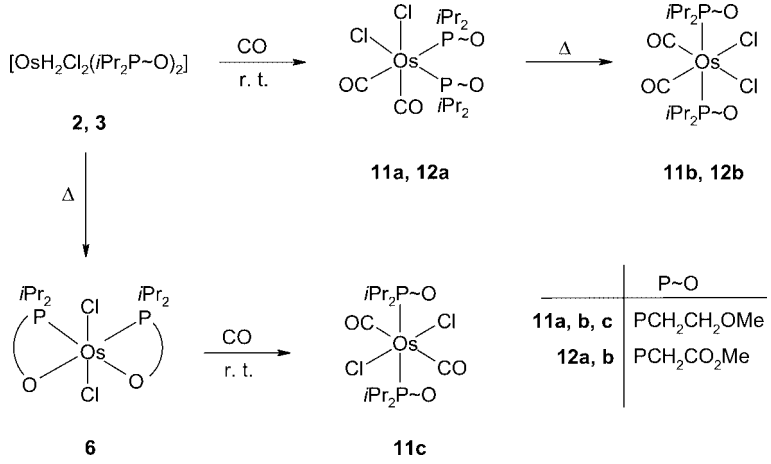
compounds **2**–**4**, as was shown by the thermal conversion of **3** to **6** in benzene under reflux. An alternative method of synthesis of **6**–**8** consists of the reaction of **2**–**4** in benzene in the presence of ethene, which affords the required osmium(II) complexes in nearly quantitative yield. If the conversion was carried out in C_6D_6 in an NMR tube, ethane could be detected as a by-product. Under these conditions it was also possible to observe the formation of the ethene derivatives **9** and **10** as intermediates. Similar to the IR spectra of **3** and **4**, those of **9** and **10** also display two ν(C=O) stretching modes at 1710 and 1605 cm^{-1} (for **9**) and 1705 and 1610 cm^{-1} (for **10**), which is consistent with the coordination of one monodentate and one bidentate $iPr_2PCH_2CO_2R$ ligand. This proposal is supported by the ^{31}P NMR spectra of **9** and **10**, in which two signals corresponding to an AB spin system are observed. The large $^{31}P,^{31}P$ coupling constants of 324.0 Hz (for **9**) and 325.6 Hz (for **10**) suggest that the two phosphorus atoms are *trans*-disposed. The ^1H NMR spectra of **9** and **10** show in each case a single resonance at δ = 4.01 ppm (for **9**) and δ = 4.05 ppm (for **10**), which is split into a triplet due to $^1H,^{31}P$ coupling. Since for a rigid structure two signals for the ethene protons should be observed, we assume that a rapid rotation of the ethene ligand around the metal–olefin axis occurs, making these protons equivalent. With regard to the stereochemistry of the six-coordinate osmium(II) complexes **6**–**8**, we favor a *cis*,*cis*,*trans* configuration (see Scheme 1), which is not only consistent with the spectroscopic data but also with the molecular structure of the related ruthenium(II) compound $[RuCl_2\{\kappa^2(P,O)\text{-}Ph_2PCH_2CH_2OMe\}_2]$.[8]

Similar to $[OsH_2Cl_2(PtBu_2Me)_2]$,[1] the osmium(IV) complexes **2** and **3** react with CO at room temperature within a few minutes by elimination of H_2. While with **2** as starting material the all-*cis* isomer **11a** (Scheme 2) is exclusively formed, in the case of **3** a mixture of **12a** (all-*cis*) and **12b** (*cis*,*cis*,*trans*) is generated under these conditions. Typical spectroscopic features for **11a** are two CO stretching modes in the IR spectrum, two doublet resonances in the ^{31}P NMR spectrum, two singlets for the methoxy protons in the ^1H NMR spectrum, and two signals for the carbon atoms of the stereochemically different CO ligands in the ^{13}C NMR spectrum. One of these ^{13}C NMR signals is split into a triplet and assigned to the carbonyl ligand *trans* to the chlorido ligand, while the other is split into a doublet of doublets and assigned to the carbonyl ligand *cis*-disposed to one and *trans*-disposed to the other phosphorus atom. The ^1H and ^{31}P NMR spectroscopic data of **12a** are very similar to those of **11a**.

If a solution of **11a** in benzene is stirred under reflux for 3 h, a complete conversion of the all-*cis* to the *cis*,*cis*,*trans* isomer **11b** occurs. The related complex **12b** is obtained upon heating a solution of the isomeric mixture of **12a** and **12b** in refluxing benzene for 5 h. Like the dibromidoosmium(II) compounds all-*trans*-$[OsBr_2(CO)_2\{\kappa(P)\text{-}R_2PCH_2CH_2OMe\}_2]$ (R = Ph, Cy), prepared by Lindner and co-workers,[9] the stereochemically different dichlorido complexes **11a**,**12a** and **11b**,**12b** are white solids, which are air-stable and readily soluble in benzene, toluene and chlorinated aliphatic hydrocarbons. In contrast to **11a** and **12a**, the ^{31}P NMR spectra of **11b** and **12b** display only one resonance for the equivalent phosphorus atoms and the ^1H NMR spectra of **11b** and **12b** only one signal for the methoxy protons. The IR spectra of **11b** and **12b** show two CO stretching modes, which is in agreement with a *cis* disposition of the carbonyl ligands.

In addition to **11a** and **11b** a third isomer **11c** of the general composition $[OsCl_2(CO)_2\{\kappa(P)\text{-}iPr_2PCH_2CH_2OMe\}_2]$ was obtained by passing a slow stream of CO through a solution of **6** in benzene at room temperature. The proposed all-*trans* configuration of **11c** is supported by the appearance of only one ν(C=O) band in the IR spectrum and of a single resonance in the ^{31}P NMR spectrum. The $^{31}P,^{187}Os$ coupling constant of 162.8 Hz is also in agreement with the *trans* position of the phosphorus atoms.[10]

In contrast to **6**, the corresponding phosphane–ester complexes **7** and **8** react with CO in toluene/dichloromethane at room temperature to give the monocarbonyl compounds **13** and **14** as yellow, air-stable solids in about 75% yield. Even if the solutions are stirred under CO for 12 h,

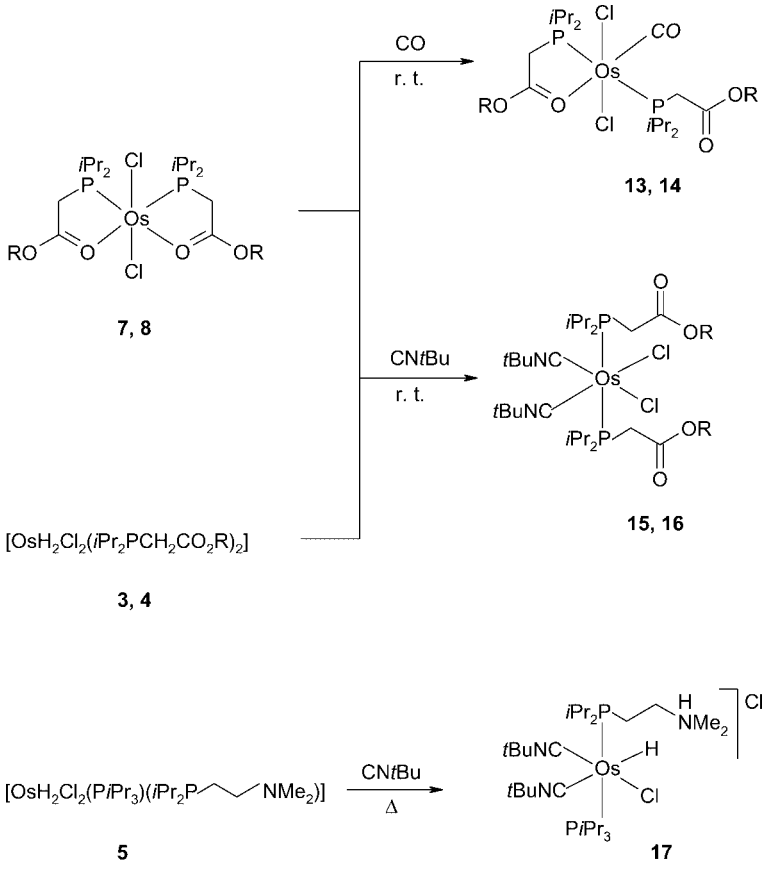


Scheme 2.

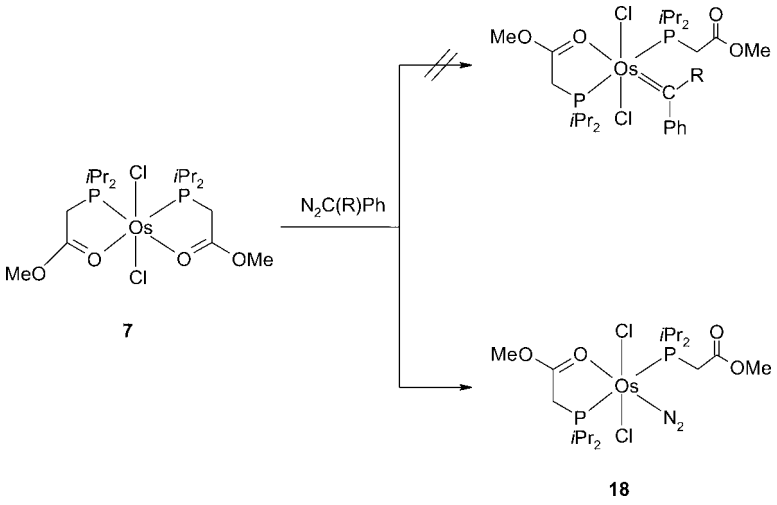
the expected dicarbonyl complexes, structurally related to **11a**, **11b** or **11c**, are not formed. The IR spectra of **13** and **14** display besides the strong ν(CO) band for the carbonyl ligand at 1915 cm^{-1} (for **13**) and 1905 cm^{-1} (for **14**) two ν(C=O) stretching modes for the free and the coordinated C=O ester function at 1710 and 1615 cm^{-1} (for **13**) and 1705 and 1610 cm^{-1} (for **14**). The observation of an AB spin system in the ^{31}P NMR spectra supports the different bonding mode of the $iPr_2PCH_2CO_2R$ ligands and the size of the $^{31}P,^{187}Os$ coupling constant the *trans* position of the phosphorus atoms. If we take this (and the supposed octahedral structure) into consideration, there remain two alternatives for the coordination site of the carbonyl ligand: it could be *trans* to the chlorido ligand or *trans* to the oxygen atom of the C=O ester group. Since the splitting pattern of the signals of the $CHCH_3$ protons and the $CHCH_3$ carbon atoms in the ^1H and ^{13}C NMR spectra of **13** and **14** indicate the presence of a mirror plane in the molecules, the second alternative, shown in Scheme 3, should be correct.

Under the same conditions, under which the monocarbonyl complexes **13** and **14** are obtained, the osmium(II) precursors **7** and **8** react with *tert*-butyl isocyanide to afford the disubstituted compounds **15** and **16**. Based on the NMR spectroscopic data, we assume that exclusively the *cis*,*cis*,*trans* isomers are formed. In analogy to the structurally related dicarbonyl derivatives **11b** and **12b**, the ^{31}P NMR spectra of **15** and **16** display one singlet for the equivalent phosphorus atoms, while the IR spectra show two ν(C≡N) stretching modes in the expected region. We note that prior to our work on the reactivity of the osmium(II) compounds **7** and **8**, we found that the analogous ruthenium(II) complex $[RuCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2CO_2Me\}_2]$ reacts with CO to give the monocarbonyl compound $[RuCl_2(CO)\{\kappa(P)\text{-}iPr_2PCH_2CO_2Me\}\{\kappa^2(P,O)\text{-}iPr_2PCH_2CO_2Me\}]$ whereas with *t*BuNC the bis(isocyanide) complex $[RuCl_2(CNtBu)_2\{\kappa(P)\text{-}iPr_2PCH_2CO_2Me\}_2]$ (having in contrast to **15** the all-*trans* configuration) was obtained. The corresponding 1:1 adduct $[RuCl_2(CNtBu)\{\kappa(P)\text{-}iPr_2PCH_2CO_2Me\}\{\kappa^2(P,O)\text{-}iPr_2PCH_2CO_2Me\}]$ was isolated as an intermediate.[11]

The dihydridoosmium(IV) compounds **3** and **4** behave similarly to **7** and **8** and upon treatment with excess *t*BuNC in benzene at room temperature give the bis(isocyanide) complexes **15** and **16** in good to excellent yield. In contrast, the reaction of the phosphane–amine complex **5** with *tert*-butyl isocyanide in benzene under reflux led to the formation of the ionic product **17**, the conductivity of which in nitromethane is in agreement with that of a 1:1 electrolyte.



Scheme 3.

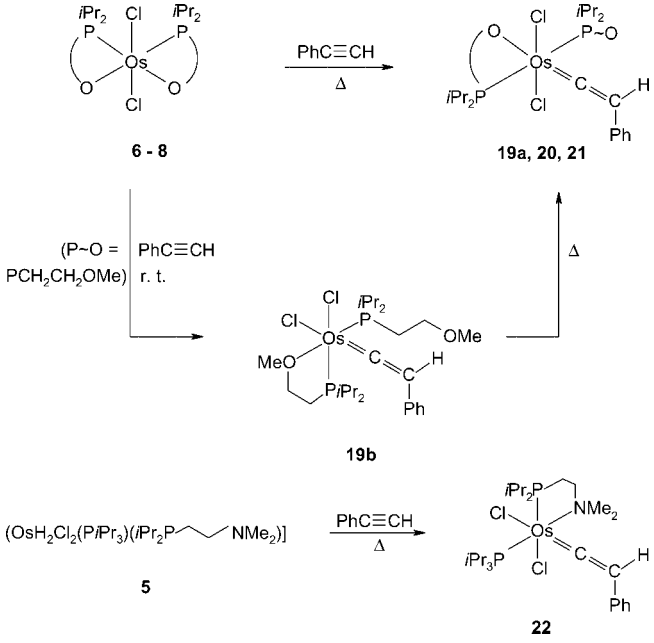


Scheme 4.

The ^{1}H NMR spectrum of **17** displays for the hydrido ligand a resonance at δ = –7.48 ppm, which due to the coupling with two different ^{31}P nuclei is split into a doublet of doublets. The presence of the OsH unit is also indicated by the {^{1}H}-decoupled ^{31}P NMR spectrum, in which the two singlet signals of the AB spin system are split into doublets. The large ^{31}P,^{31}P coupling constant of 245.8 Hz supports the *trans* position of the two phosphane ligands.

Attempts to prepare a (carbene)osmium(II) complex [$OsCl_2$(=CRPh){κ(*P*)-*i*$Pr_2PCH_2CO_2Me$}{κ^2(*P*,*O*)-*i*$Pr_2PCH_2CO_2Me$}] (R = H, Ph) from **6** and phenyl- or diphenyldiazomethane led unexpectedly to the formation of the dinitrogen compound **18** (see Scheme 4). A similar observation was already made in the course of studies on the reactivity of the dimer [RhCl(P*i*$Pr_3)_2]_2$, which upon treatment with $PhCHN_2$ gave the mononuclear complex *trans*-[RhCl(N_2)(P*i*$Pr_3)_2$].[12] As we failed to separate **18** from organic by-products by column chromatography or fractional crystallization, the dinitrogenosmium(II) compound was characterized spectroscopically. Diagnostic for the coordination of the N_2 ligand is the N–N stretching mode at 2060 cm^{-1} in the IR spectrum, which appears at a similar position as for the complexes [$OsCl_2(N_2)(L_3)$] (L = PMe_2Ph, PEt_2Ph, PEt_3)[13] and is consistent with an "end-on" coordination of the dinitrogen molecule.[14] Since the IR spectrum of **18** displays two ν(C=O) stretching modes at almost the same wavenumbers as for the monocarbonyl complex **13**, and since also the ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data of the two compounds are quite similar, we assume that the two chlorido ligands, the two phosphorus atoms, and the ester C=O group and the N_2 ligand are *trans*-disposed.

The reactions of the bis(chelate) osmium(II) precursors **6**–**8** with phenylacetylene in benzene under reflux gave the six-coordinate vinylidene complexes **19a**, **20** and **21** in 48–95% yield (Scheme 5). They are possibly formed via the isomeric alkyne- and alkynyl(hydrido) compounds as intermediates, although in contrast to the reactions of [RhCl{κ(*P*)-*i*$Pr_2PCH_2CH_2OMe$}{κ^2(*P*,*O*)-*i*$Pr_2PCH_2CH_2OMe$}] and [IrCl(C_2H_4){κ(*P*)-*i*$Pr_2PCH_2CO_2Me$}$_2$] with phenylacetylene,[15,16] species with an Os(PhC≡CH) or OsH(C≡CPh) unit could not be observed. The most characteristic spectroscopic features of **19a**, **20** and **21** are (1) the signal of the =C*H*Ph proton at $\delta \approx$ 2.0–2.6 ppm in the ^{1}H NMR spectra and (2) the low-field resonances at δ = 291.8 and 108.9 ppm (for **19a**), 297.1 and 109.3 ppm (for **20**), and 297.3 and 108.3 ppm (for **21**) in the ^{13}C NMR spectra. The latter are assigned to the α-C and β-C vinylidene carbon atoms. The chemical shifts of the ^{1}H and ^{13}C NMR signals are quite similar to those of the related five-coordinate phenylvinylidene complexes [$OsCl_2$(=C=CHPh)(P*i*$Pr_3)_2$][17] and [$OsCl_2$(=C=CHPh)($PPh_3)_2$].[18]



Scheme 5.

At room temperature, compounds **19a**, **20** and **21** are fluxional in solution, as can be seen by the appearance of one broad singlet in the ^{31}P NMR spectra. The dynamic

process is frozen out at low temperature, and thus in the spectra of **19a** (in $CDCl_3$ at –90 °C), **20** (in $C_6D_5CD_3$ at –80 °C), and **21** (in $C_6D_5CD_3$ at –20 °C) the typical pattern of an AB spin system is observed. The large $^{31}P,^{31}P$ coupling constants of about 320–333 Hz are consistent with the *trans* position of the phosphorus atoms. From the coalescence temperatures and the difference in the chemical shifts of the two signals $\Delta G^{\neq}$ values of approximately 40 kJ mol^{-1} (for **19a**), 51 kJ mol^{-1} (for **20**), and 54 kJ mol^{-1} (for **21**) can be calculated. The observed phenomenon is reversible and explained by a rapid exchange in the chelating behavior of the two phosphane ligands. It is interesting to note that neither the monocarbonyl complexes **13** and **14** nor the dinitrogen derivative **18** are fluxional in solution at room temperature.

The proposed stereochemistry of **20** with the phosphanes and the chlorido ligands in *trans* disposition was confirmed by a single-crystal X-ray diffraction investigation.[19] The Os–C–C unit is almost linear [176.7(5)°] and the Os–C bond length [1.802(6) Å] slightly shorter than in some other (vinylidene)osmium(II) complexes such as $[OsCl_2(=C=CHPh)(P\textit{i}Pr_3)\{\kappa^2(\textit{P},\textit{N})\text{-}\textit{i}Pr_2PCH_2CH_2NMe_2\}]$ [1.82(1) Å],[3b] $[OsCl(=C=CHSiMe_3)(CH=CHSiMe_3)(P\textit{i}Pr_3)_2]$ [1.82(3) Å],[20] $[OsCl(=C=CHPh)(PPh_3)\{1,3\text{-}(PPh_2CH_2)_2C_6H_4\}]$ [1.819(6) Å],[21] and $[OsCl_2(=C=CHPh)(H_2O)(PPh_3)_2]$ [1.812(7) Å].[18] The smallest corner–center–corner angle of the octahedron is found for P–Os–O (80.0(1)°], which is probably due to the ring strain in the five-membered $OsPC_2O$ chelating system.

If the reaction of **6** with phenylacetylene in benzene was carried out at room temperature instead of under reflux, the red, moderately air-stable *cis,cis*-configured compound **19b** was generated (see Scheme 5). Under the same conditions, **7** and **8** are inert towards PhC≡CH. Upon heating, **19b** rearranges quickly to the thermodynamically preferred isomer **19a**. In contrast to **19a**, the ^{31}P NMR spectrum of **19b** displays two sharp doublets at room temperature, which indicates that in solution the molecule is non-fluxional on the NMR time scale under these conditions. The chemical shift of the two doublets (δ = 19.0 and –10.4 ppm) and the $^{31}P,^{31}P$ coupling constant (9.2 Hz) are similar to those of the phenylvinylidene complex **22** (δ = 15.4 and –11.2 ppm, $^2J_{P,P}$ = 6.7 Hz), which was prepared from **5** and excess phenylacetylene in benzene under reflux and characterized crystallographically.[3b] The X-ray crystal structure analysis of **22** revealed a slightly distorted octahedral geometry with the phosphorus atoms and the chlorido ligands in *cis* disposition and bond angles Cl–Os–Cl and P–Os–P of 85.10(9)° and 105.80(9)°, respectively. The P–Os–N angle of the chelate ring amounts to 82.4(1)° and is thus similar to the corresponding P–Os–O angle of **20**.

Conclusion

The present work has shown that osmium(II) complexes of the general composition $[OsCl_2(P\text{–}O)_2]$ with the phosphane–ether $\textit{i}Pr_2PCH_2CH_2OMe$ and the phosphane–esters $\textit{i}Pr_2PCH_2CO_2R$ (R = Me, Et) as chelate ligands are accessible from dichloridodihydridoosmium(IV) compounds as precursors. Due to the lability of the Os–O bond, the osmium(II) complexes react smoothly with carbon monoxide and *tert*-butyl isocyanide by partial opening of the chelate ring. Depending on the reaction conditions, different isomers of the dicarbonyl compounds $[OsCl_2(CO)_2(\textit{i}Pr_2PCH_2CH_2OMe)_2]$ and $[OsCl_2(CO)_2(\textit{i}Pr_2PCH_2CO_2Me)_2]$ are formed. The monocarbonyl complexes $[OsCl_2(CO)(\textit{i}Pr_2PCH_2CO_2R)_2]$ and the dinitrogen derivative $[OsCl_2(N_2)(\textit{i}Pr_2PCH_2CO_2Me)_2]$, each of them containing one monodentate and one bidentate phosphane ligand, have also been obtained. The reactions of the chelate compounds $[OsCl_2(P\text{–}O)_2]$ with phenylacetylene afford the phenylvinylidene complexes $[OsCl_2(=C=CHPh)(P\text{–}O)_2]$, which in solution at room temperature are fluxional on the NMR time scale. The phosphane–amine complex $[OsCl_2(=C=CHPh)(P\textit{i}Pr_3)(\textit{i}Pr_2PCH_2CH_2NMe_2)]$ was prepared from $[OsH_2Cl_2(P\textit{i}Pr_3)(\textit{i}Pr_2PCH_2CH_2NMe_2)]$ and phenylacetylene and characterized crystallographically.

Experimental Section

General: All operations were carried out under argon using Schlenk techniques. The osmium complex **1**[1] and the phosphane derivatives $\textit{i}Pr_2PCH_2CH_2OMe$,[16] $\textit{i}Pr_2PCH_2CH_2NMe_2$,[16] and $\textit{i}Pr_2PCH_2CO_2R$ (R = Me, Et)[7] were prepared as described in the literature. NMR: Bruker AC 200 and AMX 400. IR: Perkin–Elmer 397 and 1320. MS: Varian CH 7 MAT (70 eV). The molar conductivity Λ_M was determined in nitromethane. Melting points were determined by DTA. Abbreviations used: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; vt: virtual triplet; br.: broad signal; $N = {}^3J_{P,H} + {}^5J_{P,H}$ or ${}^2J_{P,C} + {}^4J_{P,C}$.

1. Preparation of $[OsH_2Cl_2(\textit{i}Pr_2PCH_2CH_2OMe)_2]$ (2): A suspension of **1** (145 mg, 0.25 mmol) in pentane (10 mL) was treated with $\textit{i}Pr_2PCH_2CH_2OMe$ (142 μL, 0.75 mmol) and stirred at room temperature for 24 h. A pale-yellow solid precipitated, which was filtered, washed three times with 5-mL portions of pentane and dried; yield 144 mg (94%); m.p. 65 °C (decomp.). MS: *m*/*z* (I_r) = 614 (0.4) [M^+], 578 (2.8) [M^+ – HCl], 542 (2.4) [M^+ – 2 HCl]. IR (KBr): $\tilde{\nu}$ = 2225 [ν(OsH)] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.65 (m, 4 H, OCH_2), 3.49 (s, 6 H, OCH_3), 2.53 (m, 4 H, $PCHCH_3$), 1.99 (m, 4 H, PCH_2), 1.24 (dd, $^3J_{P,H}$ = 16.2, $^3J_{H,H}$ = 7.1 Hz, 12 H, $PCHCH_3$), 1.23 (dd, $^3J_{P,H}$ = 13.9, $^3J_{H,H}$ = 7.0 Hz, 12 H, $PCHCH_3$), –12.39 (t, $^2J_{P,H}$ = 26.8 Hz, 2 H, OsH_2) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 72.4 (s, OCH_2), 60.5 (s, OCH_3), 28.0 (d, $^1J_{P,C}$ = 35.7 Hz, $PCHCH_3$), 27.3 (d, $^1J_{P,C}$ = 33.7 Hz, PCH_2), 19.2, 18.8 (2 s, $PCHCH_3$) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 25.2 (s, t in off-resonance) ppm. $C_{18}H_{44}Cl_2O_2OsP_2$ (615.7): calcd. C 35.11, H 7.20; found C 35.38, H 7.32.

2. Preparation of $[OsH_2Cl_2\{\kappa^2(\textit{P},\textit{O})\text{-}\textit{i}Pr_2PCH_2C(=O)OMe\}\{\kappa(\textit{P})\text{-}\textit{i}Pr_2PCH_2CO_2Me\}]$ (3): This compound was prepared as described for **2**, with **1** (134 mg, 0.29 mmol) and $\textit{i}Pr_2PCH_2CO_2Me$ (135 μL, 0.69 mmol) as starting materials and hexane (10 mL) as solvent. Colorless solid; yield 106 mg (72%); m.p. 80 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2140 [ν(OsH)], 1720, 1630 [ν(C=O)] cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 6 H, OCH_3), 3.31 (d, $^2J_{P,H}$ = 9.9 Hz, 4 H, PCH_2), 2.38 (m, 4 H, $PCHCH_3$), 1.29 (dd, $^3J_{P,H}$ = 15.9, $^3J_{H,H}$ = 7.0 Hz, 12 H, $PCHCH_3$), 1.13 (dd, $^3J_{P,H}$ = 14.5, $^3J_{H,H}$ = 6.7 Hz, 12 H, $PCHCH_3$), –9.97 (t, $^2J_{P,H}$ = 18.2 Hz, 2 H, OsH_2)

ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 177.4 (s, *C*O_2Me), 53.9 (s, OCH_3), 31.8 (d, $^1J_{P,C}$ = 25.0 Hz, PCH_2), 27.8 (d, $^1J_{P,C}$ = 32.7 Hz, P*C*HCH$_3$), 18.8, 18.5 (2 s, PCH*C*H$_3$) ppm. ^{31}P NMR (36.2 MHz, C_6D_6, 295 K): δ = 15.8 (s, t in off-resonance) ppm. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 183 K): δ = 18.0, 9.7 (2 br., $J_{P,P}$ not resolved) ppm. $C_{18}H_{40}Cl_2O_4OsP_2$ (643.6): calcd. C 33.59, H 6.26; found C 33.54, H 6.22.

3. Preparation of [OsH$_2$Cl$_2${κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OEt}{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Et}] (4): This compound was prepared as described for **2**, with **1** (98 mg, 0.17 mmol) and *i*Pr$_2$PCH$_2$CO$_2$Et (120 μL, 0.51 mmol) as starting materials and hexane (10 mL) as solvent. Colorless solid; yield 99 mg (88%); m.p. 112 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2140 [ν(OsH)], 1755, 1665 [ν(C=O)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.25 (q, J = 4 H, $^3H_{H,H}$ = 7.1 Hz, OC*H*$_2$CH$_3$), 3.29 (d, $^2J_{P,H}$ = 9.8 Hz, 4 H, PCH_2), 2.32 (m, 4 H, PC*H*CH$_3$), 1.28 (dd, $^3J_{P,H}$ = 16.4, $^3J_{H,H}$ = 7.0 Hz, 12 H, PCHC*H*$_3$), 1.26 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$), 1.11 (dd, $^3J_{P,H}$ = 14.3, $^3J_{H,H}$ = 6.9 Hz, 12 H, PCHC*H*$_3$), –9.90 (t, $^2J_{P,H}$ = 18.3 Hz, 2 H, OsH$_2$) ppm. ^{31}P NMR (36.2 MHz, C_6D_6, 295 K): δ = 15.5 (s, t in off-resonance) ppm. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 183 K): δ = 19.0, 9.8 (2 br., $J_{P,P}$ not resolved) ppm. $C_{20}H_{44}Cl_2O_4OsP_2$ (671.6): calcd. C 35.77, H 6.60; found C 35.43, H 6.63.

4. Preparation of [OsH$_2$Cl$_2$(P*i*Pr$_3$)(*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$)] (5): This compound was prepared as described for **2**, with **1** (200 mg, 0.35 mmol) and *i*Pr$_2$PCH$_2$CH$_2$NMe$_2$ (218 μL, 1.03 mmol) as starting materials and benzene (8 mL) as solvent. Time of reaction 3 h. Pale-yellow solid; yield 185 mg (88%); m.p. 98 °C (decomp.). MS: *m*/*z* (I_r) = 576 (17.6) [M$^+$ – HCl)], 540 (0.8) [M$^+$ – 2 HCl]. IR (KBr): $\tilde{\nu}$ = 2180, 2140 [ν(OsH)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.80 (s, 6 H, NCH_3), 2.71, 2.57, 2.53 (3 m, 7 H, C*H*$_2$NMe$_2$ and PC*H*CH$_3$), 1.78 (m, 2 H, PCH_2), 1.30 (dd, $^3J_{P,H}$ = 13.2, $^3J_{H,H}$ = 7.2 Hz, 12 H, PCHC*H*$_3$ of P*i*Pr$_3$), 1.24 (dd, $^3J_{P,H}$ = 13.2, $^3J_{H,H}$ = 7.1 Hz, 6 H, PCHC*H*$_3$ of P*i*Pr$_2$), 1.21 (dd, $^3J_{P,H}$ = 14.5, $^3J_{H,H}$ = 7.2 Hz, 6 H, PCHC*H*$_3$ of P*i*Pr$_2$), –12.22 (dd, $^2J_{P,H}$ = $^2J_{P',H}$ = 18.2 Hz, 2 H, OsH$_2$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 63.3 (s, NCH_2), 54.0 (s, NCH_3), 30.2 (d, $^1J_{P,C}$ = 33.5 Hz, P*C*HCH$_3$ of P*i*Pr$_2$), 26.4 (d, $^1J_{P,C}$ = 31.5 Hz, P*C*HCH$_3$ of P*i*Pr$_3$), 20.9 (d, $^1J_{P,C}$ = 27.7 Hz, PCH_2), 19.7 (s, PCH*C*H$_3$ of P*i*Pr$_3$), 18.7, 18.6 (2 s, PCH*C*H$_3$ of P*i*Pr$_2$) ppm. ^{31}P NMR (162.0 MHz, $CDCl_3$, 295 K): δ = 30.8, 14.2 (2 br. s, both t in off-resonance) ppm. $C_{19}H_{47}Cl_2NOsP_2$ (612.6): calcd. C 37.25, H 7.73, N 2.29; found C 37.03, H 7.75, N 2.25.

5. Preparation of [OsCl$_2${κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$CH$_2$OMe}$_2$] (6). (a) A suspension of **1** (305 mg, 0.52 mmol) in hexane (70 mL) was treated dropwise with *i*Pr$_2$PCH$_2$CH$_2$OMe (351 μL, 1.57 mmol) and heated at 110 °C in a closed vessel for 4 h. After the reaction mixture was cooled to room temperature, an orange solid precipitated. The solution was concentrated to ca. 2 mL, the yellow precipitate was filtered, washed twice with 5-mL portions of pentane (0 °C) and dried; yield 154 mg (48%). **(b)** A stream of ethene was passed through a solution of **2** (206 mg, 0.34 mmol) in benzene (10 mL) for 1 min and, after the ethene was replaced by argon, the solution was stirred under reflux for 30 min. After the reaction mixture was cooled to room temperature, the solvent was evaporated. The remaining oily residue was suspended in pentane (5 mL, 0 °C) and the suspension was stirred until an orange solid precipitated. The isolation of the product was analogous to the one described in (a); yield 156 mg (76%); m.p. 96 °C (decomp.). ^{1}H NMR (200 MHz, C_6D_6): δ = 3.60 (s, 6 H, OCH_3), 3.56 (m, 4 H, OCH_2), 2.78 (m, 4 H, PC*H*CH$_3$), 1.84 (m, 4 H, PCH_2), 1.21 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 7.3 Hz, 12 H, N = 13.2 Hz), 1.19 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 7.4 Hz, 12 H, N = 13.0 Hz) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 75.0 (s, CH_2O), 62.6 (s, OCH_3), 29.0 (X part of an ABX spin system, $J_{A,X}$ = 28.6 Hz, P*C*HCH$_3$), 26.3 (X part of an ABX spin system, $J_{A,X}$ = 23.0 Hz, PCH_2), 20.7, 20.5 (2 s, PCH*C*H$_3$) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = –0.6 (s, $^1J_{Os,P}$ = 361.8 Hz) ppm. $C_{18}H_{42}Cl_2O_2OsP_2$ (613.6): calcd. C 35.23, H 6.86; found C 35.22, H 6.90.

6. Preparation of [OsCl$_2${κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OMe}$_2$] (7). (a) A suspension of **1** (119 mg, 0.20 mmol) in hexane (15 mL) was treated dropwise with *i*Pr$_2$PCH$_2$CO$_2$Me (120 μL, 0.16 mmol) and heated at 110 °C in a closed vessel for 4 h. The reaction mixture was worked up as described for **6**; yield 118 mg (90%). **(b)** A stream of ethene was passed through a solution of **3** (515 mg, 0.80 mmol) in benzene (20 mL) for 1 min and, after the ethene was replaced by argon, the solution was stirred under reflux for 1 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated. The remaining oily residue was dissolved in benzene (20 mL) and the solution refluxed again for 1 h. After the solution was cooled and the solvent removed, the residue was suspended in pentane (5 mL, 0 °C) and the suspension was stirred until an orange solid precipitated; yield 467 mg (91%). **(c)** A suspension of **3** (101 mg, 0.17 mmol) in benzene (20 mL) was heated under reflux for 12 h. The hot reaction mixture was filtered, the filtrate was brought to drynes in vacuo, and the oily residue worked up as described for **6**. Orange microcrystalline solid; yield 96 mg (87%); m.p. 69 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1630 [ν(C=O)] cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 3.41 (s, 6 H, OCH_3), 3.13 (d, $^2J_{P,H}$ = 9.1 Hz, 4 H, PCH_2), 2.43 (m, 4 H, PC*H*CH$_3$), 1.21 (dd, $^3J_{P,H}$ = 14.3, $^3J_{H,H}$ = 7.1 Hz, 12 H, PCHC*H*$_3$), 1.15 (dd, $^3J_{P,H}$ = 13.6, $^3J_{H,H}$ = 7.1 Hz, 12 H, PCHC*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 185.3 (s, *C*O_2Me), 55.0 (s, OCH_3), 35.7 (X part of an ABX spin system, $J_{A,X}$ = 23.7 Hz, PCH_2), 28.3 (X part of an ABX spin system, $J_{A,X}$ = 29.5 Hz, P*C*HCH$_3$), 19.1, 18.8 (2 s, PCH*C*H$_3$) ppm. ^{31}P NMR (162.0 MHz, C_6D_6): δ = 2.8 (s, $^1J_{Os,P}$ = 341.4 Hz) ppm. $C_{18}H_{38}Cl_2O_4OsP_2$ (641.5): calcd. C 33.70, H 5.97; found C 34.02, H 6.15.

7. Preparation of [OsCl$_2${κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OEt}$_2$] (8). (a) A suspension of **1** (353 mg, 0.61 mmol) in hexane (60 mL) was treated dropwise with *i*Pr$_2$PCH$_2$CO$_2$Et (434 μL, 1.82 mmol) and heated at 110 °C in a closed vessel for 4 h. The reaction mixture was worked up as described for **6**; yield 180 mg (44%). **(b)** A stream of ethene was passed through a solution of **4** (150 mg, 0.22 mmol) in benzene (10 mL) for 1 min and, after the ethene was replaced by argon, the solution was stirred under reflux for 1 h. The reaction mixture was worked up as described for **6**. Orange microcrystalline solid; yield 133 mg (89%); m.p. 56 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1630 [ν(C=O] cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 4.05 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, OC*H*$_2$CH$_3$), 3.14 (d, $^2J_{P,H}$ = 9.1 Hz, 4 H, PCH_2), 2.43 (m, 4 H, PC*H*CH$_3$), 1.22 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 7.7 Hz, 12 H, N = 14.6 Hz), 1.15 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 6.8 Hz, 12 H, N = 13.9 Hz), 0.88 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, OC*H*$_2$CH$_3$) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 185.3 (t, $^2J_{P,C}$ = 3.3 Hz, *C*O_2Et), 65.4 (s, O*C*H$_2$CH$_3$), 36.6 (X part of an ABX spin system, $J_{A,X}$ = 23.1 Hz, PCH_2), 30.0 (X part of an ABX spin system, $J_{A,X}$ = 29.6 Hz, P*C*HCH$_3$), 19.8, 19.6 (2 s, PCH*C*H$_3$), 14.5 (s, OCH_2CH_3) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 3.2 (s, $^1J_{Os,P}$ = 341.4 Hz) ppm. $C_{20}H_{42}Cl_2O_4OsP_2$ (669.6): calcd. C 35.87, H 6.32; found C 36.26, H 6.85.

8. Generation of [OsCl$_2$(C$_2$H$_4$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OMe}-{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (9): A slow stream of ethene was passed through a solution of **3** (40 mg, 0.06 mmol) in C_6D_6 (1 mL) in an NMR tube for 1 min. The ethene was replaced by argon, and the solution was stirred at 70 °C for 5 min. After it was cooled to room

temperature, the ^1H NMR spectrum indicated that a 1:1 mixture of **7** and **9** had formed. Attempts to separate the two compounds by chromatography or fractional crystallization failed. Data for **9**: IR (CH_2Cl_2): $\tilde{\nu}$ = 1710, 1605 [ν(C=O)], 1590 [ν(C=C)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 4.01 (t, $^3J_{P,H}$ = 3.7 Hz, 4 H, C_2H_4), 3.60 (br. d, $^2J_{P,H}$ = 6.6 Hz, 2 H, PCH_2), 3.29 (s, 6 H, OCH_3), 2.90, 2.61 (2 m, 2 H each, $PCHCH_3$), 2.89 (br. d, $^2J_{P,H}$ = 9.1 Hz, 2 H, PCH_2), 1.45, 1.15 (2 m, 12 H each, $PCHCH_3$) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): AB spin system: δ_A = –0.1, δ_B = –15.3 ($^2J_{P,P}$ = 324.0 Hz) ppm.

9. Generation of [$OsCl_2(C_2H_4)$\{κ²(*P*,*O*)-*i*$Pr_2PCH_2C(=O)OEt$\}-\{κ(*P*)-*i*$Pr_2PCH_2CO_2Et$\}] (10): This compound was generated as described for **9**, with **4** (38 mg, 0.05 mmol) and ethene as starting materials. The ^1H NMR spectrum indicated that a 2:1 mixture of **8** and **10** had formed. Attempts to separate the two compounds by chromatography or fractional crystallization failed. Data for **10**: IR (CH_2Cl_2): $\tilde{\nu}$ = 1705, 1610 [ν(C=O)], 1585 [ν(C=C)] cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 4.05 (t, $^3J_{P,H}$ = 3.1 Hz, 4 H, C_2H_4), 3.64 (d, $^2J_{P,H}$ = 7.2 Hz, 2 H, PCH_2), 2.95, 2.64 (2 m, 2 H each, $PCHCH_3$), 2.93 (br. d, $^2J_{P,H}$ = 9.0 Hz, 2 H, PCH_2), 1.50, 1.08 (2 m, 12 H each, $PCHCH_3$), 0.97 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): AB spin system: δ_A = –0.5, δ_B = –15.4 ($^2J_{P,P}$ = 325.6 Hz) ppm.

10. Preparation of all-*cis*-[$OsCl_2(CO)_2$\{κ(*P*)-*i*$Pr_2PCH_2CH_2OMe$\}$_2$] (11a): A slow stream of CO was passed through a solution of **2** (96 mg, 0.16 mmol) in a 5:1 mixture of toluene and dichloromethane (12 mL) at room temperature for 10 min. The solvent was evaporated in vacuo and the oily residue dissolved in a 1:10 mixture of acetone/diethyl ether (5 mL). After the solution had been stored at –78 °C for 12 h, colorless crystals precipitated, which were washed twice with 2-mL portions of hexane and dried; yield 48 mg (46%); m.p. 102 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2005, 1940 [ν(CO)] cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.76 (m, 4 H, OCH_2), 3.40, 3.38 (2 s, 3 H each, OCH_3), 3.02, 2.82, 2.64, 2.56 (4 m, 8 H, PCH_2 and $PCHCH_3$), 1.50–1.22 (br. m, 24 H, $PCHCH_3$) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 175.2 (t, $^2J_{P,C}$ = 8.9 Hz, OsCO *trans* to Cl), 174.8 (dd, $^2J_{P,C}$ = 100.5 and 8.9 Hz, OsCO *trans* to P), 68.8, 68.7 (2 s, OCH_2), 59.0, 58.9 (2 s, OCH_3), 28.6 (d, $^1J_{P,C}$ = 25.4 Hz, $PCHCH_3$), 27.9 (d, $^1J_{P,C}$ = 28.0 Hz, $PCHCH_3$), 26.8 (d, $^1J_{P,C}$ = 29.2 Hz, PCH_2), 25.0, 23.7 (2 d, $^1J_{P,C}$ = 25.4 Hz, $PCHCH_3$), 21.5 (d, $^1J_{P,C}$ = 22.9 Hz, PCH_2), 20.2, 20.0, 19.7, 19.3, 18.9 (5 s, $PCHCH_3$), 19.1 (br., $PCHCH_3$) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 2.3 (d, $^2J_{P,P}$ = 14.5, $^1J_{Os,P}$ = 222.0 Hz), –12.3 (d, $J_{P,P}$ = 14.5, $J_{Os,P}$ = 151.3 Hz) ppm. $C_{20}H_{42}Cl_2O_4OsP_2$ (669.6): calcd. C 35.88, H 6.32; found C 36.20, H 6.47.

11. Preparation of *cis*,*cis*,*trans*-[$OsCl_2(CO)_2$\{κ(*P*)-*i*$Pr_2PCH_2CH_2OMe$\}$_2$] (11b): A solution of **11a** (48 mg, 0.07 mmol) in benzene (10 mL) was stirred under reflux for 3 h. After the solution had cooled to room temperature, the solvent was evaporated in vacuo. The oily residue was treated with a small quantity of hexane (ca. 2 mL) and stirred until small crystals precipitated. The crystallization was completed while the mixture was stored at –78 °C for 12 h. The colorless solid was filtered, washed twice with 2-mL portions of hexane and dried; yield 45 mg (94%); m.p. 98 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2000, 1940 [ν(CO)] cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.73 (m, 4 H, OCH_2), 3.31 (s, 6 H, OCH_3), 2.74, 2.67 (2 m, 4 H each, PCH_2 and $PCHCH_3$), 1.31 (m, 24 H, $PCHCH_3$) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 176.4 (t, $^2J_{P,C}$ = 7.4 Hz, OsCO), 69.0 (s, OCH_2), 59.1 (s, OCH_3), 25.3 (vt, *N* = 13.8 Hz, PCH_2), 20.8 (vt, *N* = 13.4 Hz, $PCHCH_3$), 19.4, 19.1 (2 s, $PCHCH_3$) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 3.6 (s, $^1J_{Os,P}$ = 149.7 Hz) ppm. $C_{20}H_{42}Cl_2O_4OsP_2$ (669.6): calcd. C 35.88, H 6.32; found C 36.14, H 6.53.

12. Preparation of all-*trans*-[$OsCl_2(CO)_2$\{κ(*P*)-*i*$Pr_2PCH_2CH_2OMe$\}$_2$] (11c): A slow stream of CO was passed through a solution of **6** (50 mg, 0.08 mmol) in benzene (10 mL) at room temperature for 5 min. The solvent was evaporated in vacuo and the oily residue worked up as described for **11b**. Pale-orange crystals; yield 34 mg (63%); m.p. 105 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1960 [ν(CO)] cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.71 (m, 4 H, OCH_2), 3.32 (s, 6 H, OCH_3), 2.66 (m, 4 H, PCH_2), 2.48 (m, 4 H, $PCHCH_3$), 1.32 (m, 24 H, $PCHCH_3$) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = –4.7 (s, $^1J_{Os,P}$ = 162.8 Hz) ppm. $C_{20}H_{42}Cl_2O_4OsP_2$ (669.6): calcd. C 35.88, H 6.32; found C 35.41, H 6.65.

13. Preparation of a Mixture of all-*cis*- and *cis*,*cis*,*trans*-[$OsCl_2(CO)_2$\{κ(*P*)-*i*$Pr_2PCH_2CO_2Me$\}$_2$] (12a,b): A slow stream of CO was passed through a solution of **3** (46 mg, 0.07 mmol) in a 1:1 mixture of toluene/dichloromethane (4 mL) at room temperature for 10 min. The solvent was evaporated in vacuo, and the oily residue dissolved in diethyl ether (1 mL). After the solution had been stored at –78 °C for 24 h, a colorless solid precipitated which was filtered, washed twice with 2-mL portions of pentane and dried. According to the NMR spectroscopic data, the product consisted of a mixture of **12a** and **12b** in a ratio of 7:3; yield 32 mg (65%). IR (KBr): $\tilde{\nu}$ = 2060, 1965 [ν(CO)], 1725, 1715 [ν(C=O)] cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 4.11 (dd, $^2J_{P,H}$ = 15.1, $^4J_{H,H}$ = 12.2 Hz, PCH_2 of **12a**), 3.81 (m, PCH_2 of **12a/b**), 3.25 (dd, $^2J_{P,H}$ = 14.6, $^4J_{H,H}$ = 9.4 Hz, PCH_2 of **12a**), 3.17, 3.16, 3.15 (3 s, OCH_3), 2.83, 2.51, 2.33 (3 m, $PCHCH_3$ of **12a**), 2.74 (m, $PCHCH_3$ of **12b**), 1.49 (dd, $^3J_{P,H}$ = 15.4, $^3J_{H,H}$ = 7.2 Hz, $PCHCH_3$ of **12a**), 1.48 (dd, $^3J_{P,H}$ = 14.1, $^3J_{H,H}$ = 7.0 Hz, $PCHCH_3$ of **12a**), 1.32 (dvt, *N* = 16.1 Hz, $^3J_{H,H}$ = 7.3 Hz, $PCHCH_3$ of **12b**), 1.17 (dvt, *N* = 14.6 Hz, $^3J_{H,H}$ = 7.5 Hz, $PCHCH_3$ of **12b**), 1.18–0.96 (br. m, $PCHCH_3$ of **12a**) ppm. ^{31}P NMR (162.0 MHz, C_6D_6): δ = 6.2 (s, P of **12b**), 4.9, –9.0 (2 d, $^2J_{P,P}$ = 15.2 Hz, P of **12a**) ppm. $C_{20}H_{38}Cl_2O_6OsP_2$ (697.6): calcd. C 34.44, H 5.49; found C 34.12, H 5.15.

14. Preparation of *cis*,*cis*,*trans*-[$OsCl_2(CO)_2$\{κ(*P*)-*i*$Pr_2PCH_2CO_2Me$\}$_2$] (12b): A solution of **12a**,**b** (32 mg, 0.05 mmol) in benzene (3 mL) was stirred under reflux for 5 h. After the solution had cooled to room temperature, the solvent was evaporated in vacuo, and the oily residue layered with diethyl ether (1 mL). The mixture was vigorously stirred until a colorless solid precipitated. The precipitate was filtered, washed twice with 2-mL portions of pentane and dried; yield 12 mg (39%); m.p. 85 °C (decomp). IR (KBr): $\tilde{\nu}$ = 2020, 1945 [ν(CO)], 1710 [ν(C=O)] cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 3.81 (vt, 4 H, *N* = 9.5 Hz, PCH_2), 3.15 (s, 6 H, OCH_3), 2.74 (m, 4 H, $PCHCH_3$), 1.32 (dvt, $PCHCH_3$, $^3J_{H,H}$ = 7.3 Hz, 12 H, *N* = 16.1 Hz), 1.17 (dvt, $PCHCH_3$, $^3J_{H,H}$ = 7.5 Hz, 12 H, *N* = 14.6 Hz) ppm. ^{31}P NMR (162.0 MHz, C_6D_6): δ = 6.2 (s, $^1J_{Os,P}$ = 151.6 Hz) ppm. $C_{20}H_{38}Cl_2O_6OsP_2$ (697.6): calcd. C 34.44, H 5.49; found C 33.99, H 5.43.

15. Preparation of *trans*,*trans*-[$OsCl_2(CO)$\{κ²(*P*,*O*)-*i*$Pr_2PCH_2C(=O)OMe$\}\{κ(*P*)-*i*$Pr_2PCH_2CO_2Me$\}] (13): A slow stream of CO was passed through a solution of **7** (52 mg, 0.08 mmol) in a 3:2 mixture of toluene/dichloromethane (10 mL) at room temperature for 10 min. A change of color from orange to yellow occurred. The solvent was evaporated in vacuo, the remaining yellow oil was dissolved in methanol (2 mL) and the solution was layered with diethyl ether (4 mL). After the mixture had been stored at –78 °C for 12 h, a lemon-yellow microcrystalline solid precipitated, which was filtered, washed twice with 2-mL portions of diethyl ether and dried; yield 42 mg (77%); m.p. 116 °C (decomp.). IR (CH_2Cl_2): $\tilde{\nu}$ = 1915 [ν(CO)], 1710, 1615 [ν(C=O)] cm^{-1}. ^1H NMR (400 MHz, $C_6D_5CD_3$): δ = 3.83 (d, $^2J_{P,H}$ = 8.4 Hz, 2 H, PCH_2), 3.53, 3.52 (2 s, 3 H each, OCH_3), 3.31, 2.97 (2 m, 2 H each, $PCHCH_3$), 2.94 (d,

$^2J_{P,H}$ = 9.0 Hz, 2 H, PCH_2), 1.67 (dd, $^3J_{P,H}$ = 16.0, $^3J_{H,H}$ = 7.1 Hz, 6 H, PCHCH_3), 1.56 (dd, $^3J_{P,H}$ = 13.4, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHCH_3), 1.50 (dd, $^3J_{P,H}$ = 16.3, $^3J_{H,H}$ = 7.4 Hz, 6 H, PCHCH_3), 1.31 (dd, $^3J_{P,H}$ = 14.1, $^3J_{H,H}$ = 9.3 Hz, 6 H, PCHCH_3) ppm. ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 186.9 [dd, $^2J_{P,C}$ = 14.5, $^3J_{P',C}$ = 6.0 Hz, *C*(=O)OMe], 177.7 (dd, $^2J_{P,C}$ = $^2J_{P',C}$ = 8.5 Hz, OsCO), 170.8 (d, $^2J_{P,C}$ = 8.5 Hz, *C*O_2Me), 55.8 (s, OCH_3), 30.7 (d, $^2J_{P,C}$ = 22.2 Hz, PCH_2), 23.0 (d, $^2J_{P,C}$ = 12.8 Hz, PCH_2), 22.7 (dd, $^1J_{P,C}$ = 23.9, $^3J_{P',C}$ = 3.4 Hz, P*C*HCH$_3$), 21.3 (dd, $^1J_{P,C}$ = 23.0, $^3J_{P',C}$ = 3.4 Hz, P*C*HCH$_3$), 18.6 (d, $^2J_{P,C}$ = 2.6 Hz, PCH*C*H$_3$), 18.0 (s, PCH*C*H$_3$), 16.5 (d, $^2J_{P,C}$ = 2.6 Hz, PCH*C*H$_3$), 16.2 (s, PCH*C*H$_3$) ppm. ^{31}P NMR (36.2 MHz, $CDCl_3$): AB spin system: δ_A = 24.8, δ_B = 9.6 ($^2J_{P,P}$ = 290.2 Hz) ppm.

16. Preparation of *trans*,*trans*-[OsCl$_2$(CO){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OEt}{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Et}] (14): This compound was prepared as described for **13**, with **8** (45 mg, 0.07 mmol) and CO as starting materials. Yellow solid; yield 34 mg (73%); m.p. 108 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 1905 [ν(CO)], 1705, 1610 [ν(C=O)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.40, 4.13 (2 q, $^3J_{H,H}$ = 7.2 Hz, OCH_2CH$_3$, 2 H each), 3.35, 3.13 (2 d, $^2J_{P,H}$ = 8.8 Hz, PCH_2, 2 H each), 2.94 (m, 4 H, PC*H*CH$_3$), 1.40 (m, 12 H, PCHCH_3), 1.38–1.32 (br. m, 15 H, PCHCH_3 and OCH$_2$CH_3), 1.27 (t, $^3J_{H,H}$ = 7.2 Hz, OCH$_2$CH_3) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): AB spin system: δ_A = 24.1, δ_B = 11.2 ($^2J_{P,P}$ = 289.1 Hz) ppm. $C_{21}H_{42}Cl_2O_5OsP_2$ (697.6): calcd. C 36.16, H 6.07; found C 36.39, H 6.33.

17. Preparation of *cis*,*cis*,*trans*-[OsCl$_2$(CN*t*Bu)$_2${κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}$_2$] (15). (a) A solution of **3** (62 mg, 0.10 mmol) in benzene (10 mL) was treated with *tert*-butyl isocyanide (200 μL, 1.77 mmol) and stirred at room temperature for 10 min. The solvent was evaporated in vacuo, and the oily residue layered with hexane (1 mL). The mixture was vigorously stirred until a pale-yellow solid precipitated. The precipitate was filtered, washed twice with 1-mL portions of pentane (0 °C) and dried; yield 64 mg (83%). **(b)** Similarly as described for (a), but with **7** (65 mg, 0.10 mmol) as starting material; yield 63 mg (77%); m.p. 87 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2065, 2025 [ν(CN)], 1715 [ν(C=O)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.57 (s, 6 H, OCH_3), 3.23 (vt, 4 H, *N* = 7.2 Hz, PCH_2), 2.73 (m, 4 H, PC*H*CH$_3$), 1.44 (s, 18 H, CNCCH$_3$), 1.32–1.14 (br. m, 24 H, PCHCH_3) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 172.7 (vt, *N* = 6.6 Hz, *C*O_2Me), 138.6 (br. s, *C*NCCH$_3$), 56.9 (s, CN*C*CH$_3$), 51.9 (s, OCH_3), 25.1 (vt, *N* = 11.0 Hz, PCH_2), 24.4 (vt, *N* = 25.0 Hz, P*C*HCH$_3$), 18.3, 17.6 (2 s, PCH*C*H$_3$) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = –2.9 (s, $^1J_{Os,P}$ = 187.1 Hz) ppm. $C_{28}H_{56}Cl_2N_2O_4OsP_2$ (807.8): calcd. C 41.63, H 6.99, N 3.47; found C 42.05, H 7.18, N 3.35.

18. Preparation of *cis*,*cis*,*trans*-[OsCl$_2$(CN*t*Bu)$_2${κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Et}$_2$] (16): This compound was prepared as described for **15**, either with **4** (50 mg, 0.07 mmol) or **8** (59 mg, 0.09 mmol) and *tert*-butyl isocyanide (200 μL, 1.77 mmol) as starting materials. Pale-yellow solid; yield 50 mg (81%) using **3** as starting material, or 56 mg (76%) using **8** as starting material; m.p. 95 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 2065, 2040 [ν(CN)], 1705 [ν(C=O)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.99 (q, $^3J_{H,H}$ = 6.9 Hz, 4 H, OCH_2CH$_3$), 3.17 (vt, 4 H, *N* = 7.4 Hz, PCH_2), 2.71 (m, 4 H, PC*H*CH$_3$), 1.42 (s, 18 H, CNCCH$_3$), 1.31–1.11 (br. m, 30 H, PCHCH_3 and OCH$_2$CH_3) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = –2.9 (s) ppm. $C_{30}H_{60}Cl_2N_2O_4OsP_2$ (835.9): calcd. C 43.11, H 7.23, N 3.35; found C 43.50, H 7.38, N 3.54.

19. Preparation of [OsHCl(CN*t*Bu)$_2$(P*i*Pr$_3$)(*i*Pr$_2$PCH$_2$CH$_2$NHMe$_2$)]Cl (17): A solution of **5** (60 mg, 0.10 mmol) in benzene (15 mL) was treated with *tert*-butyl isocyanide (33 μL, 0.29 mmol) and stirred under reflux for 10 min. After the solution had cooled to room temperature, the solvent was evaporated in vacuo, and the oily residue layered with hexane (3 mL). The mixture was vigorously stirred until a white solid precipitated. The precipitate was filtered, washed twice with 1-mL portions of hexane and dried; yield 60 mg (78%); m.p. 122 °C (decomp.); Λ_M = 65 Ω^{-1}cm^{2}mol^{-1}. IR (KBr): $\tilde{\nu}$ = 3400 [ν(NH)], 2160 [ν(OsH)], 2110, 2010 [ν(CN)] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.86 (br. s, 1 H, N*H*Me$_2$), 3.62, 3.48 (2 m, 1 H each, CH_2NHMe$_2$), 2.73 (s, 6 H, NCH_3), 2.52 (m, 3 H, PC*H*CH$_3$ of P*i*Pr$_3$), 2.39 (m, 2 H, PC*H*CH$_3$ of P*i*Pr$_2$), 1.23, 2.08 (2 m, 1 H each, PCH_2), 1.43 (s, 9 H, CNCCH$_3$), 1.26 (dd, $^3J_{P,H}$ = 12.5, $^3J_{H,H}$ = 7.3 Hz, 18 H, PCHCH_3 of P*i*Pr$_3$), 1.19 (s, 9 H, CNCCH$_3$), –7.48 (dd, $^2J_{P,H}$ = 24.4, $^2J_{P',H}$ = 21.9 Hz, 1 H, OsH); signal for PCHCH_3 protons of of P*i*Pr$_2$, and second signals for PCHCH_3 protons of P*i*Pr$_3$ and for CNCCH$_3$ protons of CN*t*Bu overlap and could not be exactly located. ^{31}P NMR (162.0 MHz, $CDCl_3$): AB spin system: δ_A = 28.4, δ_B = 24.5 ($^2J_{P,P}$ = 245.8 Hz, 2 d in off-resonance) ppm. $C_{29}H_{65}Cl_2N_3OsP_2$ (778.9): calcd. C 44.72, H 8.41, N 5.39; found C 44.28, H 8.69, N 5.52.

20. Generation of *trans*,*trans*-[OsCl$_2$(N$_2$){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OMe}{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (18): A solution of **7** (84 mg, 0.13 mmol) in dichloromethane (10 mL) was treated with diphenyldiazomethane (26 mg, 0.13 mmol) and stirred at room temperature for 30 min. The solvent was evaporated in vacuo, and the red residue was extracted with diethyl ether (5 mL). The extract was dried in vacuo and the residue was recrystallized from dichloromethane/diethyl ether/hexane (1:2:10). After the solution had been stored at –30 °C for 12 h, a red solid precipitated, which was filtered, washed twice with 2-mL portions of hexane and dried. According to the ^{1}H NMR spectrum, the precipitate contained besides compound **18** some organic by-products, which could not be separated neither by fractional crystallization nor column chromatography. A similar mixture of products was obtained from **7** and excess of phenyldiazomethane in benzene. Data for **18**: IR (KBr): $\tilde{\nu}$ = 2060 [ν(N$_2$)], 1725, 1620 [ν(C=O)] cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 3.77 (d, $^2J_{P,H}$ = 8.0 Hz, 2 H, PCH_2), 3.38, 3.22 (2 s, 3 H each, OCH_3), 3.30, 2.98 (2 m, 2 H each, PC*H*CH$_3$), 2.70 (d, $^2J_{P,H}$ = 8.5 Hz, 2 H, PCH_2), 1.55 (dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 6.6 Hz, 6 H, PCHCH_3), 1.48 (dd, $^3J_{P,H}$ = 13.0, $^3J_{H,H}$ = 6.6 Hz, 6 H, PCHCH_3), 1.40 (dd, $^3J_{P,H}$ = 15.6, $^3J_{H,H}$ = 6.5 Hz, 6 H, PCHCH_3), 1.20 (dd, $^3J_{P,H}$ = 13.8, $^3J_{H,H}$ = 5.4 Hz, 6 H, PCHCH_3) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = 189.5 [dd, $^2J_{P,C}$ = 15.3, $^3J_{P',C}$ = 5.1 Hz, *C*(=O)OMe], 171.3 (dd, $^2J_{P,C}$ = 10.2, $^2J_{P',C}$ = 3.2 Hz, *C*O_2Me), 56.6, 51.4 (2 s, OCH_3), 31.7 (d, $^2J_{P,C}$ = 22.9 Hz, PCH_2), 23.9 (d, $^1J_{P,C}$ = 21.6 Hz, P*C*HCH$_3$), 22.6 (d, $^1J_{P,C}$ = 22.9 Hz, P*C*HCH$_3$), 22.3 (d, $^2J_{P,C}$ = 30.5 Hz, PCH_2), 19.5, 18.6, 17.5, 17.3 (4 s, PCH*C*H$_3$) ppm. ^{31}P NMR (162.0 MHz, C_6D_6): AB spin system: δ_A = 15.1, δ_B = 1.4 ($^2J_{P,P}$ = 316.0 Hz) ppm.

21. Preparation of *trans*,*trans*-[OsCl$_2$(=C=CHPh){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$CH$_2$OMe}{κ(*P*)-*i*Pr$_2$PCH$_2$CH$_2$OMe}] (19a): A solution of **6** (54 mg, 0.16 mmol) in benzene (10 mL) was treated with phenylacetylene (20 μL, 0.18 mmol) and stirred under reflux for 3 h. After the solution had cooled to room temperature, the solvent was evaporated in vacuo. The oily residue was recrystallized from a 1:5 mixture of diethyl ether/pentane (3 mL) to give an orange microcrystalline solid. This was filtered, washed twice with 2-mL portions of pentane and dried; yield 29 mg (48%); m.p. 170 °C (decomp.). IR (CH_2Cl_2): $\tilde{\nu}$ = 1610 [ν(C=C)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.00, 6.77, 6.59 (3 m, 5 H, C_6H_5), 3.75 (m, 4 H, OCH_2), 3.33 (s, 6 H each, OCH_3), 2.76 (m, 4 H, PC*H*CH$_3$), 2.04 (m, 4 H, PCH_2), 1.97 (t, $^4J_{P,H}$ = 3.1 Hz, 1 H, =C*H*Ph), 1.24 (m, 24 H, PCHCH_3) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 291.8 (t, $^2J_{P,C}$ = 10.2 Hz, =*C*=CHPh), 130.7 (s, *i*-C of C_6H_5), 127.4, 124.5,

122.3 (3 s, C_6H_5), 108.9 (s, =C=*C*HPh), 71.1 (s, OCH_2), 60.6 (s, OCH_3), 22.9 (vt, *N* = 26.6 Hz, P*C*HCH$_3$), 21.4 (vt, *N* = 24.1 Hz, PCH_2), 19.0, 18.7 (2 s, PCH*C*H$_3$) ppm. ^{31}P NMR (36.2 MHz, $CDCl_3$, 298 K): δ = –4.1 (br.) ppm. ^{31}P NMR (36.2 MHz, $CDCl_3$, 183 K): AB spin system: δ_A = 7.9, δ_B = –15.7 ($^2J_{P,P}$ = 319.5 Hz) ppm. $C_{26}H_{48}Cl_2O_2OsP_2$ (715.7): calcd. C 43.63, H 6.76; found C 43.26, H 6.51.

22. Preparation of *cis*-(*P*)-[OsCl$_2$(=C=CHPh){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$-CH$_2$OMe}{κ(*P*)-*i*Pr$_2$PCH$_2$CH$_2$OMe}] (19b): A solution of **6** (42 mg, 0.07 mmol) in benzene (2 mL) was treated with phenylacetylene (16 μL, 0.14 mmol) and slowly stirred at room temperature for 30 min. The solvent was evaporated in vacuo and pentane (5 mL) added to the oily residue. The mixture was stirred until a red solid precipitated. The solid was filtered, washed twice with 2-mL portions of pentane and dried; yield 24 mg (48%); m.p. 164 °C (decomp.). IR (CH_2Cl_2): $\tilde{\nu}$ = 1600 [ν(C=C)] cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.20, 6.78 (2 m, 5 H, C_6H_5), 3.83, 3.26 (2 s, 3 H each, OCH_3), 3.80, 3.62 (2 m, 2 H each, OCH_2), 2.84, 2.71, 2.60, 2.32, 1.98 (5 m, 8 H, PCH_2 and PC*H*CH$_3$), 1.79 (br. s, 1 H, =C*H*Ph), 1.31 (m, 24 H, PCHC*H*$_3$) ppm. ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 19.0, –10.4 (2 d, $^2J_{P,P}$ = 9.2 Hz) ppm. $C_{26}H_{48}Cl_2O_2OsP_2$ (715.7): calcd. C 43.63, H 6.76; found C 43.38, H 6.45.

23. Preparation of *trans*,*trans*-[OsCl$_2$(=C=CHPh){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OMe}{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}] (20): A solution of **7** (304 mg, 0.47 mmol) in benzene (20 mL) was treated with phenylacetylene (104 μL, 0.95 mmol) and stirred under reflux for 3 h. After the solution had cooled to room temperature, the solvent was evaporated in vacuo. The oily residue was disolved in benzene (3 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm). With benzene, a red fraction was eluted which was dried in vacuo. The residue was recrystallized from pentane (3 mL) to give a salmon-red microcrystalline solid. This was filtered, washed twice with 2-mL portions of pentane (0 °C) and dried; yield 333 mg (95%); m.p. 154 °C (decomp.). MS: *m*/*z* (*I*$_r$) = 743 (6.3) [M$^+$]. IR (KBr): $\tilde{\nu}$ = 1715, 1640 [ν(C=O)] cm^{-1}. ^{1}H NMR (400 MHz, $C_6D_5CD_3$, 60 °C): δ = 7.38, 6.95 (2 m, 5 H, C_6H_5), 3.52 (br. s, 10 H, OCH_3 and PCH_2), 3.20 (m, 4 H, PC*H*CH$_3$), 2.64 (t, $^4J_{P,H}$ = 5.9 Hz, 1 H, =C*H*Ph), 1.55 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 7.2 Hz, 12 H, *N* = 14.5 Hz), 1.52 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 7.0 Hz, 12 H, *N* = 14.6 Hz) ppm. ^{13}C NMR (22.5 MHz, C_6D_6): δ = 297.1 (t, $^2J_{P,C}$ = 11.0 Hz, Os=*C*=CHPh), 129.7, 128.2, 125.2, 123.5 (4 s, C_6H_5), 109.3 (t, $^3J_{P,C}$ = 6.1 Hz, Os=C=*C*HPh), 53.3 (s, OCH_3), 27.5 (br. s, PCH_2), 23.4 (vt, *N* = 25.6 Hz, P*C*HCH$_3$), 18.5, 18.3 (2 s, PCH*C*H$_3$) ppm; signal for *C*O$_2$CH$_3$ could not be exactly located. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 313 K): δ = 2.6 (s) ppm. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 193 K): AB spin system: δ_A = 9.5, δ_B = –2.9 ($^2J_{P,P}$ = 331.9 Hz) ppm. $C_{26}H_{44}Cl_2O_4OsP_2$ (743.5): calcd. C 42.00, H 5.93; found C 42.34, H 5.72.

24. Preparation of *trans*,*trans*-[OsCl$_2$(=C=CHPh){κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$C(=O)OEt}{κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Et}] (21): This compound was prepared as described for **20**, with **8** (74 mg, 0.11 mmol) and phenylacetylene (36 μL, 0.33 mmol) as starting materials. Red microcrystalline solid; yield 69 mg (81%); m.p. 152 °C (decomp.). IR (KBr): $\tilde{\nu}$ 1700, 1635 [ν(C=O)] cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.32, 7.22, 6.77 (3 m, 5 H, C_6H_5), 3.82 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, C*H*$_2$CH$_3$), 3.42, 3.05 (2 m, 4 H each, PCH_2 and PC*H*CH$_3$), 2.58 (t, $^4J_{P,H}$ = 5.9 Hz, 1 H, =C*H*Ph), 1.40 (dvt, PCHC*H*$_3$, $^3J_{H,H}$ = 7.2 Hz, 12 H, *N* = 14.5 Hz), 1.30 (m, 12 H, PCHC*H*$_3$), 0.82 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, $C_6D_5CD_3$, 253 K): δ = 297.3 (t, $^2J_{P,C}$ = 11.1 Hz, Os=*C*=CHPh), 185.4 [dd, $^2J_{P,C}$ = 12.1, $^2J_{P',C}$ = 3.2 Hz, *C*(=O)OEt], 170.6 (d, $^2J_{P,C}$ = 6.6 Hz, *C*O$_2$Et), 131.3, 128.3, 125.3, 123.3 (4 s, C_6H_5), 108.3 (s, Os=C=*C*HPh), 65.2, 60.4 (2 s, *C*H$_2$CH$_3$), 32.4 (d, $^1J_{P,C}$ = 22.8 Hz, PCH_2), 23.1 (m, P*C*HCH$_3$), 18.9 (d, $^1J_{P,C}$ = 22.9 Hz, PCH_2), 17.4 (br. s, PCH*C*H$_3$), 13.7, 13.5 (2 s, CH$_2$*C*H$_3$) ppm. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 333 K): δ = 8.0 (s) ppm. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 253 K): AB spin system: δ_A = 13.2, δ_B = 4.4 ($^2J_{P,P}$ = 333.1 Hz) ppm. $C_{28}H_{48}Cl_2O_4OsP_2$ (771.7): calcd. C 43.58, H 6.27; found C 43.68, H 6.53.

25. Preparation of *cis*,*cis*-[OsCl$_2$(=C=CHPh)(P*i*Pr$_3$){κ^2(*P*,*N*)-*i*Pr$_2$PCH$_2$CH$_2$NMe$_2$}] (22): This compound was prepared as described for **20**, method (a), with **5** (80 mg, 0.13 mmol) and phenylacetylene (43 μL, 0.39 mmol) as starting materials. Pale-red microcrystalline solid; yield 77 mg (82%); m.p. 170 °C (decomp.). MS: *m*/*z* (*I*$_r$) = 710 (0.1) [M$^+$]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11, 7.00, 6.66 (3 m, 5 H, C_6H_5), 3.46 (m, 2 H, PCH_2 or NCH_2), 2.76 (br. s, 4 H each, NCH_3 and =C*H*Ph), 2.57 (s, 3 H, NCH_3), 2.46, 2.33, 2.09, 2.02 (4 m, 7 H, PCH_2 or NCH_2 and PC*H*CH$_3$), 1.38 (dd, $^3J_{P,H}$ = 12.6, $^3J_{H,H}$ = 6.9 Hz, 6 H, PCHC*H*$_3$), 1.30 (br. m, 12 H, PCHC*H*$_3$), 1.23 (dd, $^3J_{P,H}$ = 12.7, $^3J_{H,H}$ = 7.1 Hz, 6 H, PCHC*H*$_3$), 1.17 (dd, $^3J_{P,H}$ = 13.5, $^3J_{H,H}$ = 7.3 Hz, 6 H, PCHC*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 294.0 (dd, $^2J_{P,C}$ = $^2J_{P',C}$ = 12.3 Hz, Os=*C*=CHPh), 129.3, 128.8, 126.0, 124.2 (4 s, C_6H_5), 114.5 (s, Os=C=*C*HPh), 62.8 (s, NCH_2), 54.8, 49.2 (2 s, NCH_3), 28.6 (d, $^1J_{P,C}$ = 26.9 Hz, P*C*HCH$_3$), 28.2 (d, $^1J_{P,C}$ = 32.9 Hz, PCH_2), 25.7 (d, $^1J_{P,C}$ = 26.2 Hz, P*C*HCH$_3$), 20.2 (d, $^1J_{P,C}$ = 28.8 Hz, P*C*HCH$_3$), 21.9, 21.8, 20.8, 20.6, 20.1, 20.0 (6 s, PCH*C*H$_3$) ppm. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 15.4 (d, $^2J_{P,P}$ = 6.7, $J_{Os,P}$ = 239.1 Hz), –11.2 (d, $^2J_{P,P}$ = 6.7, $J_{Os,P}$ = 252.5 Hz) ppm. $C_{27}H_{51}Cl_2NOsP_2$ (712.8): calcd. C 45.50, H 7.21, N 1.97; found C 44.98, H 7.05, N 1.97.

[1] M. Aracama, M. A. Esteruelas, F. J. Lahoz, J. A. Lopez, U. Meyer, L. A. Oro, H. Werner, *Inorg. Chem.* **1991**, *30*, 288–293.

[2] H. Werner, S. Jung, B. Weberndörfer, J. Wolf, *Eur. J. Inorg. Chem.* **1999**, 951–957.

[3] Carbyne complexes: a) J. Espuelas, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, N. Ruiz, *J. Am. Chem. Soc.* **1993**, *115*, 4683–4689; b) B. Weber, P. Steinert, B. Windmüller, J. Wolf, H. Werner, *J. Chem. Soc., Chem. Commun.* **1994**, 2595–2596; c) G. J. Spivak, J. N. Coalter, M. Oliván, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 999–1001.

[4] Vinylidene complexes: a) M. A. Esteruelas, L. A. Oro, N. Ruiz, *Organometallics* **1994**, *13*, 1507–1509; b) M. Bourgault, A. Castillo, M. A. Esteruelas, E. Oñate, N. Ruiz, *Organometallics* **1997**, *16*, 636–645; c) P. Crochet, M. A. Esteruelas, A. M. López, M.-P. Matrinez, M. Oliván, E. Oñate, N. Ruiz, *Organometallics* **1998**, *17*, 4500–4509.

[5] H. Werner, B. Weber, O. Nürnberg, J. Wolf, *Angew. Chem.* **1992**, *104*, 1105–1107; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1025–1027.

[6] For reviews on transition metal complexes with hemilabile phosphanes, see: a) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110; b) E. Lindner, S. Pautz, M. Haustein, *Coord. Chem. Rev.* **1996**, *155*, 145–162; c) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233–350; d) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702–722; *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699.

[7] W. Wolfsberger, W. Burkart, S. Bauer, A. Hampp, J. Wolf, H. Werner, *Z. Naturforsch., Teil B* **1994**, *49*, 1659–1673.

[8] E. Lindner, U. Schober, R. Fawzi, W. Hiller, U. Englert, P. Wegner, *Chem. Ber.* **1987**, *120*, 1621–1628.

[9] E. Lindner, H. Rothfuß, R. Fawzi, W. Hiller, *Chem. Ber.* **1992**, *125*, 541–550.

[10] R. Benn, H. Brenneke, E. Joussen, H. Lehmkuhl, F. L. Ortiz, *Organometallics* **1990**, *9*, 756–761.

[11] H. Werner, A. Stark, P. Steinert, C. Grünwald, J. Wolf, *Chem. Ber.* **1995**, *128*, 49–62.
[12] H. Werner, N. Mahr, M. E. Schneider, M. Bosch, J. Wolf, *Polyhedron* **2004**, *23*, 2645–2657.
[13] J. Chatt, G. J. Leigh, R. L. Richards, *J. Chem. Soc. A* **1970**, 2243–2246.
[14] J. Chatt, J. R. Dilworth, R. L. Richards, *Chem. Rev.* **1978**, *78*, 589–625.
[15] H. Werner, A. Hampp, K. Peters, E. M. Peters, L. Walz, H. G. von Schnering, *Z. Naturforsch., Teil B* **1990**, *45*, 1548–1558.
[16] P. Steinert, H. Werner, *Organometallics* **1994**, *13*, 2677–2681.
[17] R. Castarlenas, M. A. Esteruelas, E. Gutiérrez-Puebla, E. Oñate, *Organometallics* **2001**, *20*, 1545–1554.
[18] T. B. Wen, W. Y. Hung, Z. Y. Zhou, M. F. Lo, I. D. Williams, G. Jia, *Eur. J. Inorg. Chem.* **2004**, 2837–2846.
[19] O. Nürnberg, Dissertation, Universität Würzburg **1993**.
[20] D. Huang, M. Oliván, J. C. Huffman, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *21*, 4700–4706.
[21] T. B. Wen, Y. K. Cheung, J. Yao, W.-T. Wong, Z. Y. Zhou, G. Jia, *Organometallics* **2000**, *19*, 3803–3809.
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