New Five- and Six-Coordinate Nitrosylosmium(0) and Nitrosylosmium(II) Complexes Prepared from the Stable 16-Electron Species $[OsCl(NO)(PR_3)_2]$☆

Helmut Werner*, Ruth Flügel, and Bettina Windmüller

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

Received October 19, 1996

Keywords: Osmium(0) complexes / Nitrosyl complexes / Oxidative addition reactions / Alkynyl(hydrido)osmium complexes / Diynyl(hydrido)osmium complexes

The coordinatively unsaturated starting materials *trans*-$[OsCl(NO)(PiPr_3)_2]$ (**2**) and *trans*-$[OsCl(NO)(PiPr_2Ph)_2]$ (**3**), for which a new one-pot synthesis is reported, react with isocyanides, SO_2 and O_2 to give the corresponding 1:1 adducts $[OsCl(NO)(L)(PiPr_2R)_2]$ (**4**–**7**). The corresponding methyleneosmium complex $[OsCl(NO)(=CH_2)(PiPr_3)_2]$ (**9**), on treatment with SO_2 and HCl, affords the six-coordinate osmium(II) compounds $[OsCl(NO)\{\kappa^2(C,O)\text{-}CH_2S(O)O\}(PiPr_3)_2]$ (**10**) and $[OsCl_2(NO)(CH_3)(PiPr_3)_2]$ (**11**), respectively. The reactions of **2** and **3** with HCl, I_2, CH_3I, CH_2=CHBr, $R'CO_2H$, PhSH, CH_3OH, PhCOSH, and R'CHO lead by oxidative addition to the corresponding octahedral osmium(II) complexes $[OsCl(NO)(X)(Y)(PiPr_2R)_2]$ (**12**–**24**). The initially formed compound $[OsHCl(NO)\{SC(=O)Ph\}(PiPr_3)_2]$ (**20a**) rearranges smoothly to the more stable S-bonded isomer $[OsHCl(NO)\{OC(=S)Ph\}(PiPr_3)_2]$ (**20b**). Alkynyl(hydrido)- and diynyl(hydrido)osmium(II) complexes **26**–**31** and **34**, **35** are obtained from **2** or **3** and HC≡CCO_2Me, propargylic alcohols HC≡CCPh(R')OH or the diyne HC≡CC≡$CCPh_2OH$. The compounds $[OsHCl(NO)\{C{\equiv}CCPh(R')OH\}(PiPr_3)_2]$ (**30**, **31**) react with aqueous HCl in benzene to give the η^1-allenylosmium(II) derivatives $[OsCl_2(NO)\{\eta^1\text{-}CH{=}C{=}C(Ph)R'\}(PiPr_3)_2]$ (**32**, **33**). $[OsHCl(NO)(C{\equiv}CC{\equiv}CCPh_2OH)(PiPr_3)_2]$ (**34**) has been characterized by X-ray structural analysis.

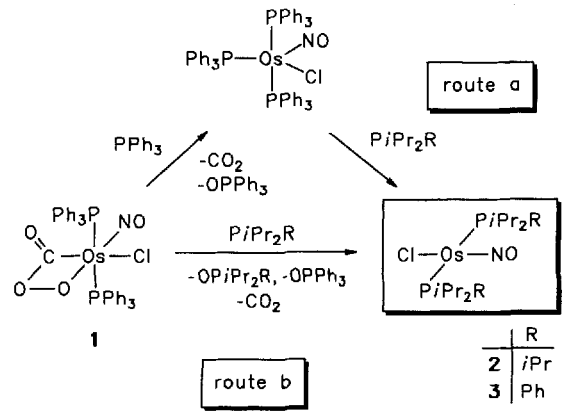
Recently, we described the preparation of four-coordinate osmium(0) complexes of the type *trans*-$[OsCl(NO)(PR_3)_2]$ (PR_3 = $PiPr_3$, $PiPr_2Ph$) in which the metal centre has only a 16-electron configuration[1]. As the X-ray crystal structure analysis of *trans*-$[OsCl(NO)(PiPr_3)_2]$ revealed[1a], these compounds are in structural terms completely analogous to the Vaska-type complexes *trans*-$[IrCl(CO)(PR_3)_2]$ for which a rich chemistry has been reported[2]. After we found in our initial studies that the coordinatively unsaturated nitrosylosmium(0) derivatives readily form 1:1 adducts with Lewis bases (e.g., with CO, CH_2, CS_2, SCNPh etc.)[1,3] and also undergo oxidative addition reactions (e.g., with H_2, HC≡CPh etc.)[1] to form stable 18-electron complexes, we became interested to further explore the synthetic potential of the new type of osmium(0) species. It should be mentioned that most recently we also succeeded in preparing the ruthenium counterparts *trans*-$[RuCl(NO)(PR_3)_2]$ (PR_3 = $PiPr_3$, $PiPr_2Ph$)[4] which are, probably due to the bulkiness of the phosphane ligands, significantly more stable than the analogous compounds with PR_3 = PPh_3[5], $PMePh_2$ or PMe_2Ph[6].

In this paper we report a simplified preparative route to the square-planar starting materials and illustrate that an extensive series of five-coordinate osmium(0) and six-coordinate osmium(II) complexes, both being electronically saturated, are accessible by addition reactions. Some preliminary results have already been communicated[1a].

Improved Synthesis of *trans*-$[OsCl(NO)(PR_3)_2]$ (2, 3)

The original synthetic route (Scheme 1, route a) to the target compounds **2** and **3** consisted of two steps. In the first of these, the peroxocarbonylosmium(II) derivative **1** was treated with a 2.5-fold excess of PPh_3 to give the 18-electron complex $[OsCl(NO)(PPh_3)_3]$[7], which on subsequent treatment with $PiPr_3$ or $PiPr_2Ph$ in benzene at room temperature afforded the 16-electron species **2** and **3**[1].

Scheme 1



The new method (Scheme 1, route b) leads directly from **1** to **2** or **3**. Stirring a solution of **1** in benzene with a threefold excess of $PiPr_3$ or $PiPr_2Ph$ at 60°C for 20 min results in a color change from yellow to dark-green, accompanied by an evolution of gas (CO_2). Subsequent work-up of the mixture affords the nitrosylosmium(0) complexes **2** and **3** as dark-green solids in almost quantitative yield. The ^{31}P-NMR spectra of the mother liquors display signals of both $OPPh_3$ and $OPiPr_3$ or $OPiPr_2Ph$, respectively, which confirms that the phosphane ligands coordinated in **1** as well as excess $PiPr_3$ or $PiPr_2Ph$ behave as oxygen acceptors.

  0009–2940/97/0404–0493 $ 17.50+.50/0

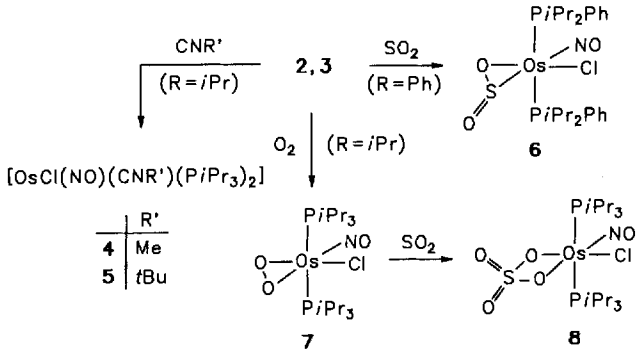
Attempts to apply the new route to P*i*PrPh$_2$ as reacting substrate were unsuccessful. Under the same conditions used for the preparation of **2** and **3**, the reaction of **1** and P*i*PrPh$_2$ afforded a mixture of products which could not be separated and in which neither [OsCl(NO)(P*i*PrPh$_2$)$_2$] nor [OsCl(NO)(P*i*PrPh$_2$)$_3$] could unequivocally be detected. When CO was passed through the solution of these products, a change of color from green to yellow occurred, with the formation of a new product. The IR spectrum of the solution showed a strong absorption at 1900 cm^{-1} which could be assigned to the CO stretching frequency of [OsCl(NO)(CO)(P*i*PrPh$_2$)$_2$] (cf: [OsCl(NO)(CO)(P*i*Pr$_3$)$_2$], ν(CO) = 1895 cm^{-1}; [OsCl(NO)(CO)(P*i*Pr$_2$Ph)$_2$], ν(CO) = 1896 cm^{-1})[1b]. The new complex can either be formed by addition of CO to [OsCl(NO)(P*i*PrPh$_2$)$_2$] or by ligand exchange from [OsCl(NO)(P*i*PrPh$_2$)$_3$]. We assume that possibly for steric reasons[8], P*i*PrPh$_2$ is a borderline case and upon interaction with the [OsCl(NO)]-fragment does not give (like PPh$_3$) a stable tris(phosphane)- or (like P*i*Pr$_3$ and P*i*Pr$_2$Ph) a stable bis(phosphane)osmium(0) complex.

Addition Reactions of 2 and 3 with Isocyanides, SO_2 and O_2

After we had shown that the starting materials **2** and **3** form stable five-coordinate osmium(0) derivatives [OsCl(NO)(CO)(P*i*Pr$_2$R)$_2$] and [OsCl(NO)(=CH$_2$)(P*i*Pr$_2$R)$_2$] (R = *i*Pr, Ph) on treatment with CO and CH$_2$N$_2$, respectively, we became interested to extend these studies to other two-electron donor ligands as substrates. As summarized in Scheme 2, stable 1:1 adducts of **2** and **3** with CNMe, CN*t*Bu, SO$_2$, and O$_2$ have been obtained in 60–75% yield. The yellow (**4**, **5**), orange (**6**), or red-brown (**7**) solids, which are air-stable and soluble in most organic solvents, were characterized by elemental analysis and spectroscopic techniques. Since the ^{1}H- and ^{31}P-NMR spectra of **4** and **5** confirm that the two phosphane ligands are equivalent and probably *trans* to each other, four isomers **A**–**D** could exist which are depicted in Figure 1. From these stereoisomers, we consider **D** as unlike due to the *trans* disposition of the two π-acceptor ligands NO and CNR′. For five-coordinate osmium(0) compounds in general, the trigonal-bipyramidal configuration seems to be favored[9], and this has been substantiated inter alia by Roper et al. by the X-ray crystal structural analyses of [OsCl(NO)(=CH$_2$)(PPh$_3$)$_2$][7] and [OsCl(NO)(=CF$_2$)(PPh$_3$)$_2$][10]. The energy difference between the trigonal-bipyramidal and square-pyramidal geometries may, however, be quite small[11] and thus predictions about which of the possible stereoisomers **A**–**D** is preferred in the case of **4** and **5** can only be made with great caution.

Although SO$_2$ and O$_2$ are undoubtedly also two-electron donor ligands and behave like other Lewis bases in coordination chemistry[12,13], the configuration of **6**, obtained from **3** and SO$_2$, and of **7**, obtained from **2** and O$_2$, is slightly different from that of the isocyanide complexes **4** and **5**. In particular, the IR data of **6** and **7** indicate that the O$_2$ unit is bonded side-on[12] and that the SO$_2$ ligand coordinated via S *and* O[13], thus the geometry around the osmium centre is closer to pseudo-octahedral than to trigonal-bipyramidal. The structural difference between **6**, **7** and **4**, **5** is also illustrated by the difference in the N–O stretching vibration, which appears for **6** at 1802 cm^{-1} and for **7** at 1767 cm^{-1}, while for **4** and **5** it is observed at significantly lower frequencies (1639 and 1595 cm^{-1}, respectively).

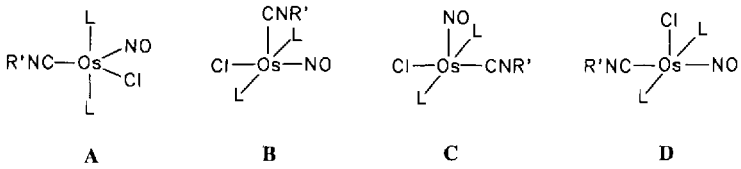
Scheme 2



Compound **7**, which in the absence of any substrate slowly decomposes in solution, reacts almost instantaneously with SO$_2$ in toluene at room temperature to give the sulfatoosmium(II) derivative **8** (see Scheme 2) as an orange, crystalline solid in ca. 70% yield. The O$_2$-adduct **7** thus resembles some other d^8 transition metal complexes containing dioxygen as a ligand, which on treatment with SO$_2$ also afford sulfatometal compounds[14]. In the IR spectrum of **8**, four ν(SO) vibrations appear between 1300 and 860 cm^{-1} pointing to a pseudo-C_{2v} symmetry of the SO$_4$ unit with a bidentate linkage via two oxygens to the metal. This bonding arrangement has been confirmed for the analogous ruthenium complex [RuCl(NO){κ^2(O,O)-O$_2$SO$_2$}-(P*i*Pr$_3$)$_2$] by X-ray crystallography[4].

Not only the Os(O$_2$) compound **7**, but also the related carbene complex **9** reacts with SO$_2$ in dichloromethane. Under a pressure of 2 bar of SO$_2$, the reaction proceeds smoothly as evidenced by a change of color from orange to yellow. After work-up, a yellow, air-stable solid with the analytical composition corresponding to **10** (Scheme 3) is isolated in 64% yield. In close analogy to other M(CH$_2$SO$_2$) derivatives, which are also obtained from M(=CH$_2$) precursors and SO$_2$[15], we assume that the generated sulfene ligand is coordinated via C and O but not, as recently found in cationic Ru(CH$_2$SO$_2$) complexes, via C and S to the metal[16]. The most salient features of the spectroscopic data of **10** are the three ν(SO) bands in the IR spectrum at 1138, 1098, and 795 cm^{-1}, typical for *C,O*-bonded sulfenes[15], and the two signals, corresponding to an AB spin system, in the ^{31}P-NMR spectrum at δ = 5.8 and 3.4. Although the latter observation indicates a non-equivalence of the two phosphanes, they are nevertheless most probably *trans* disposed, as is indicated by the large P–P coupling constant of 326 Hz. The non-equivalence of the P*i*Pr$_3$ ligands, which is also shown in the ^{1}H-NMR spectrum by the appearance of *four* signals for the PCHC*H*$_3$ protons (instead of two as for compound **8**) is best explained by the assumption that the terminal S=O unit of the sulfene does not lie in the

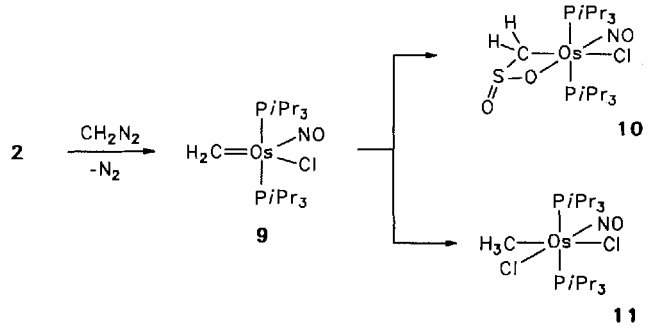
Figure 1. Possible stereoisomers for compounds **4**, **5** with *trans*-disposed phosphane ligands (L = P*i*Pr$_3$; R′ = Me, *t*Bu)



A **B** **C** **D**

[Os,C,S,O] plane but points in the direction of one of the phosphane ligands. The necessary condition that **10** has a rigid structure at room temperature is certainly fulfilled since all the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra display very sharp lines. Finally, we note that the resonance of the sulfene carbon atom appears at $\delta = 7.6$ as a doublet of doublets with P–C coupling constants of 5.4 and 4.1 Hz, an observation which is also in agreement with the structure proposed for **10** shown in Scheme 3.

Scheme 3



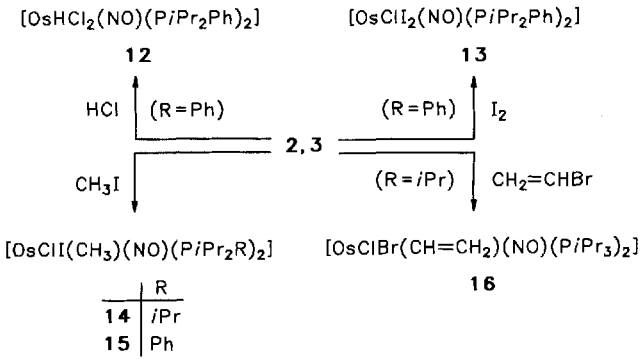
The nucleophilic behavior of the CH_2 carbon of **9** is also illustrated by the reaction with HCl. As in the case of SO_2, the starting material reacts slowly with a solution of HCl in benzene and, after 24 h at room temperature, gives the methyl(nitrosyl) complex **11** in 56% yield. The orange, moderately air-stable solid is an analogue of the Roper compound $[OsCl_2(CH_3)(NO)(PPh_3)_2]$[7b], which has been prepared via a similar route. Since the ^{1}H-NMR spectrum of **11** displays, besides the triplet for the Os-CH_3 protons at $\delta = 2.42$, *two* doublets of virtual triplets for the CH_3 protons of the isopropyl groups, we conclude that the two chloro ligands are *cis* disposed. If they were, like the phosphane ligands, *trans* to one another, the methyl groups of the phosphanes would not be diastereotopic and would give rise to only one signal in the ^{1}H-NMR spectrum.

Oxidative Addition Reactions of 2 and 3 with Brønsted Acids and Other Electrophiles

We have already reported that both compounds **2** and **3** react quite rapidly with H_2 to give the expected dihydridoosmium(II) complexes $[OsH_2Cl(NO)(PiPr_2R)_2]$ (R = *i*Pr, Ph) almost quantitatively[11b]. The corresponding reactions of **3** with HCl and I_2 also proceed under mild conditions (25°C) in toluene. They lead to the dichloro(hydrido)- and chloro(diiodo)osmium(II) derivatives **12** and **13** in 78% and 96% yield. These compounds are yellow, air-stable solids for which, in view of the appearance of one sharp singlet in the ^{31}P-NMR spectra, a transoid arrangement of the two phosphanes in the octahedral coordination sphere is proposed. Since both the hydrido and the nitrosyl ligands exert a strong *trans* influence, we assume that for **12** the configuration with the chlorides in a *cis* orientation is preferred.

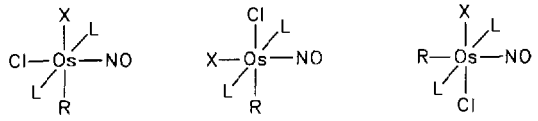
For the diiodoosmium(II) compound **13**, however, a transoid arrangement of the iodides seems most likely. The ^{1}H-NMR spectrum of **13** displays instead of four (as in the case of **12**) only two signals for the methyl protons of the isopropyl groups indicating that *two* mirror planes exist, one passing through Os, H, NO, and the iodides and the other through Os, H, NO, and the two phosphorus atoms. For the mechanism of formation of **13**, it is conceivable that in the initial step an "end-on" attack of the iodine molecule at the metal occurs. This could generate an $Os(\eta^1\text{-}I_2)$ intermediate[17] which, after heterolytic cleavage of the I–I bond and *trans* addition of the thus formed iodide ion, would yield the final product. In this context we note that oxidative addition reactions of other square-planar d^8-metal complexes with I_2 also lead to compounds in which the two iodides are *trans* disposed[18].

Scheme 4



Methyl iodide and vinyl bromide behave similarly to HCl and I_2 toward **2** and **3** and react in toluene even at 0°C to give the six-coordinate complexes **14**–**16** as orange, air-stable solids in good to excellent yields. On the basis of the ^{1}H- and ^{31}P-NMR spectra of **14**–**16**, a *trans* orientation of the two phosphane ligands can be proposed, hence three stereoisomers **E**, **F**, and **G** could exist which are depicted in Figure 2. Although a *trans* addition of CH_3I and CH_2=CHBr to the metal centre seems to be most likely[19], we cannot conclude from the spectroscopic data whether the expected isomer **E** was indeed formed. In the IR spectra of **14**–**16**, the NO stretching frequency appears at 1770–1775 cm^{-1}, which is very similar in position to the ν(NO) band of **13** at 1785 cm^{-1}. In the ^{1}H-NMR spectra of **14** and **15**, the protons of the metal-bound CH_3 group

Figure 2. Possible stereoisomers for compounds **14**–**16** with *trans*-disposed phosphane ligands (L = P*i*Pr$_3$, P*i*Pr$_2$Ph)



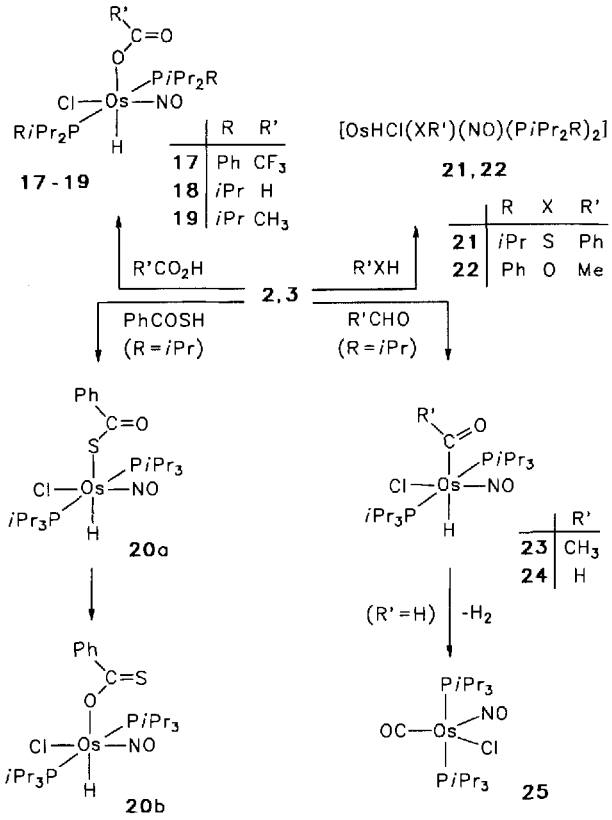
E **F** **G**

give rise to signals at δ = 2.68 and 2.37, respectively, which appear as triplets due to P–H coupling.

The reactions of **2** and **3** with carboxylic acids, methanol, thiophenol, and aldehydes are outlined in Scheme 5. Treatment of **2** and **3** with HCO_2H, CH_3CO_2H, or CF_3CO_2H in benzene leads to an almost instantaneous change of color from green to yellow or orange and affords the carboxylato(hydrido)osmium(II) compounds **17**–**19** in 80–90% yield. For the preparation of **17** it is important that precisely equimolar amounts of **3** and CF_3CO_2H are used since an excess of acid initiates decomposition. While **18** is a yellow oil at room temperature, the related complexes **17** and **19** are moderately air-stable solids which are thermally quite stable. They have been characterized by elemental analysis and spectroscopic techniques. The IR spectra of **17**–**19** confirm that the carboxylato ligands are monodentate[20], which is in agreement with the expected octahedral configuration of the products. The reaction of **2** with thiobenzoic acid is particularly interesting insofar as in the initially formed product **20a** the thiobenzoate ligand is most probably S-bonded as indicated by the strong ν(C=O) vibration at 1619 cm^{-1} in the IR spectrum. However, on storage of this compound for 8 days in benzene solution at room temperature, a complete rearrangement occurs and the thermodynamically more stable O-bonded isomer **20b** is formed. This rearrangement is accompanied by the disappearance of the IR band at 1619 cm^{-1} and a shift of the NO stretching absorption from 1750 to 1795 cm^{-1}. In the ^{1}H-NMR spectrum of **20a**, the hydride signal is observed at δ = −5.56 while in that of **20b** it appears at δ = −4.19. The ^{13}C- and ^{31}P-NMR spectra of **20a** and **20b** also reveal some minor differences which support the assumption that isomeric species with a similar structure are present.

Whereas compound **2** in the presence of PhSH behaves as expected and yields the hydrido(thiophenolato)osmium(II) complex **21** almost quantitatively, the corresponding reaction of the analogous starting material **3** with methanol deserves a special comment. As is apparent from a literature survey[21], transition metal compounds having both hydride and methoxo ligands are quite rare, which could be due to the fact that an energetically preferred pathway going from $L_nM(OCH_3)$ to $L_nMH(O{=}CH_2)$, $L_nMH_2(CHO)$ and finally to $L_nMH(CO)$ usually exists. By using areneosmium complexes as starting materials, we have previously shown that in the coordination sphere of Os, in the presence of a hydrogen acceptor such as $CH_2{=}CHtBu$, a clean metal-mediated cleavage of ethanol into H_2, CO, H, and CH_3 (the last three species remaining coordinated to osmium) takes place[22]. The hydrido(methoxo) compound **22** is unusually stable

Scheme 5



and decomposes on heating only at 154 °C. Since the ^{1}H-NMR spectrum of **22** displays the signal for the OsH proton at relatively low field (δ = −2.31), it is conceivable that the hydride ligand is *trans* to NO, although as in **17**–**21** a transoid arrangement of H and OCH_3 seems more likely.

Not only acetic acid, but also acetaldehyde reacts quite rapidly with **2** to give the acetyl(hydrido)osmium(II) complex **23** in ca. 80% yield. The yellow solid is somewhat more air-sensitive than the methoxy derivative **22** but can be stored under argon at 0 °C for days without decomposition. It should be mentioned that Roper et al. reported the synthesis of an acetyl(hydrido)osmium(II) complex $[OsH\{\eta^1\text{-}C(=O)CH_3\}(CO)_2(PPh_3)_2]$ from $[Os(CO)_2(PPh_3)_3]$ and acetaldehyde[23], although acetylosmium as well as acetylruthenium compounds are more commonly obtained by insertion of CO into an M–CH_3 bond[24]. Characteristic spectroscopic features of **23** are the C=O stretching frequency in the IR spectrum at 1653 cm^{-1}, the high-field signal of the hydride ligand in the ^{1}H-NMR spectrum at δ = −4.25, and the resonance of the acetyl carbon atom in the ^{13}C-NMR spectrum at δ = 173.3.

Although the reaction of **2** with gaseous formaldehyde takes place in toluene even at −40 °C and is complete within a few minutes, we failed to isolate the supposed formyl(hydrido)osmium(II) complex **24** in an analytically pure state. The yellow-brown oil, which was isolated upon facile work-up of the reaction mixture at low temperature, exhibits a broad singlet at δ = 11.81 and a triplet at δ = −6.79 [*J*(PH) = 27.5 Hz] in its ^{1}H-NMR spectrum in $CDCl_3$,

These signals can be assigned to the formyl proton and the hydride ligand, respectively. The ^{13}C-NMR spectrum (in $CDCl_3$ at −40 °C) displays a signal at δ = 194.5 which, by comparison with the data of Roper's compound $[OsH(\eta^1\text{-}CHO)(CO)_2(PPh_3)_2]$[25], seems to be typical for a metal-bonded CHO carbon atom. IR and ^{13}C-NMR spectra, recorded after storage of the oily substance for 2 h at −40 °C, clearly indicated that the product consisted mainly of the carbonyl complex **25**, which was originally prepared from **2** and CO[1].

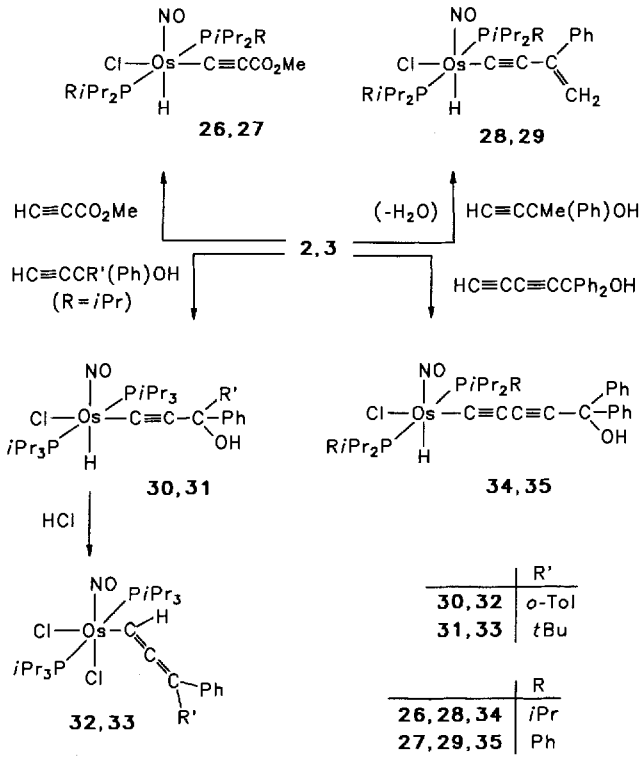
Reactions of 2 and 3 with Terminal Alkynes and Diynes

Since our first attempts to prepare nitrosylosmium complexes containing the metal-vinylidene fragment Os=C=CHPh had been unsuccessful[1b], we tried to use $HC{\equiv}CCO_2Me$ as a more appropriate starting material. It was known from our recent work that treatment of $[OsCl_2\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(OMe){=}O\}_2]$ with $HC{\equiv}CCO_2Me$ leads to the exclusive formation of the corresponding vinylidene derivative $[OsCl_2(=C{=}CHCO_2Me)\{\kappa(P)iPr_2PCH_2CO_2Me\}\{\kappa^2(P,O)\text{-}iPr_2PCH_2C(OMe){=}O\}]$[26].

In contrast to this and other results[27], the starting materials **2** and **3** react with $HC{\equiv}CCO_2Me$ in benzene at room temperature to give instead of the vinylidene complexes the isomeric six-coordinate alkynyl(hydrido)osmium(II) compounds **26** and **27** in excellent yield. The red solids, which are formed by oxidative addition of the terminal alkyne to the osmium(0) centre, are air-stable and are readily soluble in most organic solvents. The most characteristic feature of the ^{1}H-NMR spectra of **26** and **27** is the signal of the Os*H* proton, which appears at unusually low field (δ = −0.90 and −0.84, respectively). From this we conclude that the hydride is *trans* disposed to the strong π-acceptor ligand NO and, therefore, the octahedral configuration shown in Scheme 6 for **26** and **27** seems most likely. Attempts to rearrange the alkynyl(hydrido) complexes to the vinylidene isomers failed. While on heating of a solution of **26** or **27** in benzene to 60 °C for several hours no reaction occurred, irradiation with UV light led to rapid decomposition. Thus the question remains as to whether compounds of the general composition $[OsCl(=C{=}CHR')(NO)(PR_3)_2]$ are stable or not.

The starting materials **2** and **3** react with the propargylic alcohol HC≡CCMe(Ph)OH in a somewhat different manner than with $HC{\equiv}CCO_2Me$. After 24 hours in toluene at room temperature red solids are formed, which, on the basis of their elemental analyses and spectroscopic data, correspond to the enynyl(hydrido)osmium(II) derivatives **28** and **29** (Scheme 6). The ^{1}H-NMR spectra display two resonances for the vinyl protons at δ = 5.36 and 4.93 for **28** and at δ = 5.30 and 4.34 for **29**, which confirms that the two hydrogens of the CH_2 group are not equivalent. In the ^{13}C-NMR spectra, the signal of the CH_2 carbon is observed at δ = 114.9 (**28**) and 116.0 (**29**), while that of the quaternary carbon atom appears at δ = 133.9 (**28**) and 133.4 (**29**), respectively. With regard to the mechanism of formation of the enynyl(hydrido) complexes, we assume that initially an intermediate containing the OH-functionalized alkynyl ligand C≡CCMe(Ph)OH is generated, elimination of water from which yields the final product. It should be mentioned that Bruce et al. recently reported the preparation of the ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru\{C{\equiv}CC(PPh_3){=}CH_2\}(PPh_3)_2]PF_6$[28] containing a similar enynyl unit to that in **28** and **29**.

Scheme 6



The reactions of **2** and **3** with HC≡CCPh(*o*-Tol)OH and HC≡CCPh(*t*Bu)OH proceed analogously to those with $HC{\equiv}CCPh_2OH$[1b] and afford the octahedral alkynyl(hydrido) compounds **30** and **31**. According to the spectroscopic data there is no doubt that the ligand arrangement of **26**–**29** and of **30**, **31** is the same. In the IR spectra, the C≡C stretching absorption appears at 2030 cm^{-1} (for **30**) and 2056 cm^{-1} (for **31**), while in the ^{1}H-NMR spectra the hydride bonded to osmium is observed at δ = −0.86 (for **30**) and −1.02 (for **31**). The ^{13}C-NMR spectra display a triplet at δ ca. 75 for the α-alkynyl and a singlet at δ ca. 118 for the β-alkynyl carbon atom.

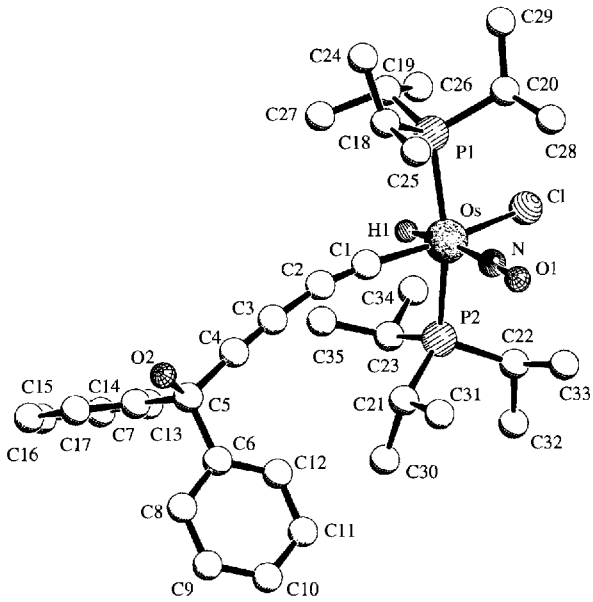
On treatment of **30** and **31** with a 37% aqueous solution of HCl, elimination of water accompanied by the addition of HCl takes place, and instead of the desired allenylideneosmium(0) complexes $[OsCl\{{=}C{=}C{=}C(Ph)R'\}(NO)(PiPr_3)_2]$ (R′ = *o*-Tol, *t*Bu), the allenylosmium(II) derivatives **32** and **33** are obtained. With regard to the course of the reaction, we assume that in the initial step attack at the OH group by the HCl proton and elimination of H_2O results in the formation of a cationic allenylidene(hydrido)osmium(II) species. Following a 1,2-hydrogen shift from the metal to the α-C atom of the allenylidene ligand, a five-coordinate intermediate $[OsCl\{CH{=}C{=}C(Ph)R'\}(NO)(PiPr_3)_2]^+$ could be generated, which by addition of chloride

would then give the final product. Support for this proposal comes from the observation that if a 37% aqueous solution of DCl is used, no deuterium is found at the α-position of the CH=C=C(Ph)R′ unit. In this context we note that although most of the known η^1-allenyl transition metal complexes have been prepared by oxidative addition of propargyl or allenyl halides to nucleophilic metal precursors[29], there is precedence for the formation of allenyl ligands from propargylic alcohols HC≡CCPh(R)OH by our own work[1b] as well as by that of others[30]. Characteristic spectroscopic features of **32** and **33** are the C=C=C stretching frequency in the IR spectra at about 1880 cm^{-1} and the three resonances in the ^{13}C-NMR spectra at δ = 77.4, 201.8, 102.1 (for **32**) and 75.5, 200.3, 109.1 (for **33**) for the α-, β-, and γ-allenyl carbon atoms. Only the first of these is split into a triplet. In the ^{1}H-NMR spectra of **32**, the allenyl proton Os*CH* also gives rise to a triplet, which is observed at δ = 8.08.

Finally, the reactivity of the square-planar osmium(0) compounds **2** and **3** toward the diynol HC≡CC≡CCPh$_2$OH was also investigated. The diynol reacts almost instantaneously with **2** and **3** in benzene at room temperature and upon chromatographic work-up of the reaction mixture, the OH-functionalized diynyl(hydrido)osmium(II) complexes **34** and **35** are isolated as red crystals in 65–70% yield. The preparative procedure given in the Experimental Section has to be followed very carefully, otherwise the diynol (possibly also the product) undergoes polymerization reactions. In dichloromethane, rapid decomposition of the complexes occurs. The IR- and NMR-spectroscopic data of **34** and **35** are in some respects similar to those of **26**, **27** and **30**, **31** and indicate that, as in those cases, an oxidative addition of the alkyne has taken place. The ^{13}C-NMR spectra of **34** and **35** display five distinct signals for the carbon atoms of the Os–C≡C–C≡C–C chain between δ = 104 and 74, of which surprisingly that of the β-C atom is least shielded.

In order to confirm the proposed structure for **34** (and indirectly also that for the other six-coordinate alkynyl(hydrido)osmium(II) complexes summarized in Scheme 6), a single-crystal X-ray diffraction investigation was carried out. The crystals were found to contain one diethyl ether molecule per osmium atom, the atoms of which could be anisotropically refined. The SCHAKAL drawing of **34** (Figure 3) reveals that the geometry around the metal centre is distorted octahedral with the chloride and nitrosyl ligands *cis* and the two phosphanes *trans* to each other. The P1–Os–P2 axis is significantly bent [bond angle 160.58(3)°] towards the hydride ligand, a situation which has also been found in other six-coordinate bis(triisopropylphosphane)hydridometal compounds[31]. Due to this bending, the largest corner-to-center-to-corner angles of the octahedron are found for Cl–Os–N [99.5(1)°], P1–Os–N [99.4(1)°] and P2–Os–N [100.0(1)°], respectively. The Os–N–O unit is almost linear [175.1(4)°] and the N–O bond length [1.154(4) Å] is practically identical to that in the free NO molecule[32]. Although the position of the metal-bonded hydrogen H1 was found in a difference Fourier analysis, the calculated distance Os–H1 of 1.33(3) Å seems to be too small, even when the *trans* influence of the nitrosyl ligand is taken into account. Similar observations regarding the distance of hydride ligands to 4d and 5d transition-metals have also been made in other cases[31b,33].

Figure 3. Molecular structure of **34**; selected bond lengths [Å] and angles [°]: Os–P1 2.407(1), Os–P2 2.422(1), Os–N 1.784(4), Os–Cl 2.428(1), Os–H1 1.33(3), Os–C1 2.016(4), N–O1 1.154(4), C1–C2 1.194(5), C2–C3 1.369(5), C3–C4 1.187(5), C4–C5 1.480(5), C5–O2 1.432(4); Cl–Os–P1 88.04(3), Cl–Os–P2 89.01(4), Cl–Os–N 99.5(1), Cl–Os–C1 166.2(1), Cl–Os–H1 88(1), P1–Os–P2 160.58(3), P1–Os–N 99.4(1), P1–Os–C1 91.5(1), P1–Os–H1 86(1), P2–Os–N 100.0(1), P2–Os–C1 86.9(1), P2–Os–H1 75(1), N–Os–C1 94.1(2), N–Os–H1 171(1), Cl–Os–H1 78(1), Os–N–O1 175.1(4), Os–C1–C2 173.2(3), C1–C2–C3 168.7(4), C2–C3–C4 175.5(4), C3–C4–C5 176.3(4)



In contrast to the six-coordinate ruthenium(II) complexes all-*trans*-[Ru(C≡C–C≡CR)$_2$(CO)$_2$(PEt$_3$)$_2$] (R = H, SiMe$_3$), in which the diynyl ligands are nearly linear[34], the bond angle C1–C2–C3 [168.7(4)°], and to a lesser extent that of Os–C1–C2 [173.2(3)°], deviates somewhat more from linearity. The reason for this is not clear but may originate in some steric hindrance between the diynyl carbon atoms and the triisopropylphosphane ligands. The C–C distances in the C$_5$ chain alternate and lie in the same range as found for other diynylmetal compounds[34,35]. The bond lengths Os–C1 of 2.016(4) Å is almost identical to that found for the Os–C(sp) single bond in [Os(C≡CCO$_2$Me)-{κ^2(*C*,*O*)-CH=CHC(OMe)=O}(CO)(P*i*Pr$_3$)$_2$] [1.977(4) Å][36], but is slightly shorter than that in the related derivative [Os(C≡CPh){κ^2(*N*,*C*)-NH=C(Ph)C$_6$H$_4$}(CO)(P*i*Pr$_3$)$_2$] [2.074(7) Å][37]. The Os–P and Os–Cl distances correspond to what could be expected for octahedral complexes of osmium(II) containing two *trans* disposed P*i*Pr$_3$ ligands[1b,3,36,37] and merit no further comments.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We thank the *Degussa AG* for generous gifts of chemicals, Mrs. *R. Schedl* and Mr. *C. P. Kneis* for performing the elemental analyses and DTA measurements, Mrs. Dr. *G. Lange* and Mr. *F. Dadrich* for recording the

mass spectra, and Mrs. *M.-L. Schäfer* and Dr. *W. Buchner* for carrying out NMR measurements.

Experimental Section

All operations were carried out under argon using Schlenk-tube techniques. The starting materials **1**[7a], **9**[1b], $PiPr_2Ph$[38], and $HC{\equiv}CC{\equiv}CCPh_2OH$[39] were prepared according to published procedures. $PiPr_3$ was a commercial product from Strem. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400. Abbreviations used: dvt = doublet of virtual triplets. – MS: Finnigan 90 MAT (70 eV).

1. Simplified Preparative Procedure for [OsCl(NO)(PiPr$_2$R)$_2$] (**2, 3**): A suspension of 166 mg (0.20 mmol) of **1** in 15 ml of benzene was treated with 114 µl (0.60 mmol) of $PiPr_3$ or with 130 µl (0.60 mmol) of $PiPr_2Ph$, respectively. The reaction mixture was stirred for 20 min at 60°C which led to a change of color from yellow to dark-green. After cooling the solution to room temp., it was concentrated to ca. 3 ml in vacuo and then 5 ml of hexane was added. A dark-green microcrystalline solid precipitated which was separated from the mother liquor, washed with 10 ml portions of pentane and ethanol, and dried in vacuo; yield 104 mg (91%) of **2** and 123 mg (97%) of **3**. Both complexes were characterized by IR and ^{1}H-NMR spectroscopy[1b].

2. Preparation of trans-[OsCl(NO)(CNMe)(PiPr$_3$)$_2$][(**4**): A solution of 125 mg (0.22 mmol) of **2** in 8 ml of benzene was treated at 10°C with 13 µl (0.22 mmol) of methyl isocyanide which led to an instantaneous change of color from dark-green to yellow. The solvent was removed in vacuo, and the oily residue was stirred with 8 ml of pentane. After 2–3 h, a yellow solid was formed which was filtered off, washed with 3 ml of pentane and dried; yield 102 mg (76%), m.p. 86°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2127 cm^{-1} [ν(CN)], 1639 [ν(NO)]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.43 (s, br, 3H, $CNCH_3$), 2.76 (m, 6H, $PCHCH_3$), 1.26 [dvt, *N* = 13.7, *J*(HH) = 7.2 Hz, 18H, $PCHCH_3$], 1.23 [dvt, *N* = 14.0, *J*(HH) = 7.2 Hz, 18H, $PCHCH_3$]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 144.1 [t, *J*(PC) = 4.1 Hz, $CNCH_3$], 20.8 (s, $CNCH_3$), 20.1 (vt, *N* = 28.1 Hz, $PCHCH_3$), 19.4 (s, br, $PCHCH_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 20.6 (s). – $C_{20}H_{45}ClN_2OOsP_2$ (617.2): calcd. C 38.92, H 7.35, N 4.54; found C 39.39, H 7.81, N 4.76.

3. Preparation of [OsCl(NO)(CNtBu)(PiPr$_3$)$_2$] (**5**): Compound **5** was prepared analogously to **4**, by using 156 mg (0.27 mmol) of **2** and 31 µl (0.27 mmol) of *t*BuCN as starting materials; yellow microcrystalline solid, yield 104 mg (58%), m.p. 95°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2118 cm^{-1} [ν(CN)], 1595 [ν(NO)]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.44 (m, 6H, $PCHCH_3$), 1.41 [s, 9H, $NC(CH_3)_3$], 1.24 [dvt, *N* = 14.7, *J*(HH) = 7.1 Hz, 18H, $PCHCH_3$], 1.22 [dvt, *N* = 14.2, *J*(HH) = 7.0 Hz, 18H, $PCHCH_3$]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 58.7 [s, $NC(CH_3)_3$], 30.8 [s, $NC(CH_3)_3$], 26.5 (vt, *N* = 24.7 Hz, $PCHCH_3$), 20.1 (s, br, $PCHCH_3$), signal of *C*N*t*Bu not exactly located. – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 17.9 [s, $J(^{187}Os^{31}P)$ = 162.0 Hz]. – $C_{23}H_{51}ClN_2OOsP_2$ (659.3): calcd. C 41.90, H 7.80, N 4.25; found C 41.74, H 7.68, N 4.13.

4. Preparation of [OsCl(NO){κ^2(O,S)-SO$_2$}(PiPr$_2$Ph)$_2$] (**6**): A slow stream of SO_2 was passed through a solution of 80 mg (0.12 mmol) of **3** in 5 ml of benzene for 1 min at room temp. A smooth change of color from dark-green to orange occurred. The solution was concentrated to ca. 2 ml in vacuo, and after 5 ml of pentane was added, an orange solid precipitated. This was separated from the mother liquor, washed twice with 5 ml portions of pentane and dried; yield 64 mg (73%), m.p. 46°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1802 cm^{-1} [ν(NO)], 1112, 874 [ν(SO_2)]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.67–7.24 (m, 10H, C_6H_5), 3.34 (m, 2H, $PCHCH_3$), 3.17 (m, 2H, $PCHCH_3$), 1.24 [dvt, *N* = 14.9, *J*(HH) = 7.4 Hz, 6H, $PCHCH_3$], 1.21 [dvt, *N* = 15.2, *J*(HH) = 6.8 Hz, 6H, $PCHCH_3$], 1.19 [dvt, *N* = 14.3, *J*(HH) = 6.4 Hz, 6H, $PCHCH_3$]; one signal of $PCHCH_3$ protons partly obscured by signal at δ = 1.24. – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 9.2 (s). – $C_{24}H_{38}ClNO_3OsP_2S$ (708.2): calcd. C 40.70, H 5.41, N 1.98, S 4.52; found C 40.86, H 5.06, N 2.40, S 4.56.

5. Preparation of [OsCl(NO)(η^2-O$_2$)(PiPr$_3$)$_2$] (**7**): A slow stream of oxygen was passed through a solution of 78 mg (0.14 mmol) of **2** in 8 ml of benzene for 1 min at room temp. A rapid change of color from dark-green to red occurred. After the solution was worked-up analogously as described for **6**, a red-brown microcrystalline solid was isolated; yield 61 mg (74%), m.p. 96°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1767 cm^{-1} [ν(NO)], 882 [ν(O_2)]. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.57 (m, 6H, $PCHCH_3$), 1.33 [dvt, *N* = 14.6, *J*(HH) = 7.3 Hz, 18H, $PCHCH_3$], 1.29 [dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 18H, $PCHCH_3$]. – ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 33.3 (s). – $C_{18}H_{42}ClNO_3OsP_2$ (608.1): calcd. C 35.55, H 6.96, N 2.30; found C 35.74, H 7.27, N 2.14.

6. Preparation of [OsCl(NO){κ^2(O,O)-O$_2$SO$_2$}(PiPr$_3$)$_2$] (**8**): A slow stream of SO_2 was passed through a solution of 97 mg (0.16 mmol) of **7** in 8 ml of benzene for 1 min at room temp. A change of color from red to orange-brown occurred. The solvent was removed, the residue was dissolved in 2 ml of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With benzene, an orange fraction was eluted, from which the solvent was removed in vacuo. The remaining orange solid was washed with 5 ml of pentane and dried; yield 74 mg (69%), m.p. 137°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1798 cm^{-1} [ν(NO)], 1297, 1166, 890, 867 [ν(SO)]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.38 (m, 6H, $PCHCH_3$), 1.37 [dvt, *N* = 14.5, *J*(HH) = 7.1 Hz, 18H, $PCHCH_3$], 1.29 [dvt, *N* = 14.2, *J*(HH) = 6.9 Hz, 18H, $PCHCH_3$]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 22.8 (vt, *N* = 22.0 Hz, $PCHCH_3$), 20.8, 20.3 (both s, $PCHCH_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 6.9 (s). – $C_{18}H_{42}ClNO_5OsP_2S$ (672.1): calcd. C 32.17, H 6.30, N 2.08, S 4.76; found C 32.53, H 6.80, N 2.47, S 4.61.

7. Preparation of [OsCl(NO){κ^2(C,O)-CH$_2$S(O)O}(PiPr$_3$)$_2$] (**10**): A slow stream of SO_2 was passed through a solution of 132 mg (0.22 mmol) of **9** in 8 ml of CH_2Cl_2 for 3 min at room temp. After closure of the Schlenk tube, the solution was stirred under 2 bar of SO_2 for 8 h which led to a smooth change of color from orange to yellow. The pressure was reduced to 1 bar, 5 ml of ethanol was added, and the mixture of solvents was evaporated until crystallization started. The concentrated solution was then stored at –78°C for 12 h, the yellow precipitate was filtered off, washed with 5 ml of ethanol and dried in vacuo; yield 94 mg (64%), m.p. 164°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1770 cm^{-1} [ν(NO)], 1138, 1098, 795 [ν(SO)]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.24 (m, 2H, CH_2SO_2), 3.20 (m, 3H, $PCHCH_3$), 3.18 (m, 3H, $PCHCH_3$), 1.45 [dvt, *N* = 14.7, *J*(HH) = 7.2 Hz, 9H, $PCHCH_3$], 1.42 [dvt, *N* = 14.1, *J*(HH) = 7.4 Hz, 9H, $PCHCH_3$], 1.41 [dvt, *N* = 13.8, *J*(HH) = 7.1 Hz, 9H, $PCHCH_3$]; one signal of $PCHCH_3$ protons partly obscured by signal at δ = 1.41. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 24.7 (vt, *N* = 29.6 Hz, $PCHCH_3$), 24.6 (vt, *N* = 30.8 Hz, $PCHCH_3$), 21.1, 20.5, 20.3, 19.5 (all s, $PCHCH_3$), 7.6 [dd, $J(P_1C)$ = 5.4, $J(P_2C)$ = 4.1 Hz, CH_2SO_2]. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): AB spin system, δ_A = 5.8, δ_B = 3.4 [*J*(PP) = 326 Hz]. – $C_{19}H_{44}ClNO_3OsP_2S$ (654.2): calcd. C 34.89, H 6.78, N 2.14, S 4.89; found C 34.53, H 6.81, N 2.55, S 4.72.

8. Preparation of [OsCl$_2$(CH$_3$)(NO)(PiPr$_3$)$_2$] (**11**): A solution of 101 mg (0.17 mmol) of **9** in 5 ml of benzene was treated with a

few drops of a saturated solution of HCl in benzene and stirred for 24 h at room temp. The solvent was removed, the partly oily residue was treated with 5 ml of pentane, and the suspension was stirred until precipitation occurred. The orange solid was filtered off, washed twice with 3 ml portions of pentane and dried in vacuo; yield 60 mg (56%), m.p. 141 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1771 cm^{-1} [ν(NO)]. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.97 (m, 6H, PC*H*CH_3), 2.42 [t, *J*(PH) = 4.1 Hz, 3H, OsCH_3], 1.21 [dvt, *N* = 14.1, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.19 [dvt, *N* = 14.0, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$]. – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = −14.2 (s). – $C_{19}H_{45}Cl_2NOOsP_2$ (626.6): calcd. C 36.42, H 7.24, N 2.23; found C 36.14, H 6.86, N 1.98.

9. Preparation of [OsHCl$_2$(NO)(PiPr$_2$Ph)$_2$] (**12**): To a solution of 182 mg (0.28 mmol) of **3** in 12 ml of toluene, a saturated solution of HCl in ether was added dropwise until a change of color from dark-green to yellow occurred. The solvent was removed, the yellow residue was washed three times with 5 ml portions of ether and dried in vacuo; yield 150 mg (78%), m.p. 128 °C (dec.). – IR (THF): $\tilde{\nu}$ = 2170 cm^{-1} [ν(OsH)], 1775 [ν(NO)]. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 8.31–7.79 (m, 10H, C_6H_5), 3.10 (m, 2H, PC*H*CH_3), 2.78 (m, 2H, PC*H*CH_3), 1.37 [dvt, *N* = 14.9, *J*(HH) = 6.7 Hz, 6H, PCHC*H*$_3$], 1.26 [dvt, *N* = 14.4, *J*(HH) = 6.8 Hz, 6H, PCHC*H*$_3$], 1.08 [dvt, *N* = 13.9, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$], 1.01 [dvt, *N* = 14.4, *J*(HH) = 6.8 Hz, 6H, PCHC*H*$_3$], −5.78 [t, *J*(PH) = 16.0 Hz, 1H, OsH]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 135.8, 129.3 (both vt, *N* = 9.8 and 10.1 Hz, *o*-C and *m*-C of C_6H_5), 131.7 (s, *p*-C of C_6H_5), 126.6 (vt, *N* = 38.6 Hz, *ipso*-C of C_6H_5), 25.7 (vt, *N* = 32.8 Hz, PCHCH$_3$), 23.3 (vt, *N* = 29.3 Hz, PCHCH$_3$), 19.2, 19.0, 18.3, 17.7 (all s, PCHC*H*$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 12.5 (s, d in off-resonance). – $C_{24}H_{39}Cl_2NOOsP_2$ (680.6): calcd. C 42.35, H 5.78, N 2.06; found C 42.82, H 5.73, N 1.81.

10. Preparation of [OsCl$_2$I$_2$(NO)(PiPr$_2$Ph)$_2$] (**13**): To a solution of 205 mg (0.32 mmol) of **3** in 15 ml of toluene was added 82 mg (0.32 mmol) of iodine and the mixture was stirred for 1 h at room temp. The solution was concentrated to ca. 3 ml in vacuo and after 10 ml of pentane was added, a yellow microcrystalline solid precipitated. It was separated from the mother liquor, washed with 5 ml of methanol (0 °C) and 5 ml of ether (0 °C), and dried; yield 274 mg (96%), m.p. 188 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1785 cm^{-1} [ν(NO)]. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.81–7.32 (m, 10H, C_6H_5), 3.98 (m, 4H, PC*H*CH_3), 1.41 [dvt, *N* = 14.9, *J*(HH) = 7.1 Hz, 12H, PCHC*H*$_3$], 1.29 [dvt, *N* = 14.4, *J*(HH) = 7.2 Hz, 12H, PCHC*H*$_3$]. – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = −9.6 (s). – $C_{24}H_{38}Cl_2I_2NOOsP_2$ (898.0): calcd. C 32.10, H 4.27, N 1.56; found C 32.47, H 4.15, N 1.48; mol. mass 897 (MS).

11. Preparation of [OsClI(CH$_3$)(NO)(PiPr$_3$)$_2$] (**14**): To a solution of 178 mg (0.31 mmol) of **2** in 13 ml of toluene was added 29 µl (0.32 mmol) of CH_3I and the mixture was stirred for 1 h at 0 °C. A change of color from dark-green to orange occurred. The solvent was removed in vacuo, and the residue was extracted twice with 5 ml portions of ethanol. The combined extracts were concentrated to ca. 3 ml and after 5 ml of pentane was added, an orange microcrystalline solid precipitated. It was separated from the mother liquor, washed with 5 ml of pentane and dried; yield 189 mg (85%), m.p. 139 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1775 cm^{-1} [ν(NO)]. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.08 (m, 6H, PC*H*CH_3), 2.68 [t, *J*(PH) = 4.3 Hz, 3H, OsCH_3], 1.27 [dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.24 [dvt, *N* = 13.6, *J*(HH) = 6.4 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.1 (vt, *N* = 23.4 Hz, PCHCH$_3$), 19.9, 19.8 (both s, PCHC*H*$_3$), −9.4 [t, *J*(PC) = 5.0 Hz, OsCH_3]. – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = −14.2 (s). – $C_{19}H_{45}ClINOOsP_2$ (718.1): calcd. C 31.78, H 6.32, N 1.95; found C 31.43, H 6.67, N 1.85.

12. Preparation of [OsClI(CH$_3$)(NO)(PiPr$_2$Ph)$_2$] (**15**): Compound **15** was prepared analogously to **14**, by using 154 mg (0.24 mmol) of **3** and 23 µl (0.25 mmol) of CH_3I as starting materials; orange air-stable solid; yield 161 mg (86%), m.p. 134 °C (dec.). – IR (THF): $\tilde{\nu}$ = 1770 cm^{-1} [ν(NO)]. – ^1H NMR (C_6D_6, 400 MHz): δ = 7.68–7.08 (m, 10H, C_6H_5), 3.81 (m, 2H, PC*H*CH_3), 3.42 (m, 2H, PC*H*CH_3), 2.37 [t, *J*(PH) = 4.9 Hz, 3H, OsCH_3], 1.53 [dvt, *N* = 14.6, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$], 1.44 [dvt, *N* = 14.5, *J*(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.30 [dvt, *N* = 14.4, *J*(HH) = 7.1 Hz, 6H, PCHC*H*$_3$], 1.24 [dvt, *N* = 14.4, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$]. – ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = −13.7 (s). – $C_{25}H_{41}ClINOOsP_2$ (786.1): calcd. C 38.20, H 5.26, N 1.78; found C 38.68, H 5.33, N 1.54.

13. Preparation of [OsClBr(CH=CH$_2$)(NO)(PiPr$_3$)$_2$] (**16**): A solution of 154 mg (0.27 mmol) of **2** in 10 ml of toluene was treated at −78 °C with an excess (ca. 100 µl) of vinyl bromide. After warming to 0 °C, the mixture was stirred for 3 h. A change of color from dark-green to orange occurred. The solution was worked-up as described for **14**; orange microcrystalline solid; yield 122 mg (67%), m.p. 133 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1771 cm^{-1} [ν(NO)], 1552 [ν(C=C)]. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.53 [m, in $^1H\{^{31}P\}$ dd, $J(H^1H^2)$ = 17.9, $J(H^1H^3)$ = 10.5 Hz, 1H, Os-CH^1], 5.87 [m, in $^1H\{^{31}P\}$ dd, $J(H^1H^3)$ = 10.5, $J(H^2H^3)$ = 2.0 Hz, 1H, =C*H*^{3}H (*cis* to H^1)], 4.89 [m, in $^1H\{^{31}P\}$ dd, $J(H^1H^2)$ = 17.9, $J(H^2H^3)$ = 2.0 Hz, 1H, =CH*H*^{2} (*trans* to H^1)], 3.14 (m, 6H, PC*H*CH_3), 1.39 [dvt, *N* = 14.0, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.34 [dvt, *N* = 13.5, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 141.9 [t, *J*(PC) = 7.3 Hz, OsCH], 119.6 (s, br, =CH_2), 25.6 (vt, *N* = 23.2 Hz, PCHCH$_3$), 20.5, 20.1 (both s, PCHC*H*$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = −9.6 (s). – $C_{20}H_{45}BrClNOOsP_2$ (683.1): calcd. C 35.16, H 6.64, N 2.05; found C 34.99, H 6.18, N 1.73.

14. Preparation of [OsHCl(η^1-O$_2$CCF$_3$)(NO)(PiPr$_2$Ph)$_2$] (**17**): A solution of 87 mg (0.14 mmol) of **3** in 10 ml of benzene was treated with 11 µl (0.14 mmol) of trifluoroacetic acid at room temp. which led to a rapid change of color from dark-green to orange. The solvent was removed, and the partly oily residue was stirred with 10 ml of hexane. After 4–5 h, an orange solid was formed which was separated from the mother liquor, washed three times with 3 ml portions of hexane and dried; yield 90 mg (88%), m.p. 167 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2219 cm^{-1} [ν(OsH)], 1807 [ν(NO)], 1681 [$\nu(OCO_{as})$], 1421 [$\nu(OCO_{sym})$]. – ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.92–7.24 (m, 10H, C_6H_5), 3.04 (m, 2H, PC*H*CH_3), 2.98 (m, 2H, PC*H*CH_3), 1.32 [dvt, *N* = 15.5, *J*(HH) = 7.5 Hz, 6H, PCHC*H*$_3$], 1.22 [dvt, *N* = 13.7, *J*(HH) = 6.5 Hz, 6H, PCHC*H*$_3$], 1.15 [dvt, *N* = 15.3, *J*(HH) = 7.8 Hz, 6H, PCHC*H*$_3$], 1.11 [dvt, *N* = 14.9, *J*(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], −8.12 [t, *J*(PH) = 16.1 Hz, 1H, OsH]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 161.8 [q, *J*(CF) = 36.4 Hz, *C*O$_2$CF$_3$], 134.3, 128.4 (both vt, *N* = 9.2 and 9.6 Hz, *o*-C and *m*-C of C_6H_5), 131.2 (*p*-C of C_6H_5), 124.6 (vt, *N* = 42.2 Hz, *ipso*-C of C_6H_5), 114.8 [q, *J*(CF) = 291.2 Hz, CO$_2$*C*F$_3$], 23.9 (vt, *N* = 31.5 Hz, PCHCH$_3$), 23.2 (vt, *N* = 29.0 Hz, PCHCH$_3$), 18.0, 18.0, 17.3, 16.9 (all s, PCHC*H*$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 21.5 (s, d in off-resonance). – ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ = −75.3 (s). – $C_{26}H_{39}ClF_3NO_3OsP_2$ (758.2): calcd. C 41.19, H 5.18, N 1.85; found C 40.91, H 5.43, N 2.03.

15. Preparation of [OsHCl(η^1-O$_2$CH)(NO)(PiPr$_3$)$_2$] (**18**): A solution of 124 mg (0.22 mmol) of **2** in 8 ml of benzene was treated with 8 µl (0.22 mmol) of formic acid at 10 °C. An almost instan-

taneous change of color from dark-green to yellow occurred. The solvent was removed, the oily residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, a yellow fraction was eluted, from which the solvent was removed in vacuo. A yellow oil was obtained; yield 110 mg (82%). – IR (C_6H_6): $\tilde{\nu}$ = 2132 cm^{-1} [ν(OsH)], 1772 [ν(NO)], 1648 [$\nu(OCO_{as})$], 1387 [$\nu(OCO_{sym})$]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.43 (m, 6H, PC*H*CH$_3$), 1.99 (s, 1H, CO_2H), 1.40 [dvt, *N* = 14.4, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$], 1.34 [dvt, *N* = 15.0, *J*(HH) = 7.3 Hz, 18H, PCHC*H*$_3$], –4.23 [t, *J*(PH) = 14.3 Hz, 1H, OsH]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 173.2 (s, CO_2H), 23.7 (vt, *N* = 22.2 Hz, P*C*HCH$_3$), 20.0, 18.9 (both s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 23.6 (s, d in off-resonance). – $C_{19}H_{44}ClNO_3OsP_2$ (622.2): calcd. C 36.68, H 7.13, N 2.25; found C 36.74, H 7.29, N 2.48.

16. Preparation of [OsHCl(η^1-O$_2$CCH$_3$)(NO)(PiPr$_3$)$_2$] (**19**): A solution of 123 mg (0.21 mmol) of **2** in 8 ml of benzene was treated with 12 μl (0.21 mmol) of acetic acid at room temp. An almost instantaneous change of color from dark-green to yellow occurred. The solvent was removed, the residue was dissolved in 3 ml of pentane, and the solution was stored for 24 h at –60 °C. A yellow solid precipitated which was separated from the mother liquor, washed three times with 2 ml portions of pentane (–20 °C) and dried in vacuo; yield 110 mg (81%), m.p. 139 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2144 cm^{-1} [ν(OsH)], 1777 [ν(NO)], 1656 [$\nu(OCO_{as})$], 1375 [$\nu(OCO_{sym})$]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.42 (m, 6H, PC*H*CH$_3$), 1.74 (s, 3H, CO_2CH_3), 1.36 [dvt, *N* = 14.4, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.33 [dvt, *N* = 14.5, *J*(HH) = 7.1 Hz, 18H, PCHC*H*$_3$], –4.24 [t, *J*(PH) = 13.8 Hz, 1H, OsH]. – ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 173.4 (s, CO_2CH_3), 23.5 (vt, *N* = 25.5 Hz, P*C*HCH$_3$), 19.9, 18.9 (both s, PCH*C*H$_3$), 19.8 (s, CO_2CH_3). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 23.6 (s, d in off-resonance). – $C_{20}H_{46}ClNO_3OsP_2$ (636.2): calcd. C 37.76, H 7.29, N 2.20; found C 38.21, H 6.84, N 1.91.

17. Preparation of [OsHCl{κ(S)-SC(=O)Ph}(NO)(PiPr$_3$)$_2$] (**20a**): A solution of 139 mg (0.24 mmol) of **2** in 10 ml of benzene was treated with 28 μl (0.24 mmol) of thiobenzoic acid at room temp. An almost instantaneous change of color from dark-green to orange occurred. The solution was concentrated to ca. 2 ml in vacuo, and then chromatographed on Al_2O_3 (neutral, activity grade III, height of column 5 cm). With benzene, an orange fraction was eluted, from which the solvent was removed in vacuo. The residue was dissolved in 3 ml of pentane and after storage of the solution for 2 d at –60 °C, orange crystals were precipitated. These were separated from the mother liquor, washed twice with 2 ml portions of pentane (–20 °C) and dried; yield 128 mg (74%), m.p. 104 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2135 cm^{-1} [ν(OsH)], 1750 [ν(NO)], 1619 [ν(C=O)]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98–7.22 (m, 5H, C_6H_5), 2.65 (m, 6H, PC*H*CH$_3$), 1.34 [dvt, *N* = 14.5, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$], 1.32 [dvt, *N* = 13.8, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$], –5.56 [t, *J*(PH) = 14.0 Hz, 1H, OsH]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 196.4 (s, C=O), 141.6 (s, *ipso*-C of C_6H_5), 129.3, 128.9 (both s, *o*-C and *m*-C of C_6H_5), 128.6 (s, *p*-C of C_6H_5), 25.1 (vt, *N* = 25.8 Hz, P*C*HCH$_3$), 20.7, 20.4 (both s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 6.7 (s, d in off-resonance). – $C_{25}H_{48}ClNO_2OsP_2S$ (714.3): calcd. C 42.04, H 6.77, N 1.96, S 4.48; found C 41.79, H 6.51, N 1.83, S 4.12.

18. Isomerization of **20a** *to [OsHCl{κ(O)-OC(=S)Ph}(NO)(PiPr$_3$)$_2$]* (**20b**): A solution of 71 mg (0.10 mmol) of **20a** in 1 ml of benzene was kept for 8 d at room temp. A quantitative rearrangement occurred; orange microcrystalline solid. – IR (KBr): $\tilde{\nu}$ = 2101 cm^{-1} [ν(OsH)], 1795 [ν(NO)]. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.21–7.31 (m, 5H, C_6H_5), 2.74 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.35 [dvt, *N* = 13.8, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], –4.19 [t, *J*(PH) = 15.8 Hz, 1H, OsH]. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 201.3 (s, C=S), 142.8 (s, *ipso*-C of C_6H_5), 131.3, 129.2, 128.5 (all s, *p*-C, *o*-C, and *m*-C of C_6H_5), 25.1 (vt, *N* = 25.9 Hz, P*C*HCH$_3$), 20.9, 20.1 (both s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 17.3 (s, d in off-resonance). – $C_{25}H_{48}ClNO_2OsP_2S$ (714.3): calcd. C 42.04, H 6.77, N 1.96, S 4.48; found C 42.46, H 6.90, N 2.34, S 4.95.

19. Preparation of [OsHCl(SPh)(NO)(PiPr$_3$)$_2$] (**21**): To a solution of 145 mg (0.25 mmol) of **2** in 6 ml of benzene was added 26 μl (0.25 mmol) of thiophenol and the mixture was stirred for 5 min at room temp. A rapid change of color from dark-green to orange-red occurred. The solvent was removed, and the oily residue was stirred with 1 ml of hexane at –20 °C until an orange solid precipitated. It was separated from the mother liquor, washed three times with 2 ml portions of hexane (–20 °C) and dried in vacuo; yield 145 mg (84%), m.p. 91 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2140 cm^{-1} [ν(OsH)], 1754 [ν(NO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.47–6.83 (m, 5H, C_6H_5), 2.73 (m, 6H, PC*H*CH$_3$), 1.34 [dvt, *N* = 14.1, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$], 1.24 [dvt, *N* = 13.2, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], –7.10 [t, *J*(PH) = 14.0 Hz, 1H, OsH]. – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 144.2 (s, *ipso*-C of C_6H_5), 132.0, 127.5, 122.9 (all s, *o*-C, *m*-C, and *p*-C of C_6H_5), 23.8 (vt, *N* = 25.0 Hz, P*C*HCH$_3$), 19.7, 19.4 (both s, PCH*C*H$_3$). – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 1.6 (s, d in off-resonance). – $C_{24}H_{48}ClNOOsP_2S$ (686.2): calcd. C 42.01, H 7.05, N 2.04, S 4.66; found C 41.95, H 6.84, N 2.03, S 4.80.

20. Preparation of [OsHCl(OCH$_3$)(NO)(PiPr$_2$Ph)$_2$] (**22**): A suspension of 171 mg (0.27 mmol) of **3** in 15 ml of methanol was stirred for 2 h at 60 °C which resulted in a smooth change of color from dark-green to yellow. After cooling to room temp., the solution was concentrated to ca. 5 ml in vacuo and then stored for 3 h at –40 °C. A yellow microcrystalline solid precipitated which was separated from the mother liquor, washed twice with 5 ml portions of pentane and dried; yield 163 mg (91%), m.p. 154 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2140 cm^{-1} [ν(OsH)], 1770 [ν(NO)]. – ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.91–7.69 (m, 10H, C_6H_5), 3.43 (s, 3H, OCH_3), 3.37 (m, 2H, PC*H*CH$_3$), 3.05 (m, 2H, PC*H*CH$_3$), 1.64 [dvt, *N* = 14.1, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$], 1.54 [dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$], 1.35 [dvt, *N* = 13.7, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$], 1.28 [dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 6H, PCHC*H*$_3$], –2.31 [t, *J*(PH) = 16.7 Hz, 1H, OsH]. – ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 15.2 (s, d in off-resonance). – $C_{25}H_{42}ClNO_2OsP_2$ (676.2): calcd. C 44.41, H 6.26, N 2.07; found C 44.09, H 6.42, N 1.99.

21. Preparation of [OsHCl{η^1-C(=O)CH$_3$}(NO)(PiPr$_3$)$_2$] (**23**): To a solution of 118 mg (0.20 mmol) of **2** in 8 ml of benzene was added 11 μl (0.20 mmol) of acetaldehyde and the mixture was stirred for 2 min at room temp. An almost instantaneous change of color from dark-green to yellow occurred. The solution was concentrated to ca. 2 ml in vacuo and then 5 ml of pentane was added. After sonofication of the mixture for 10 min in an ultrasonic bath, a yellow solid was formed which was separated from the mother liquor, washed three times with 2 ml portions of pentane (–20 °C) and dried; yield 100 mg (79%), m.p. 111 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2122 cm^{-1} [ν(OsH)], 1771 [ν(NO)], 1653 [ν(C=O)]. – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.43 (m, 6H, PC*H*CH$_3$), 1.75 (s, 3H, $COCH_3$), 1.42 [dvt, *N* = 14.7, *J*(HH) = 7.4 Hz, 18H, PCHC*H*$_3$], 1.32 [dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 18H, PCHC*H*$_3$],

−4.25 [t, J(PH) = 14.0 Hz, 1H, OsH]. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 173.3 (s, $COCH_3$), 23.5 (vt, N = 25.1 Hz, $PCHCH_3$), 22.0 (s, $COCH_3$), 19.7, 18.9 (both s, $PCHCH_3$). − ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 23.6 (s, d in off-resonance). − $C_{20}H_{46}ClNO_2OsP_2$ (620.2): calcd. C 38.73, H 7.48, N 2.26; found C 38.45, H 7.56, N 1.99.

*22. Preparation of [OsCl(NO)(CO)($PiPr_3$)$_2$] (**25**) from **2** and CH_2O via [OsHCl(η^1-CHO)(NO)($PiPr_3$)$_2$] (**24**) as Intermediate:* A slow stream of formaldehyde, generated from the trimer, was passed into a solution of 105 mg (0.18 mmol) of **2** in 8 ml of toluene at −40°C. An almost instantaneous change of color from dark-green to yellow occurred. The solvent was quickly removed in vacuo and the yellow-brown oily residue, which contained **24** as the main product, was investigated by NMR spectroscopy. After storage of the oily residue for 2 h at −40°C, the IR and ^{13}C-NMR spectra showed that it now consisted mainly of **25**[11b,40]. − Spectroscopic data of **24**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 11.81 (s, br, 1H, CHO), 2.38 (m, 6H, $PCHCH_3$), 1.18 [dvt, N = 14.5, J(HH) = 7.3 Hz, 18H, $PCHCH_3$], 1.16 [dvt, N = 14.5, J(HH) = 6.9 Hz, 18H, $PCHCH_3$], −6.79 [t, J(PH) = 27.5 Hz, OsH]. − ^{13}C NMR ($CDCl_3$, 100.6 MHz, 233 K): δ = 194.5 [t, J(PC) = 8.0 Hz, CHO], 23.9 (vt, N = 26.2 Hz, $PCHCH_3$), 20.4, 20.1 (both s, $PCHCH_3$). − ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 24.4 (s).

*23. Preparation of [OsHCl(C≡CCO_2Me)(NO)($PiPr_3$)$_2$] (**26**):* To a solution of 104 mg (0.18 mmol) of **2** in 10 ml of benzene, was added 16 µl (0.18 mmol) of methyl propiolate and the mixture was stirred for 1 h at room temp. A change of color from dark-green to red occurred. The solvent was removed, and the oily residue was stirred with 2 ml of hexane until a red precipitate was formed. It was separated from the mother liquor, washed with 5 ml of hexane and dried; yield 89 mg (75%), m.p. 115°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2095 cm^{-1} [ν(OsH)], 2075 [ν(C≡C)], 1748 [ν(NO)], 1680 [$\nu(OCO_{as})$]. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.57 (s, 3H, CO_2CH_3), 2.93 (m, 6H, $PCHCH_3$), 1.30 [dvt, N = 15.7, J(HH) = 7.8 Hz, 18H, $PCHCH_3$], 1.26 [dvt, N = 13.8, J(HH) = 6.9 Hz, 18H, $PCHCH_3$], −0.90 [t, J(PH) = 22.6 Hz, 1H, OsH]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 153.7 (s, CO_2CH_3), 112.0 (s, OsC≡CR), 94.3 [t, J(PC) = 9.5 Hz, OsC≡CR], 51.6 (s, CO_2CH_3), 24.3 (vt, N = 27.9 Hz, $PCHCH_3$), 18.7, 18.5 (both s, $PCHCH_3$). − ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 20.8 (s, d in off-resonance). − $C_{22}H_{46}ClNO_3OsP_2$ (660.2): calcd. C 40.02, H 7.02, N 2.12; found C 40.43, H 7.48, N 2.36.

*24. Preparation of [OsHCl(C≡CCO_2Me)(NO)($PiPr_2Ph$)$_2$] (**27**):* Compound **27** was prepared analogously to **26**, by using 124 mg (0.19 mmol) of **3** and 17 µl (0.19 mmol) of methyl propiolate as starting materials; red air-stable solid, yield 109 mg (78%), m.p. 115°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2098 cm^{-1} [ν(OsH)], 2074 [ν(C≡C)], 1725 [ν(NO)], 1669 [$\nu(OCO_{as})$]. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.59−7.03 (m, 10H, C_6H_5), 3.42 (m, 2H, $PCHCH_3$), 3.20 (s, 3H, CO_2CH_3), 2.98 (m, 2H, $PCHCH_3$), 1.18 [dvt, N = 15.8, J(HH) = 7.6 Hz, 6H, $PCHCH_3$], 1.09 [dvt, N = 14.7, J(HH) = 6.9 Hz, 6H, $PCHCH_3$], 1.02 [dvt, N = 14.1, J(HH) = 7.1 Hz, 6H, $PCHCH_3$], 0.95 [dvt, N = 13.9, J(HH) = 6.4 Hz, 6H, $PCHCH_3$], −0.84 [t, J(PH) = 24.1 Hz, 1H, OsH]. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 153.3 (s, CO_2CH_3), 134.9, 128.2 (both vt, N = 8.3 and 9.1 Hz, *o*-C and *m*-C of C_6H_5), 130.7 (s, *p*-C of C_6H_5), 124.3 (vt, N = 45.3 Hz, *ipso*-C of C_6H_5), 115.1 (s, OsC≡CR), 90.4 [t, J(PC) = 10.2 Hz, OsC≡CR], 50.8 (s, CO_2CH_3), 24.5 (vt, N = 31.1 Hz, $PCHCH_3$), 23.1 (vt, N = 31.2 Hz, $PCHCH_3$), 17.8, 17.6, 17.3, 16.8 (all s, $PCHCH_3$). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 23.1 (s, d in off-resonance). − $C_{28}H_{42}ClNO_3OsP_2$ (728.2): calcd. C 46.18, H 5.81, N 1.92; found C 46.02, H 5.47, N 2.21.

*25. Preparation of [OsHCl{C≡CC(Ph)=CH_2}(NO)($PiPr_3$)$_2$] (**28**):* To a solution of 204 mg (0.35 mmol) of **2** in 8 ml of toluene, was added 0.44 ml (0.35 mmol) of a 0.8 M solution of HC≡CCMe(Ph)OH in toluene and the mixture was stirred for 24 h at room temp. A smooth change of color from dark-green to red-brown occurred. The solution was concentrated to ca. 2 ml in vacuo and then 5 ml of pentane was added. A yellow-brown flocculent precipitate was formed which was filtered off. The solvent was evaporated from the filtrate in vacuo, the oily residue was dissolved in 2 ml of benzene and then chromatographed on Al_2O_3 (neutral, activity grade I, height of column 5 cm). With benzene, a red fraction was eluted, from which the solvent was removed in vacuo. The partly oily residue was suspended in 5 ml of hexane and upon sonification of the suspension for 10 min in an ultrasonic bath a light-red solid was formed. It was filtered off, washed with 5 ml of hexane and dried; yield 207 mg (83%), m.p. 101°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2094 cm^{-1} [ν(OsH)], 2029 [ν(C≡C)], 1739 [ν(NO)]. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.36−7.24 (m, 5H, C_6H_5), 5.36, 4.93 (both s, both br, 1H each, $=CH_2$), 3.03 (m, 6H, $PCHCH_3$), 1.34 [dvt, N = 14.8, J(HH) = 6.9 Hz, 18H, $PCHCH_3$], 1.29 [dvt, N = 13.8, J(HH) = 6.9 Hz, 18H, $PCHCH_3$], −0.80 [t, J(PH) = 23.6 Hz, 1H, OsH]. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 140.9 (s, *ipso*-C of C_6H_5), 133.9 (s, $C=CH_2$), 128.8, 128.2, 121.1 (all s, *o*-C, *p*-C, and *m*-C of C_6H_5), 119.4 (s, OsC≡CR), 114.9 (s, $C=CH_2$), 84.9 [t, J(PC) = 10.2 Hz, OsC≡CR], 25.3 (vt, N = 28.0 Hz, $PCHCH_3$), 19.8, 19.6 (both s, $PCHCH_3$). − ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = 19.8 (s, d in off-resonance). − $C_{28}H_{50}ClNOOsP_2$ (704.3): calcd. C 47.75, H 7.16, N 1.99; found C 48.03, H 7.47, N 2.31.

*26. Preparation of [OsHCl{C≡CC(Ph)=CH_2}(NO)($PiPr_2Ph$)$_2$] (**29**):* Compound **29** was prepared analogously to **28**, by using 268 mg (0.42 mmol) of **3** and 0.52 ml (0.42 mmol) of a 0.8 M solution of HC≡CCMe(Ph)OH as starting materials; light-red solid; yield 244 mg (76%), m.p. 97°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 2105 cm^{-1} [ν(OsH)], 2045 [ν(C≡C)], 1743 [ν(NO)]. − ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.06−7.27 (m, 15H, C_6H_5), 5.30, 4.34 (both s, 1H each, $C=CH_2$), 3.44 (m, 2H, $PCHCH_3$), 3.31 (m, 2H, $PCHCH_3$), 1.43 [dvt, N = 14.3, J(HH) = 7.0 Hz, 6H, $PCHCH_3$], 1.38 [dvt, N = 14.4, J(HH) = 6.9 Hz, 6H, $PCHCH_3$], 1.34 [dvt, N = 14.0, J(HH) = 6.7 Hz, 6H, $PCHCH_3$], 1.33 [dvt, N = 13.9, J(HH) = 6.8 Hz, 6H, $PCHCH_3$], −0.53 [t, J(PH) = 25.2 Hz, 1H, OsH]. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 140.5 (s, *ipso*-C of C_6H_5), 133.4 (s, $C=CH_2$), 135.3, 128.5 (both vt, N = 8.3 and 9.2 Hz, *o*-C and *m*-C of PC_6H_5), 131.1, 129.0, 128.3, 126.6 (all s, *o*-C, *m*-C, and *p*-C of C_6H_5, *p*-C of PC_6H_5), 125.6 (vt, N = 44.4 Hz, *ipso*-C of PC_6H_5), 121.6 (s, OsC≡CR), 116.0 (s, $C=CH_2$), 82.4 [t, J(PC) = 11.1 Hz, OsC≡CR], 24.4 (vt, N = 34.2 Hz, $PCHCH_3$), 23.3 (vt, N = 29.5 Hz, $PCHCH_3$), 18.4, 18.1, 17.2, 16.6 (all s, $PCHCH_3$). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 22.1 (s, d in off-resonance). − $C_{34}H_{46}ClNOOsP_2$ (772.3): calcd. C 52.87, H 6.00, N 1.81; found C 52.76, H 6.29, N 1.54.

*27. Preparation of [OsHCl{C≡CCPh(o-Tol)OH}(NO)($PiPr_3$)$_2$] (**30**):* To a solution of 177 mg (0.31 mmol) of **2** in 10 ml of benzene was added 68 mg (0.31 mmol) of HC≡CCPh(*o*-Tol)OH and the mixture was stirred for 24 h at room temp. A smooth change of color from dark-green to red-orange occurred. The solvent was removed, the oily residue was dissolved in 1 ml of benzene and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 4 cm). With benzene, a deep-red fraction was eluted, from which the solvent was removed in vacuo. The oily residue was dissolved in 1 ml of pentane and the solution was stored for 2 d at −60°C. A red microcrystalline solid was formed which was filtered off, washed twice with 0.5 ml portions of pen-

tane (−20 °C), and dried; yield 181 mg (74%), m.p. 86 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3598 cm^{-1} [ν(OH)], 2113 [ν(OsH)], 2030 [ν(C≡C)], 1740 [ν(NO)]. − ^1H NMR (C_6D_6, 200 MHz): δ = 8.40 and 7.59 (both m, $C_6H_4CH_3$), 7.30−7.03 (m, 5H, C_6H_5), 2.89 (m, 6H, PC*H*CH_3), 2.29 (s, 1H, OH), 2.22 (s, 3H, $C_6H_4CH_3$), 1.37 [dvt, *N* = 14.6, *J*(HH) = 7.5 Hz, 18H, PCHC*H*$_3$], 1.32 [dvt, *N* = 14.2, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], −0.86 [t, *J*(PH) = 23.2 Hz, 1H, OsH]. − ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 146.8, 143.5, 135.9, 131.0, 127.9, 126.9, 126.6, 125.3, 125.2, 123.6 (all s, C_6H_5 and C_6H_4Me), 117.3 (s, OsC≡*C*R), 77.2 [t, *J*(PC) = 10.1 Hz, Os*C*≡CR], 74.8 [s, *C*Ph(*o*-Tol)OH], 23.1 (vt, *N* = 27.5 Hz, P*C*HCH$_3$), 20.3 (s, $C_6H_4CH_3$), 17.5, 17.2 (both s, PCH*C*H$_3$). − ^{31}P NMR (C_6D_6, 162.0 MHz): δ = 19.4 [s, *J*($^{187}Os^{31}P$) = 169.6 Hz]. − $C_{34}H_{56}ClNO_2OsP_2$ (798.4): calcd. C 51.15, H 7.07, N 1.75; found C 51.19, H 7.37, N 1.35.

28. Preparation of [OsHCl{C≡CCPh(t-Bu)OH}(NO)(PiPr$_3$)$_2$] (**31**): To a solution of 164 mg (0.28 mmol) of **2** in 8 ml of benzene, was added 53 mg (0.28 mmol) of HC≡CCPh(*t*-Bu)OH and the mixture was stirred for 3 d at room temp. A smooth change of color from dark-green to red-orange occurred. The solvent was removed, the residue was dissolved in 2 ml of benzene/hexane (1:1) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With hexane, a red fraction was eluted, which was worked-up as described for **30**; red crystals, yield 139 mg (64%), m.p. 105 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3611 cm^{-1} [ν(OH)], 2103 [ν(OsH)], 2056 [ν(C≡C)], 1737 [ν(NO)]. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.48−7.15 (m, 5H, C_6H_5), 2.99 (m, 6H, PC*H*CH_3), 1.79 (s, 1H, OH), 1.27 [dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.22 [dvt, *N* = 14.2, *J*(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 0.91 [s, 9H, C(CH$_3$)$_3$], −1.02 [t, *J*(PH) = 23.7 Hz, 1H, OsH]. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 144.9 (s, *ipso*-C of C_6H_5), 127.9, 126.4, 126.2 (all s, *o*-C, *m*-C, and *p*-C of C_6H_5), 119.0 (s, OsC≡*C*R), 79.9 [s, *C*Ph(*t*Bu)OH], 73.3 [t, *J*(PC) = 9.8 Hz, OsC≡CR], 25.8 [s, *C*(CH$_3$)$_3$], 24.2 (vt, *N* = 25.5 Hz, P*C*HCH$_3$), 18.8 [s, C(*C*H$_3$)$_3$], 18.6, 18.5 (both s, PCH*C*H$_3$). − ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = 19.9 (s, d in off-resonance). − $C_{31}H_{58}ClNO_2OsP_2$ (764.4): calcd. C 48.71, H 7.65, N 1.83; found C 48.38, H 7.52, N 1.46.

29. Preparation of [OsCl$_2${η^1-CH=C=CPh(o-Tol)}(NO)(PiPr$_3$)$_2$] (**32**): A solution of 178 mg (0.23 mmol) of **30** in 10 ml of benzene was treated with 23 μl (0.23 mmol) of a 37% aqueous solution of HCl and the mixture was stirred for 3 min at room temp. An almost instantaneous change of color from red to orange occurred. The solvent was removed in vacuo, the oily residue was suspended in 2 ml of pentane and the suspension was stirred for 1 h at −78 °C. An orange microcrystalline solid was formed which was filtered off, washed twice with 5 ml portions of pentane (0 °C) and dried; yield 171 mg (94%), m.p. 178 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 1883 cm^{-1} [ν(C=C=C)], 1775 [(NO)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.08 [t, *J*(PH) = 2.0 Hz, 1H, OsCH], 7.42−7.17 (m, 9H, C_6H_5 and C_6H_4), 3.22 (m, 2H, PC*H*CH$_3$), 2.94 (m, 2H, PC*H*CH$_3$), 2.19 (s, 3H, $C_6H_4CH_3$), 1.54 [dvt, *N* = 14.0, *J*(HH) = 6.8 Hz, 6H, PCHC*H*$_3$], 1.41 [dvt, *N* = 14.0, *J*(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.37 [dvt, *N* = 14.0, *J*(HH) = 6.8 Hz, 6H, PCHC*H*$_3$], 1.21 [dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 6H, PCHC*H*$_3$]. − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 201.8 (s, OsCH=*C*), 140.8, 138.7, 137.8, 132.3, 131.0, 128.3, 127.5, 126.9, 126.3, 126.1 (all s, C_6H_5 and C_6H_4Me), 102.1 [s, =*C*Ph(*o*-Tol)], 77.4 [t, *J*(PC) = 6.8 Hz, OsCH], 25.4 (vt, *N* = 23.3 Hz, P*C*HCH$_3$), 25.0 (vt, *N* = 23.2 Hz, P*C*HCH$_3$), 20.6, 20.5, 20.3, 20.1 (all s, PCH*C*H$_3$). − ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ = −4.0 (s). − $C_{34}H_{55}Cl_2NOOsP_2$ (816.8): calcd. C 49.99, H 6.79, N 1.71; found C 50.23, H 6.96, N 1.33.

30. Preparation of [OsCl$_2${η^1-CH=C=CPh(tBu)}(NO)(PiPr$_3$)$_2$] (**33**): Compound **33** was prepared analogously to **32**, by using 99 mg (0.13 mmol) of **31** and 13 μl (0.13 mmol) of a 37% aqueous solution of HCl as starting materials; orange microcrystalline solid, yield 97 mg (96%), m.p. 187 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 1879 cm^{-1} [ν(C=C=C)], 2045 [ν(C≡C)], 1799 [ν(NO)]. − ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.69 (m, 1H, OsCH), 7.68−7.13 (m, 5H, C_6H_5), 3.17 (m, 3H, PC*H*CH$_3$), 2.69 (m, 3H, PC*H*CH$_3$), 1.48 [dvt, *N* = 14.3, *J*(HH) = 7.4 Hz, 9H, PCHC*H*$_3$], 1.43 [dvt, *N* = 15.3, *J*(HH) = 6.9 Hz, 9H, PCHC*H*$_3$], 1.25 [dvt, *N* = 14.3, *J*(HH) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.12 [s, 9H, C(CH$_3$)$_3$]; one signal of PCHC*H*$_3$ protons partly obscured by signal at δ = 1.25. − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 200.3 (s, OsCH=*C*), 140.5 (s, *ipso*-C of C_6H_5), 129.9, 129.2, 129.0 (all s, *o*-C, *m*-C, and *p*-C of C_6H_5) 109.1 [s, =*C*Ph(*t*Bu)], 75.5 [t, *J*(PC) = 6.9 Hz, OsCH], 31.0 [s, *C*(CH$_3$)$_3$], 25.2 [s, C(*C*H$_3$)$_3$], 24.5 (vt, *N* = 22.3 Hz, P*C*HCH$_3$), 24.4 (vt, *N* = 24.3 Hz, P*C*HCH$_3$), 20.1, 20.0, 19.8, 19.4 (all s, PCH*C*H$_3$). − ^{31}P NMR ($CDCl_3$, 162.0 MHz): AB spin system, δ_A = −1.9, δ_B = −6.5 [*J*(PP) = 308 Hz]. − $C_{31}H_{57}Cl_2NOOsP_2$ (782.9): calcd. C 47.56, H 7.34, N 1.79; found C 47.27, H 6.87, N 1.45.

31. Preparation of [OsHCl(C≡CC≡CCPh$_2$OH)(NO)(PiPr$_3$)$_2$] (**34**): To a solution of 231 mg (0.40 mmol) of **2** in 10 ml of benzene, was added 8.0 ml (0.40 mmol) of a 0.05 M solution of HC≡CC≡CCPh$_2$OH in benzene and the mixture was stirred for 3 min at room temp. An almost instantaneous change of color from dark-green to red occurred. The solvent was removed, the residue was dissolved in 2 ml of hexane and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, an initial brown fraction was eluted which was discarded. A second red fraction was eluted with benzene, from which the solvent was evaporated in vacuo. The oily residue was dissolved in 2 ml of diethyl ether, 8 ml of pentane was added, and the solution was stored for 2 d at −60 °C. Red crystals were formed which were separated from the mother liquor, washed three times with 2 ml portions of pentane and dried; yield 224 mg (69%), m.p. 74 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3561 cm^{-1} [ν(OH)], 2194 [ν(OsH)], 2059 [ν(C≡C)], 1735 [ν(NO)]. − ^1H NMR (C_6D_6, 200 MHz): δ = 7.73−7.19 (m, 10H, C_6H_5), 2.97 (m, 6H, PC*H*CH$_3$), 2.27 (s, 1H, OH), 1.30 [dvt, *N* = 14.5, *J*(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.25 [dvt, *N* = 14.4, *J*(HH) = 7.0 Hz, 18H, PCHC*H*$_3$], −0.92 [t, *J*(PH) = 23.3 Hz, 1H, OsH]. − ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 146.6 (s, *ipso*-C of C_6H_5), 129.0, 128.1, 126.7 (all s, *o*-C, *m*-C, and *p*-C of C_6H_5), 101.7 (s, OsC≡*C*R), 82.8 [t, *J*(PC) = 10.1 Hz, Os*C*≡CR], 78.6, 75.4, 74.9 (all s, *C*≡*C*-CPh$_2$OH and *C*Ph$_2$OH), 25.0 (vt, *N* = 27.8 Hz, P*C*HCH$_3$), 19.5, 19.3 (both s, PCH*C*H$_3$). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 18.0 (s, d in off-resonance). − $C_{35}H_{54}ClNO_2OsP_2$ (808.4): calcd. C 52.00, H 6.73, N 1.73; found C 52.09, H 7.07, N 1.38.

32. Preparation of [OsHCl(C≡CC≡CCPh$_2$OH)(NO)(PiPr$_2$Ph)$_2$] (**35**): To a solution of 183 mg (0.28 mmol) of **3** in 8 ml of benzene, was added 5.6 ml (0.28 mmol) of a 0.05 M solution of HC≡CC≡CCPh$_2$OH in benzene and the mixture was stirred for 3 min at room temp. An almost instantaneous change of color from dark-green to red occurred. The solution was concentrated in vacuo to ca. 2 ml and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With benzene, a red fraction was eluted, which was worked-up as described for **34**; red microcrystalline solid, yield 162 mg (65%), m.p. 70 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3568 cm^{-1} [ν(OH)], 2193 [ν(OsH)], 2059 [ν(C≡C)], 1741 [ν(NO)]. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.74−7.16 (m, 20H, C_6H_5), 3.08 (m, 2H, PC*H*CH$_3$), 3.03 (m, 2H, PC*H*CH$_3$), 2.23 (s, 1H, OH), 1.13 [dvt, *N* = 15.8, *J*(HH) = 7.0 Hz, 6H, PCHC*H*$_3$], 1.07 [dvt, *N* = 14.7, *J*(HH) = 7.3 Hz, 6H, PCHC*H*$_3$], 1.02 [dvt,

N = 14.3, J(HH) = 7.0 Hz, 6H, PCHCH_3]; −0.88 [t, J(PH) = 24.4 Hz, 1 H, OsH]; one signal of PCHCH_3 protons partly obscured by signal at δ = 1.02. − ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 146.5 (s, *ipso*-C of C_6H_5), 135.2, 128.5 (both vt, N = 7.4 and 8.3 Hz, *o*-C and *m*-C of PC_6H_5), 131.1, 128.9, 127.9, 126.6 (all s, *o*-C, *m*-C, and *p*-C of C_6H_5, *p*-C of PC_6H_5), 124.8 (vt, N = 46.0 Hz, *ipso*-C of PC_6H_5), 104.1 (s, OsC≡*C*R), 80.7 [t, J(PC) = 11.0 Hz, Os*C*≡CR], 78.5, 75.0, 74.5 (all s, *C*≡*C*Ph_2OH and *C*Ph_2OH), 24.6 (vt, N = 28.3 Hz, P*C*HCH$_3$), 23.5 (vt, N = 28.3 Hz, PCH*C*H$_3$), 18.3, 18.1, 17.9, 17.3 (all s, PCH*C*H$_3$). − ^{31}P NMR (C_6D_6, 81.0 MHz): δ = 22.8 (s, d in off-resonance). − $C_{41}H_{50}ClNO_2OsP_2$ (876.5): calcd. C 56.19, H 5.75, N 1.60; found C 56.02, H 5.76, N 1.58.

33. Determination of the X-ray Crystal Structure of **34**[41]: Single crystals were grown from a saturated solution in diethyl ether. Crystal data (from 25 reflections, 10° < Θ < 13°): triclinic, space group *P*-1 (No. 2); a = 11.80(2) Å, b = 13.33(2) Å, c = 16.05(2) Å, α = 113.69(6)°, β = 98.27(8)°, γ = 105.46(7)°, V = 2135(5) Å^3, Z = 2, d_{calcd} = 1.33 g cm^{-3}, μ(Mo-K_α) = 31.5 cm^{-1}; crystal size 0.55 × 0.6 × 0.75 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.41); T = 293 K; ω/Θ scan, max. 2Θ = 46°; 6257 reflections measured, 5917 independent reflections, 5586 reflections with $F_o > 3\sigma(F_o)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ-scan method) was applied (minimum transmission 87.32%). The structure was solved by direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares (428 parameters, unit weights, SDP). The hydrogen atom H1 could be located by a difference Fourier analysis and was isotropically refined. The positions of all hydrogen atoms were calculated according to ideal geometry (d_{C-H} = 0.95 Å) and were used only in structure factor calculations. R = 0.019 and wR = 0.026; reflex/parameter ratio 13.1; residual electron density +0.41/−0.40 e Å^{-3}.

☆ Dedicated to Professor *Waldemar Adam* on the occasion of his 60th birthday.

[1] [1a]H. Werner, A. Michenfelder, M. Schulz, *Angew. Chem.* **1991**, *103*, 616−617; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 596−597. − [1b] H. Werner, R. Flügel, B. Windmüller, A. Michenfelder, J. Wolf, *Organometallics* **1995**, *14*, 612−618.

[2] J. D. Atwood in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson) Vol. 8, Pergamon, Oxford, **1995**, chapter 3.3.

[3] R. Flügel, O. Gevert, H. Werner, *Chem. Ber.* **1996**, *129*, 405−410.

[4] R. Flügel, B. Windmüller, O. Gevert, H. Werner, *Chem. Ber.* **1996**, *129*, 1007−1013.

[5] [5a] M. H. B. Stiddard, R. E. Townsend, *J. Chem. Soc., Chem. Commun.* **1969**, 1372. − [5b] R. D. Wilson, J. A. Ibers, *Inorg. Chem.* **1978**, *17*, 2134−2138.

[6] J. Clemens, M. Green, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1973**, 375−380.

[7] [7a] A. F. Hill, W. R. Roper, J. M. Waters, A. H. Wright, *J. Am. Chem. Soc.* **1983**, *105*, 5939−5940. − [7b] W. R. Roper, *J. Organomet. Chem.* **1986**, *300*, 167−190.

[8] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313−348.

[9] A. F. Hill in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson) Vol. 7, Pergamon, Oxford, **1995**, chapter 6.1.

[10] P. J. Brothers, W. R. Roper, *Chem. Rev.* **1988**, *88*, 1293−1326.

[11] See, e.g., the difference between the related aryl(chloro) and vinyl(chloro) complexes [IrCl(C_6H_5)(H)(P*i*Pr_3)$_2$][11a] and [OsCl(CH=CHPh)(CO)(P*i*Pr_3)$_2$][11b] of which the first is trigonal-bipyramidal and the second square-pyramidal. − [11a] H. Werner, A. Höhn, M. Dziallas, *Angew. Chem.* **1986**, *98*, 1112−1114; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1090−1092. − [11b] H. Werner, M. A. Esteruelas, H. Otto, *Organometallics* **1986**, *5*, 2295−2299.

[12] [12a] J. S. Valentine, *Chem. Rev.* **1973**, *73*, 235−245. − [12b] L. Vaska, *Acc. Chem. Res.* **1976**, *9*, 175−183. − [12c] D. T. Sawyer, *Oxygen Chemistry*, Oxford University Press, Oxford, **1991**.

[13] [13a] W. A. Schenk, *Angew. Chem.* **1987**, *99*, 101−112; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 98−109. − [13b] G. J. Kubas, *Acc. Chem. Res.* **1994**, *27*, 183−190.

[14] H. A. O. Hill, D. G. Tew in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty) Vol. 2, Pergamon, Oxford, **1987**, chapter 15.2.

[15] [15a] M. A. Gallop, W. R. Roper, *Adv. Organomet. Chem.* **1986**, *25*, 121−198. − [15b] A. K. Burell, G. R. Clark, C. E. F. Rickard, W. R. Roper, A. H. Wright, *J. Chem. Soc., Dalton Trans.* **1991**, 609−614. − [15c] W. R. Roper, J. M. Waters, A. H. Wright, *J. Organomet. Chem.* **1984**, *276*, C13−C15.

[16] [16a] W. A. Schenk, P. Urban, *J. Organomet. Chem.* **1991**, *411*, C27−C31. − [16b] W. A. Schenk, P. Urban, E. Dombrowski, *Chem. Ber.* **1993**, *126*, 679−684.

[17] For a related Pt(η^1-I_2) complex see: [17a] G. van Koten, J. Terheijden, J. A. M. van Beek, I. C. M. Wehman-Ooyevaar, F. Muller, C. H. Stam, *Organometallics* **1990**, *9*, 903−912. − [17b] J. A. M. van Beek, G. van Koten, W. J. J. Smeets, A. L. Spek, *J. Am. Chem. Soc.* **1986**, *108*, 5010−5011.

[18] [18a] J. P. Collman, C. T. Sears Jr., *Inorg. Chem.* **1968**, *7*, 27−32. − [18b] L. Vaska, J. W. DiLuzio, *J. Am. Chem. Soc.* **1962**, *84*, 679−680. − [18c] J. Vicente, M.-T. Chicote, J. Martin, P. G. Jones, C. Fittschen, *J. Chem. Soc., Dalton Trans.* **1987**, 881−884. − [18d] M. Hunziker, G. Rihs, *Inorg. Chim. Acta* **1985**, *102*, 39−43. − [18e] L. Drougge, L. I. Elding, *Inorg. Chem.* **1988**, *27*, 795−798. − [18f] R. Jones, P. F. Kelly, D. J. Williams, J. D. Woollings, *J. Chem. Soc., Dalton Trans.* **1988**, 1569−1576.

[19] [19a] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, **1988**, chapter 6.2. − [19b] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, **1987**, chapter 5. − [19c] J. A. Labinger, R. J. Braus, D. Dolphin, J. A. Osborn, *J. Chem. Soc., Chem. Commun.* **1970**, 612−613. − [19d] J. Halpern, *Acc. Chem. Res.* **1970**, *3*, 386−392. − [19e] D. G. Nocera, *Acc. Chem. Res.* **1995**, *28*, 209−217.

[20] For a detailed discussion of the IR spectra of η^1- and η^2-coordinated carboxylatometal compounds see: S. D. Robinson, M. F. Uttley, *J. Chem. Soc., Dalton Trans.* **1973**, 1912−1920.

[21] [21a] L. J. Newman, R. G. Bergman, *J. Am. Chem. Soc.* **1985**, *107*, 5314−5315. − [21b] D. S. Glueck, L. J. Newman Winslow, R. G. Bergman, *Organometallics* **1991**, *10*, 1462−1479. − [21c] F. T. Ladipo, M. Kooti, J. S. Merola, *Inorg. Chem.* **1993**, *32*, 1681−1688.

[22] S. Stahl, H. Werner, *J. Am. Chem. Soc.* **1991**, *113*, 2944−2947.

[23] C. E. L. Headford, W. R. Roper, *J. Organomet. Chem.* **1980**, *198*, C7−C10.

[24] [24a] A. F. Hill in *Comprehensive Organometallic Chemistry II* (Eds.:: E. W. Abel, F. G. A. Stone, G. Wilkinson) Vol. 7, Pergamon, Oxford, **1995**, chapter 6.4.5.2. − [24b] A. Segnitz, K. von Werner, *Methoden der Organischen Chemie* (Houben-Weyl, Ed.: A. Segnitz), 4th edition, Vol. 13/9a, G. Thieme, Stuttgart, **1986**, p. 536 and 630. − [24c] F. Calderazzo, *Angew. Chem.* **1977**, *89*, 305−317; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 299−311.

[25] [25a] G. R. Clark, C. E. L. Headford, K. Marsden, W. R. Roper, *J. Am. Chem. Soc.* **1979**, *101*, 503−505. − [25b] G. R. Clark, C. E. L. Headford, K. Marsden, W. R. Roper, *J. Organomet. Chem.* **1982**, *231*, 335−360.

[26] B. Weber, Dissertation, Universität Würzburg **1995**.

[27] [27a] H. Werner, B. Weber, O. Nürnberg, J. Wolf, *Angew. Chem.* **1992**, *104*, 1105−1107; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1025−1027. − [27b] B. Weber, P. Steinert, B. Windmüller, J. Wolf, H. Werner, *J. Chem. Soc., Chem. Commun.* **1994**, 2595−2596.

[28] M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton, A. H. White, *J. Chem. Soc., Chem. Commun.* **1996**, 1009−1010.

[29] Inter alia: [29a] T. L. Jacobs in *The Chemistry of the Allenes* (Ed.: S. R. Landor), Vol. 2, Academic Press, London, **1982**. − [29b] A. Wojcicki, C. E. Shuchart, *Coord. Chem. Rev.* **1990**, *105*, 35−60. − [29c] S. Doherty, J. F. Corrigan, A. J. Carty, E. Sappa, *Adv. Organomet. Chem.* **1995**, *37*; 39−130. − [29d] C. J. Elsevier, H. Kleijn, J. Boersma, P. Vermeer, *Organometallics* **1986**, *5*, 716−720. − [29e] R.-S. Keng, Y.-C. Lin, *Organometallics* **1990**, *9*, 289−291. − [29f] J. M. A. Wouters, R. A. Klein, C. J. Elsevier, L. Häming, C. H. Stam, *Organometallics* **1994**, *13*, 4586−4593.

[30] S. Aime, A. J. Deeming, M. B. Hursthouse, J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.* **1982**, 1625−1629.

[31] [31a] T. Rappert, O. Nürnberg, N. Mahr, J. Wolf, H. Werner, *Organometallics* **1992**, *11*, 4156–4164. – [31b] M. A. Tena, O. Nürnberg, H. Werner, *Chem. Ber.* **1993**, *126*, 1597–1602.
[32] J. D. Lee, *Course Inorganic Chemistry*, 4th edition, Chapman & Hall, Tokyo, **1991**.
[33] M. Aracama, M. A. Esteruelas, F. J. Lahoz, J. A. Lopez, U. Meyer, L. A. Oro, H. Werner, *Inorg. Chem.* **1991**, *30*, 288–293.
[34] Y. Sun, N. J. Taylor, A. J. Carty, *Organometallics* **1992**, *11*, 4293–4300.
[35] H. Werner, O. Gevert, P. Steinert, J. Wolf, *Organometallics* **1995**, *14*, 1786–1791.
[36] J. Espuelas, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, C. Valero, *Organometallics* **1993**, *12*, 663–670.
[37] M. A. Esteruelas, F. J. Lahoz, A. M. López, E. Oñate, L. A. Oro, *Organometallics* **1995**, *14*, 2496–2500.
[38] F. Kukla, Dissertation, Universität Würzburg, in preparation.
[39] J. B. Armitage, E. R. H. Jones, M. C. Whiting, *J. Chem. Soc.* **1952**, 1993–1998.
[40] **25**: IR (KBr): $\tilde{\nu}$ = 1895 cm^{-1} [ν(CO)], 1540 [ν(NO)]. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.79 (m, 6H, PC*H*CH_3), 1.22 [dvt, *N* = 14.0, *J*(HH) = 6.8 Hz, 18H, PCH*C*H_3]; one signal of PCH*C*H_3 protons partly obscured by signal at δ = 1.22. – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 191.7 [t, *J*(PC) = 11.1 Hz, CO], 26.1 (vt, *N* = 26.8 Hz, P*C*HCH$_3$), 20.4, 19.9 (both s, PCH*C*H_3). In ref. [1b] a wrong value for ν(NO) was given.
[41] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59384, the names of the authors, and the journal citation.

[96253]