Hydrido(carbene), Hydrido(diazoalkane), Aqua(carbene), and Vinyl(carbene) Complexes of Osmium(II)

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Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday

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The five-coordinate compound [OsHCl(CO)(P*i*Pr$_3$)$_2$] (**1**) reacts with CH_2N_2 and other diazoalkanes $RCHN_2$ (R = Ph, CO_2Et, $SiMe_3$) in ether or toluene at 25 °C to give instead of the expected insertion products [Os(CH$_2$R)Cl(CO)(P*i*Pr$_3$)$_2$] the isomeric hydrido(carbene)osmium(II) complexes [OsHCl(=CHR)(CO)(P*i*Pr$_3$)$_2$] (**2–5**) in excellent yields. With Me_3SiCHN_2 as the substrate, the 1:1 adduct [OsHCl(N$_2$CHSiMe$_3$)(CO)(P*i*Pr$_3$)$_2$] (**6**) was detected at low temperature as an intermediate. The reactions of **1** with Ph_2CN_2 and $Cl_4C_5N_2$ afford the hydrido(diazoalkane)compounds [OsHCl(N$_2$CR$_2$)(CO)(P*i*Pr$_3$)$_2$] (**7**, **8**), which are quite stable and do not eliminate N_2 to give the corresponding hydrido(carbene)metal derivatives. Treatment of **3** (R = Ph) with either HCl or HBF_4/H_2O leads to the cleavage of the Os-H bond and results in the formation of [OsCl$_2$(=CHPh)(CO)(P*i*Pr$_3$)$_2$] (**10**) and [OsCl(=CHPh)(OH$_2$)(CO)(P*i*Pr$_3$)$_2$]BF$_4$ (**11**), respectively. The vinyl compound [OsCl(CH=CHPh)(CO)(P*i*Pr$_3$)$_2$] (**12**) behaves similarly to **1** and affords the carbene complex [OsCl(CH=CHPh)(=CHPh)(CO)(P*i*Pr$_3$)$_2$] (**13**) upon treatment with $PhCHN_2$. Compound **13** rearranges in solution at room temperature to give the π-allyl complex [Os(η^3-PhCHCHCHPh)Cl(CO)(P*i*Pr$_3$)$_2$] (**14**) as the dominating species. The crystal and molecular structures of **4**, **5**, **10**, and **11** have been determined by X-ray crystallography.

After we found that the four- and five-coordinate iridium complexes containing [IrCl(P*i*Pr$_3$)$_2$] as a building block offer a rich chemistry, including various routes to C−H activation,[1] we started a search for related osmium compounds with a 14- or 16-electron configuration at the metal center. Attempts to prepare either [OsCl$_2$(P*i*Pr$_3$)$_2$] or [OsCl$_2$(P*i*Pr$_3$)$_3$] by treatment of $OsCl_3 \cdot 3\,H_2O$ with triisopropylphosphane in methanol led instead to the five-coordinate hydrido(carbonyl) compound [OsHCl(CO)(P*i*Pr$_3$)$_2$] (**1**) supposedly with a square-pyramidal configuration.[2] This compound reacts with a variety of small molecules such as H_2, O_2, CO, $CH_2{=}CHCN$, and acetone to give 1:1 adducts in which the entering ligand occupies the free coordination site *trans* to hydride.[2][3] However, when we used terminal alkynes $HC{\equiv}CR$ as the substrate we observed that compound **1** does not produce the expected six-coordinate hydrido(alkyne) complexes [OsHCl(CO)(η^2-HC≡CR)(P*i*Pr$_3$)$_2$] but gives the five-coordinate vinylosmium(II) derivates [OsCl(CH=CHR)(CO)(P*i*Pr$_3$)$_2$] in excellent yields.[4]

This unexpected insertion prompted us to study also the reactivity of **1** towards CH_2N_2 and other diazoalkanes with the hope that on this route, via OsH(CHR) species as intermediates, coordinatively unsaturated alkyl(carbonyl)osmium(II) compounds could be formed. From previous studies in our laboratory we knew that, by using [OsH(η^2-BH$_4$)(CO)(P*i*Pr$_3$)$_2$] as the starting material, alkylosmium(II) complexes of the general composition [OsH(CH$_2$R)(CO)$_2$(P*i*Pr$_3$)$_2$] are accessible but due to the 18-electron configuration of the metal center these compounds are quite inert.[5] After Roper reported that the reaction of diazomethane with [OsCl(*o*-Tol)(CO)(PPh$_3$)$_2$] gave the η^2-acyl compound [OsCl{η^2-C(O)*o*-Tol}(=CH$_2$)(PPh$_3$)$_2$] by migration of the aryl ligand to CO,[6] it seemed also conceivable that from **1** and CH_2N_2 even a formylosmium species [OsCl{η^2-C(O)H}(=CH$_2$)(P*i*Pr$_3$)$_2$] could be obtained.

In this paper we describe the preparation of a series of hydrido(carbene)osmium(II) complexes from CH_2N_2 and $RCHN_2$ as the carbene source, the spectroscopic characterization of a labile OsH(N$_2$CHR) intermediate as well as the isolation of stable hydrido(diazoalkane) compounds with Ph_2CN_2 and $N_2C_5Cl_4$ as ligands, the reactivity of the hydrido(carbene)metal derivatives toward Broensted acids, and the synthesis of a vinyl(carbene)osmium compound that rearranges to an isomeric η^3-allyl complex by C−C coupling. Parts of these studies have already been communicated.[7]

Results and Dicussion

The reaction of the starting material **1** with a freshly prepared solution of diazomethane in ether proceeds quite rapidly at room temperature and furnishes, after removal of the solvent, the hydrido(carbene) complex **2** in almost quantitative yield (Scheme 1). The fact, that compound **2** and not the isomeric methyl derivate [OsCl(CH$_3$)(CO)(P*i*Pr$_3$)$_2$] is formed, is confirmed by the ^{1}H-NMR spectrum

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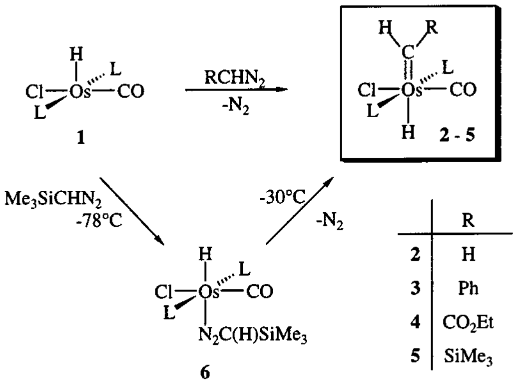
which displays besides the signals for the two phosphane ligands a triplet of triplets for the OsH proton at high field (δ −4.48) and two broadened singlets for the $OsCH_2$ protons at low field (δ 17.90 and 16.88). The ^{13}C-NMR spectrum of **2** exhibits resonances at δ = 285.0 and 182.0, which are assigned to the $OsCH_2$ and OsCO carbon atoms, respectively.



Scheme 1. L = P*i*Pr₃

Substituted diazomethanes such as $PhCHN_2$, EtO_2CCHN_2 and Me_3SiCHN_2 behave similarly to CH_2N_2 and react with the hydrido compound **1** to produce the corresponding carbene complexes **3−5** in excellent yields. The reaction of **1** with Me_3SiCHN_2 is relatively slow and needs ca. 15 h for completion at room temperature. We found that the octahedral compound $[OsHCl(CO)(PPh_3)_3]$[8] equally reacts with CH_2N_2 and $PhCHN_2$ quite smoothly but in this case the diazoalkane is converted into N_2 and the respective olefin without changing the composition of the osmium(II) derivative.

The new hydrido(carbene) complexes **3−5** are orange to yellow microcrystalline solids which are only moderately air-sensitive and which, in contrast to **2**, can be stored under argon at room temperature for weeks. The $OsCH_2$ compound **2** is more labile and, particularly in solution, decomposes slowly to give a mixture of products among which ethene was detected. The most characteristic features of the spectroscopic data of **3−5** are the hydride resonances at δ −4.5 to −5.6 in the ^1H NMR and the signal of the carbene carbon atom at δ 267−327 in the ^{13}C-NMR spectra. It should be emphasized that the signal of the OsH proton of compounds **2−5** experiences a significant downfield shift by ca. 27 ppm compared to the starting material **1**, which presumably is due to the strong influence of the carbene ligand *trans* to the hydride. The IR spectra of **2−5** (in KBr) exhibit a strong ν(CO) bond at ca. 1880−1940 cm^{-1} as well as a weaker absorption at ca. 1830−1865 cm^{-1}, which is assigned to the Os−H stretching frequency.

The molecular structures of **4** and **5** are shown in Figures 1 and 2. In both cases, the coordination geometry arround the metal center is distorted octahedral with the two phosphanes, the CO and the chloride, and the hydride and the carbene ligand occupying *trans* positions. The most noteworthy detail is the strong bending of the P−Os−P axis [144.88(2)° for **4** and 141.38(4)° for **5**] toward the (not exactly localized) position of the hydride ligand. This bending is much more pronounced than in *cis,cis,trans*-$[OsH(CH_3)(CO)_2(PiPr_3)_2]$ [165.6(1)°][5] and in the five-coordinate compound $[OsCl(CH{=}CHPh)(CO)(PiPr_3)_2]$ (**12**, see below) where the P−Os−P angle is 167.4(1)°.[4] The Os−C(carbene) distances in **4** and **5** are in the range of that of other carbene(chloro)osmium(II) complexes such as $[OsCl({=}CH_2)(NO)(PPh_3)_2]$ [1.92(1) Å] and $[OsCl({=}CF_2)(NO)(PPh_3)_2]$ [1.967(4) Å] containing NO as an additional ligand.[9]

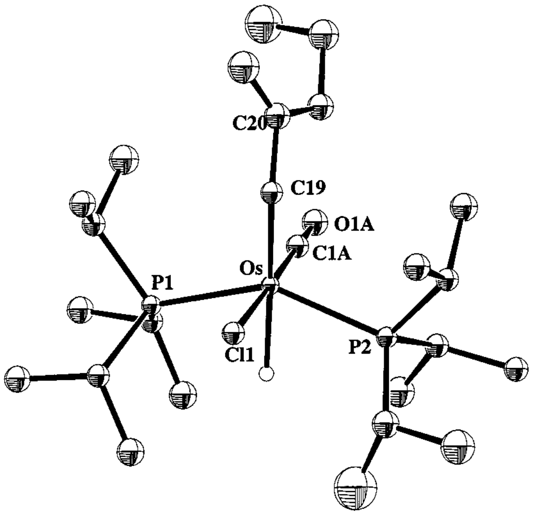


Figure 1. Molecular structure of **4**; the metal-bonded hydrogen is not exactly located, the other hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Os−Cl 2.475(1), Os−P1 2.392(1), Os−P2 2.394(1), Os−C1A 1.840(3), Os−C19 1.949(2), C1A−O1A 1.153(3), C19−C20 1.489(3); P1−Os−P2 144.88(2), P1−Os−Cl 90.47(2), P1−Os−C1A 90.2(1), P1−Os−C19 108.3(1), P2−Os−Cl 89.82(2), P2−Os−C1A 90.9(1), P2−Os−C19 106.6(1), Cl−Os−C1A 177.7(1), Cl−Os−C19 83.6(1), C1A−Os−C19 94.1(1), Os−C1A−O1A 178.9(3), Os−C19−C20 133.7(2)

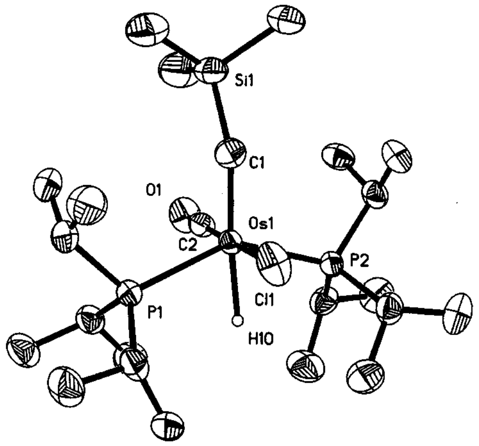
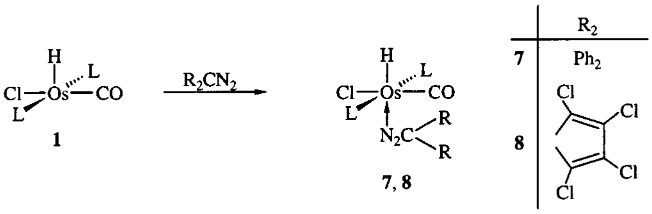


Figure 2. Molecular structure of **5**; the metal-bonded hydrogen is not exactly located, the other hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Os−Cl 2.514(1), Os−P1 2.403(1), Os−P2 2.396(1), Os−C1 1.965(5), Os−C2 1.830(5), O1−C2 1.166(5), C1−Si 1.878(5); P1−Os−P2 141.38(4), P1−Os−Cl 89.88(4), P1−Os−C1 110.4(2), P1−Os−C2 90.4(1), P2−Os−Cl 89.93(4), P2−Os−C1 107.8(2), P2−Os−C2 91.5(2), Cl−Os−C1 82.1(2), Cl−Os−C2 177.3(1), C1−Os−C2 95.3(2), Os−C1−Si 144.9(3), Os−C2−O 179.4(4)

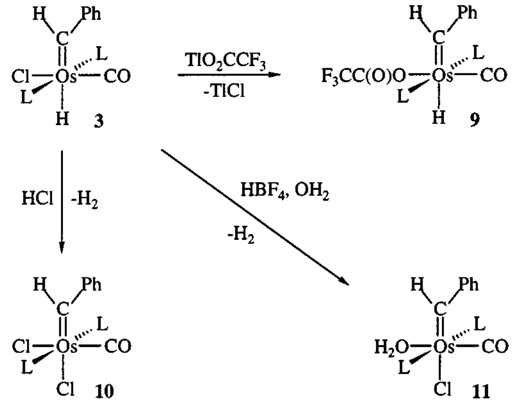
Following the observation that compound **1** reacts much more slowly with Me_3SiCHN_2 than with the other diazoalkanes, attempts were made to detect or even isolate an $Os(N_2CHR)$ species as an intermediate. Therefore, we carried out the reaction of **1** with Me_3SiCHN_2 in toluene at −78 °C and found that under these conditions a product is formed that is stable at −78 °C for several days. Evaporation of the solvent led to a slow evolution of gas (N_2) and to partial formation of the hydrido(carbene) complex **5**. This compound is formed nearly quantitatively upon warming the toluene solution to ca. −20 °C. The ^{1}H-NMR spectrum of the low-temperature product **6** displays a hydride signal at $\delta = -13.70$ (broadened singlet) and a resonance for the $Me_3SiC\mathit{H}N_2$ proton at $\delta = 2.80$. Owing to these data, we assume that the intermediate is an $OsH(N_2CHSiMe_3)$ derivative in which the trimethylsilyldiazomethane occupies the coordination position *trans* to hydride (see Scheme 1). The ^{13}C-NMR spectrum of **6** exhibits a signal for the $N_2\mathit{C}HSiMe_3$ carbon atom at $\delta = 33.4$ and the IR spectrum, apart from the ν(CO) bond at 1890 cm^{-1}, an absorption at 1933 cm^{-1} which can be assigned either to the Os-H or the N≡N stretching frequency.

If compound **1** is not treated with CH_2N_2 or a monosubstituted derivative $RCHN_2$ but with Ph_2CN_2 or $Cl_4C_5N_2$ in toluene (see Scheme 2), a reaction takes place which is not accompanied by the evolution of gas. After removal of the solvent, off-white or light brown solids are isolated which in agreement with the elemental analyses are the hydrido(diazoalkane)osmium complexes **7** and **8**. At room temperature under argon, the compounds are stable for weeks and in solution even on warming to 40 °C do not eliminate N_2 to give the corresponding hydrido(carbene) derivatives $[OsHCl(=CPh_2)(CO)(P\mathit{i}Pr_3)_2]$ and $[OsHCl(=C_5Cl_4)(CO)(P\mathit{i}Pr_3)_2]$, respectively. While the ^{1}H-NMR spectrum of **8** displays the hydride resonance at $\delta = -7.06$ as a triplet with $^2J(P,H) = 22$ Hz, the corresponding Os−H signal of **7** appears at $\delta = -11.44$ as a broad singlet at room temperature. However, upon cooling the solution of **7** in $CDCl_3$ to −10 °C the broadening disappears and a sharp triplet is observed. Since the pattern of the phosphane resonances of **7** does not change at different temperatures, we assume that the broadening of the hydride signal at 25 °C is due to the mobility of the diphenyldiazomethane ligand which could coordinate either via the terminal nitrogen atom or via the N=N bond.[10][11] Based on the IR data of **7**, it is difficult to decide whether an $Os(\eta^1\text{-}N_2CPh_2)$ or an $Os(\eta^2\text{-}N_2CPh_2)$ bonding mode exists.



Scheme 2. L = P*i*Pr$_3$

The hydrido(carbene) complexes **3−5** are thermally as well as photochemically rather inert and do not react either in the absence or in the presence of Lewis bases such as CO or CN*t*Bu to afford the corresponding five- or six-coordinate alkylosmium(II) derivatives by migratory insertion. Some other reactions aimed to displace one of the anionic ligands of compound **3** are illustrated in Scheme 3. Treatment of a solution of **3** in toluene with an equimolar amount of TlO_2CCF_3 led to the formation of the related trifluoroacetato compound **9** which is isolated as an orange, almost air-stable solid in 89% yield. A comparison of the IR data of **9** with those of other carboxylato transition-metal complexes[12] indicates that the $CF_3CO_2^-$ ligand of **9** is coordinated in a κ^1- and not in a κ^2-fashion. It should be mentioned that compound **9** like the related chloro derivative **3** does not react upon warming to 60 °C in benzene to give the corresponding isomer $[Os(CH_2Ph)(O_2CCF_3)(CO)(P\mathit{i}Pr_3)_2]$.



Scheme 3. L = P*i*Pr$_3$

While the reaction of **2** with a solution of HCl in toluene yields a mixture of products, among which the dihydrogen adduct $[OsCl_2(H_2)(CO)(P\mathit{i}Pr_3)_2]$ could be observed by ^{1}H- and ^{31}P-NMR spectroscopy,[13] the single component **10** is obtained on treatment of **3** with HCl in toluene. The isolated yield of the dark red, air-stable solid is 98%. The ^{1}H- and ^{13}C-NMR spectra of **10** both exhibit a low-field signal for the $OsC\mathit{H}$ proton at $\delta = 19.04$ and the $Os\mathit{C}H$ carbon atom at $\delta = 278.0$, respectively, and therefore confirm that a derivative of **3** still containing the carbene ligand is formed.

The structural proposal for **10** has been substantiated by X-ray crystallography. There are two independent molecules **A** and **B** in the asymmetric unit which slightly differ in the conformation of the phosphane ligands with respect to the carbene unit. As shown in Figure 3 for molecule **A**, the osmium center of compound **10** is octahedrally coordinated with the two chloro ligands in *cis* and the two triisopropylphosphanes in *trans* disposition. In contrast to the hydrido(carbene) complexes **4** and **5**, the axis P−Os−P of **10** is much less bent, the bond angle P−Os−P being 167.5(2)° for **A** and 166.3(2)° for **B**, respectively. While the Os−CO distances of **4**, **5** and **10** are almost the same, the bond length Os−C(carbene) of **10** is slightly shorter than that of

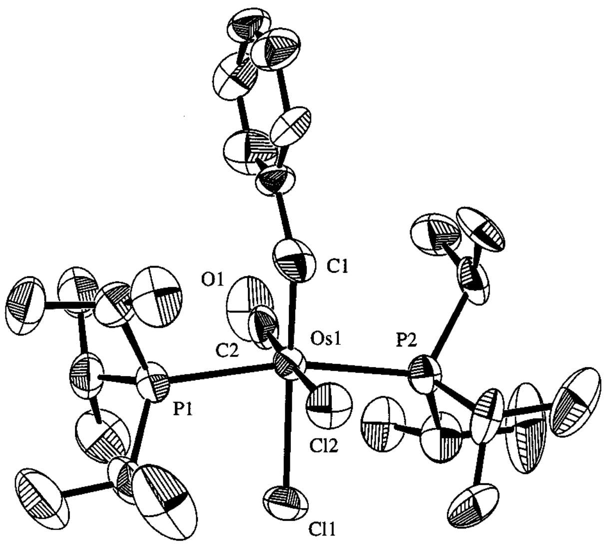


Figure 3. Molecular structure of **10**; there are two independent molecules **A** and **B** in the asymetric unit; hydrogen atoms apart from H1 are omitted for clarity; selected bond lengths [Å] and angles [°]: Molecule **A**: Os1−Cl1 2.484(4), Os1−Cl2 2.487(5), Os1−P1 2.469(5), Os1−P2 2.466(5), Os1−C1 1.95(2), Os1−C2 1.85(2), C1−C50 1.46(2), O1−C2 1.13(2); P1−Os1−P2 167.5(2), P1−Os1−Cl1 84.6(2), P1−Os1−Cl2 90.7(2), P1−Os1−C1 93.3(5), P1−Os1−C2 91.3(5), P2−Os1−Cl1 82.9(2), P2−Os1−Cl2 90.7(2), P2−Os1−C1 99.0(5), P2−Os1−C2 89.9(5), Cl1−Os1−Cl2 86.8(2), Cl1−Os1−C1 169.3(2), Cl1−Os1−C2 95.9(6), Cl2−Os1−C1 82.7(6), Cl2−Os1−C2 176.8(2), C1−Os1−C2 94.6(8), Os1−C1−C50 139(2), Os1−C2−O1 176(2), Molecule **B**: Os2−Cl3 2.489(5), Os2−Cl4 2.478(4), Os2−P3 2.466(5); Os2−P4 2.476(5), Os2−C3 1.89(2), Os2−C4 1.83(2), C3−C60 1.49(2), O3−C4 1.16(2); P3−Os2−P4 166.3(2), P3−Os2−Cl3 82.1(2), P3−Os2−Cl4 88.8(2), P3−Os2−C3 98.0(5), P3−Os2−C4 89.6(6), P4−Os2−Cl3 84.2(2), P4−Os2−Cl4 90.3(2), P4−Os2−C3 95.5(5), P4−Os2−C4 91.7(6), Cl3−Os2−Cl4 88.1(2), Cl3−Os2−C3 171.4(5), Cl3−Os2−C4 93.5(6), Cl4−Os2−C3 93.5(6), Cl4−Os2−C4 177.5(5), C3−Os2−C4 95.0(8), Os2−C3−C60 142(1), Os2−C4−O2 179(2)

5. The distance Os−C1 in molecule **A** is nearly identical with the Os−C(carbene) bond length in the related bis(triphenylphosphane)osmium(II) derivative *cis,cis,trans*-[$OsCl_2(=CHPh)(CO)(PPh_3)_2$] [1.94(1) Å],[14] whereas the distance Os−C3 in molecule **B** [1.89(2) Å] corresponds precisely to the Os−C(carbene) distance of *cis,cis,trans*-[$OsCl_2(=CHCH_2Ph)(CO)(P$*i*$Pr_3)_2$] [1.887(9) Å].[13] There is no difference in the Os−Cl bond lengths in **10** (in neither **A** nor **B**), indicating that the *trans* influences of the carbonyl and carbene ligands are virtually the same. We note in this context that the formation of **10** from **3** and HCl is uncommon insofar as analogous reactions of carbeneosmium(II) and -ruthenium(II) compounds with Broensted acids mainly proceed by attack of the proton at the carbene carbon atom to give alkylmetal derivatives.[9,14,15]

Similarly to the reaction of **3** with HCl, treatment of the starting material **3** with HBF_4 in the presence of water leads to the cleavage of the Os−H bond and affords the cationic aqua(carbene) complex **11** in 68% isolated yield. Instead of HBF_4, the carbenium salt [CPh_3]BF_4 can also be used as the electrophilic substrate. The composition of **11** (which is an orange, slightly air-sensitive solid) has been confirmed both by elemental analysis and conductivity measurements. The presence of the coordinated water molecule is clearly indicated in the IR spectrum by the strong ν(OH) bond at 3373 cm^{-1}. The ^{1}H-NMR spectrum of **11** (in CD_2Cl_2) is temperature-dependent. While at 290 K and slightly below (see Figure 4) the resonance for the OH_2 protons cannot be observed, at 266 K a relative broad signal appears which sharpens at 243 K to a singlet. This change of pattern is accompanied by a distinct separation of two resonances in the region between δ = 8.0−8.8 which are assigned to the *ortho*-hydrogen atoms of the phenyl ring. Brookhart[16] and Grubbs[17] both reported about similar observations in the case of cationic carbeneiron and -ruthenium complexes and attributed the observed effects to the interaction between the phenyl substituent and the positively charged carbene carbon atom. For **11** an analogous explanation could also be reasonable, in particular since in the ^{1}H-NMR spectrum of the related, but neutral, precursor **3** even at 213 K only one broadened resonance for the *ortho*-CH protons of the phenyl ring appears. We note that an aqua(carbene)osmium-

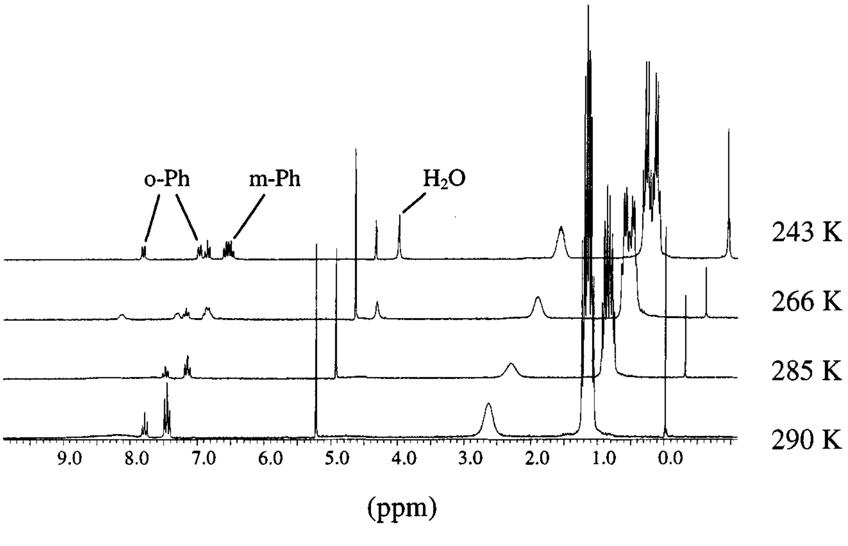


Figure 4. ^{1}H-NMR spectra of compound **11** in CD_2Cl_2 at different temperatures

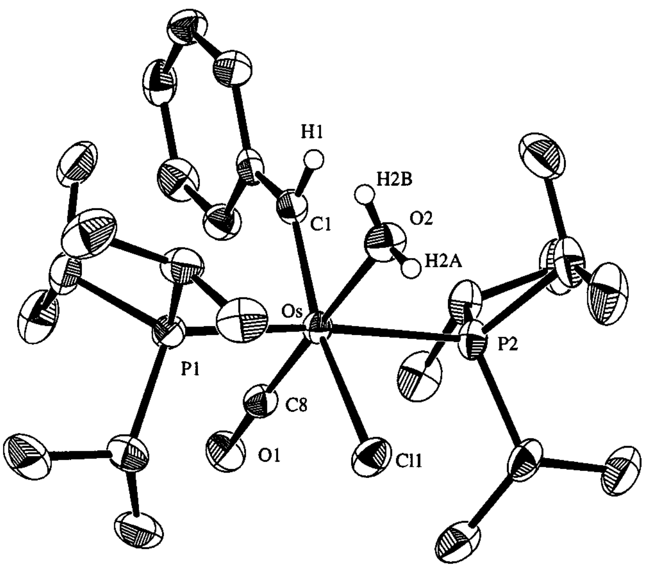


Figure 5. Molecular structure of the cation of **11**; hydrogen atoms apart from H1, H2A, and H2B are omitted for clarity; selected bond lengths [Å] and angles [°]: Os−P1 2.476(2), Os−P2 2.477(2), Os−Cl1 2.477(2), Os−C1 1.915(7), Os−C8 1.823(7), Os−O2 2.182(5), C1−C2 1.449(9), C8−O1 1.159(8); P1−Os−P2 172.90(6), P1−Os−Cl1 85.42(6), P1−Os−C1 95.3(2), P1−Os−C8 89.5(2), P1−Os−O2 89.9(2), P2−Os−Cl1 87.49(6), P2−Os−C1 91.6(2), P2−Os−C8 91.1(2), P2−Os−O2 89.3(2), Cl1−Os−C1 165.3(2), Cl1−Os−C8 98.0(2), Cl1−Os−O2 80.5(2), C1−Os−C8 96.7(3), C1−Os−O2 84.9(3), C8−Os−O2 178.4(2), Os−C8−O1 177.3(6), Os−C1−C2 140.9(5)

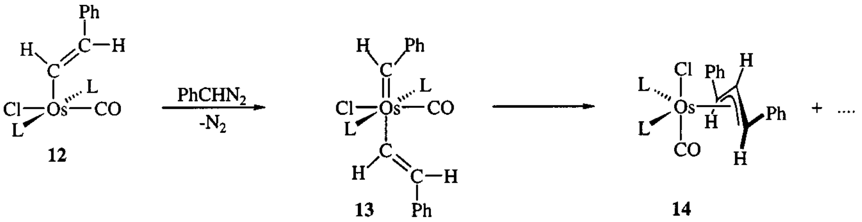
(II) compound similar to **11** with the composition [OsCl(=CHCH=CH$_2$)(H$_2$O)(CO)(P*i*Pr$_3$)$_2$]BF$_4$ has been described by Esteruelas et al. but due to the lability of this species neither NMR-spectroscopic nor structural data have been reported.[18]

The molecular structure of the cation of **11** is shown in Figure 5. Although in analogy to the other carbeneosmium(II) complexes **4**, **5**, and **10** the coordination geometry around the metal center is not perfectly octahedral, the bending of the three main axes P1−Os−P2, C8−Os−O2, and C1−Os−Cl1 is less pronounced than in the related neutral compounds with an Os−CHPh bond. The most noteworthy structural feature is that in contrast to **4**, **5**, and **10** the chloro ligand in **11** is mutually *cis* and not *trans* to the CO group. The conclusion is that in the course of the reaction of **3** with HBF$_4$/H$_2$O a rearrangement of the ligand sphere occurs. The bond length Os−C1 in **11** is slightly shorter than in the hydrido(carbene) derivatives **4** and **5**, but corresponds almost exactly to the average of the metal−carbene distances found for molecules **A** and **B** in the dichloro complex **10**.

The five-coordinate vinylosmium(II) compound **12**, which (as mentioned above) was prepared from **1** and phenylacetylene,[4] also reacts with PhCHN$_2$ to give the expected six-coordinate carbene complex **13** in 82% yield (Scheme 4). Attempts to prepare **13** on an alternative route failed because in contrast to **1** the hydrido(carbene) derivative **3** does not react with PhC≡CH by insertion of the alkyne into the Os−H bond. The ^{1}H- and ^{31}P-NMR spectra of **13** in (CDCl$_3$) reveal that in solution two isomeric species in the ratio of 2:1 are present which probably differ in the orientation of the carbene unit to the vinyl ligand. Although due to the preliminary results of an X-ray structure analysis of **13**[19] there is no doubt that in the crystal the CHPh and the CH=CHPh groups are *trans* to each other, we cannot exclude that in solution a mixture of both the *cis* and the *trans* isomer exists. With regard to the stereochemistry of the OsCH=CHPh moiety, the large H−H coupling of ca. 19 Hz between the vinyl protons indicates that the metal and the phenyl group are *trans*-disposed.

In benzene or toluene, the carbene(vinyl)osmium(II) derivative **13** is somewhat labile and rearranges slowly to a product which probably is the π-allyl complex **14**. The same reaction in chloroform leads to a mixture of at least two compounds which could not be separated by fractional crystallization or chromatographic techniques. Attempts to obtain **14** in analytically pure form also failed since during column chromatography of a solution of **14** in benzene decomposition occurred. The most typical features of the ^{1}H-NMR spectrum of **14** are the sharp triplet at δ = 6.09 for the central CH proton of the allyl moiety and the doublet of doublet resonance at δ = 4.14 (with the relative intensity of 2 H) which is assigned to the two equivalent terminal protons of the PhCHCHCHPh group. The relatively large H−H coupling constant (11.6 Hz) for these two signals indicate that the terminal protons are in *anti* position. A related compound to **14** with the composition [OsH(η^3-C$_3$H$_5$)(CO)(P*i*Pr$_3$)$_2$] exists and has been prepared in our laboratory from **1** and C$_3$H$_5$MgBr.[20]

With regard to the mechanism of formation of **14** from compound **13** we note that in rhodium and ruthenium chemistry work by Maitlis and us has already demonstrated that coupling between a vinyl group and a carbene ligand in the coordination sphere of a transition-metal occurs leading to an allyl unit.[21][22] Moreover, Hill and co-work-



Scheme 4. L = P*i*Pr$_3$

ers recently reported that the five-coordinate vinyl complex $[\mathrm{Ru(CH{=}CH_2)Cl(CO)(PPh_3)_2}]$ reacts with excess diazomethane to afford the corresponding π-allyl species $[\mathrm{RuCl(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2}]$ via a carbeneruthenium compound as an observed intermediate.[23]

Conclusion

The work presented in this paper has shown that treatment of the five-coordinate starting material **1** with $\mathrm{CH_2N_2}$ and substituted diazoalkanes $\mathrm{RCHN_2}$ does not lead to the insertion of the respective carbene into the Os−H bond and, therefore, does not afford the alkylosmium(II) complexes $[\mathrm{Os(CH_2R)Cl(CO)(P}i\mathrm{Pr_3)_2}]$. Instead, the isomeric hydrido(carbene) derivatives **2−5** are formed in excellent yields. The X-ray crystal structure analyses of two representatives **4** and **5** have confirmed that in the hydrido(carbene)osmium(II) compounds the hydride and the carbene ligand are in *trans* disposition. The same stereochemistry has been found for the related ruthenium(II) complexes $[\mathrm{RuHCl({=}CHR)(CO)(P}i\mathrm{Pr_2Ph)_2}]$ where R is H or Ph.[24] Recently, Caulton and co-workers reported that the reaction of $[\mathrm{MHCl(CO)(P}t\mathrm{Bu_2Me)_2}]$ (M = Os, Ru) with diazomethane yields at low temperature also the corresponding hydrido(methylidene) derivatives $[\mathrm{MHCl({=}CH_2)(CO)(P}t\mathrm{Bu_2Me)_2}]$ which, however, isomerize at 25°C or below to $[\mathrm{M(CH_3)Cl(CO)(P}t\mathrm{Bu_2Me)_2}]$.[25] In agreement with our studies, these authors equally observed that the osmium complex **2** decomposes unselectively to a mixture of products among which **1** and ethene could be detected. Caulton et al. assume that the remarkable ligand dependence ($\mathrm{P}t\mathrm{Bu_2Me}$ vs. $\mathrm{P}i\mathrm{Pr_3}$) is attributed to the fact that the $\mathrm{MH({=}CH_2)}$ to $\mathrm{M(CH_3)}$ isomerization of the six-coordinate compounds require phosphane dissociation and that the smaller $\mathrm{P}i\mathrm{Pr_3}$ (compared to $\mathrm{P}t\mathrm{Bu_2Me}$) fails to dissociate at a rate competitive with alternative decomposition reactions.[25] Recent ab initio MP2 calculations by Eisenstein et al.[26] are in agreement with these results. The theoretical work also reveals that for $[\mathrm{OsHCl({=}CH_2)(CO)(P}i\mathrm{Pr_3)_2}]$ the isomer, in which H and $\mathrm{CH_2}$ are mutually *cis*, is more stable than that in which these ligands are mutually *trans*.[26] Therefore, the final conclusion is that the isolated hydrido(carbene) complex **2** and probably also the analogous derivatives **3−5** are kinetically protected by a high barrier for site exchange which seems to be a prerequisite for an insertion reaction

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1**[2] and **12**[4] were prepared as described in the literature. − NMR: Bruker AC 200 and AMX 400 [dvt = doublet of virtual triplets; $N = {}^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})$ or ${}^2J(\mathrm{PC}) + {}^4J(\mathrm{PC})$, respectively]. − Melting points determined by DTA.

1. Preparation of $[\mathrm{OsHCl({=}CH_2)(CO)(P}i\mathrm{Pr_3)_2}]$ (2): A suspension of 84 mg (0.15 mmol) of **1** in 10 mL of diethyl ether was treated at room temperature with 0.80 mL of a freshly prepared 0.3 M solution of diazomethane in $\mathrm{OEt_2}$. An evolution of gas ($\mathrm{N_2}$) occurred. After the reaction mixture was stirred for 2 min, the solvent was removed and the yellow microcrystalline solid dried in vacuo; yield 86 mg (99%); m.p. 95°C (dec.). − IR (KBr): $\tilde{\nu} = 1910\ \mathrm{cm^{-1}}$ (CO), 1857 (OsH). − ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): $\delta = 17.90$, 16.88 (both br s, 1 H each, $\mathrm{OsCH_2}$), 2.46 (m, 6 H, $\mathrm{PC}H\mathrm{CH_3}$), 1.10 [dvt, $N = 14.4$, $^3J(\mathrm{H,H}) = 7.2$ Hz, 18 H, $\mathrm{PCHC}H_3$], 1.02 [dvt, $N = 14.6$, $^3J(\mathrm{H,H}) = 7.2$ Hz, 18 H, $\mathrm{PCHC}H_3$], −4.48 [tt, $^2J(\mathrm{P,H}) = 30$, $^3J(\mathrm{H,H}) = 2$ Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_6}$): $\delta = 285.0$ (br s, $\mathrm{Os{=}CH_2}$), 182.0 [t, $^2J(\mathrm{P,C}) = 8.0$ Hz, CO], 25.0 (vt, $N = 28.6$ Hz, $\mathrm{P}C\mathrm{HCH_3}$), 19.1, 18.5 (both s, $\mathrm{PCH}C\mathrm{H_3}$). − ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): $\delta = 56.5$ [s, $J(^{187}\mathrm{Os},^{31}\mathrm{P}) = 168$ Hz]. − $\mathrm{C_{20}H_{45}ClOOsP_2}$ (589.2): calcd. C 40.77, H 7.70; found C 40.50, H 8.01.

2. Preparation of $[\mathrm{OsHCl({=}CHPh)(CO)(P}i\mathrm{Pr_3)_2}]$ (3): A solution of 200 mg (0.35 mmol) of **1** in 10 mL of toluene was treated dropwise with 0.30 mL of a 1.4 M solution of $\mathrm{PhCHN_2}$ in hexane at room temperature. An evolution of gas ($\mathrm{N_2}$) occurred which was accompanied by a change of color from orange to dark yellow and finally to red (indicating excess of $\mathrm{PhCHN_2}$). After the reaction mixture was stirred for 30 min, it was worked up as described for **2**. Orange crystals; yield 230 mg (99%); m.p. 117°C (dec.). − IR (KBr): $\tilde{\nu} = 1878\ \mathrm{cm^{-1}}$ (CO), 1830 (OsH). − ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 17.45$ (m, 1 H, Os=CH), 8.20 (m, 2 H, $\mathrm{C_6H_5}$), 7.51 (m, 1 H, $\mathrm{C_6H_5}$), 7.29 (m, 2 H, $\mathrm{C_6H_5}$), 2.61 (m, 6 H, $\mathrm{PC}H\mathrm{CH_3}$), 1.10 [dvt, $N = 14.0$, $^3J(\mathrm{H,H}) = 6.8$ Hz, 36 H, $\mathrm{PCHC}H_3$)], −4.50 [dt, $^2J(\mathrm{P,H}) = 29.5$, $^3J(\mathrm{H,H}) = 4.5$ Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, $\mathrm{CDCl_3}$): $\delta = 296.8$ (br s, $\mathrm{Os{=}}C\mathrm{HPh}$), 183.4 [t, $^2J(\mathrm{P,C}) = 8.0$ Hz, CO], 157.2 (s, i-$\mathrm{C_6H_5}$), 132.1, 129.8, 129.6 (all s, $\mathrm{C_6H_5}$), 25.9 (vt, $N = 27.8$ Hz, $\mathrm{P}C\mathrm{HCH_3}$), 18.8, 18.7 (both s, $\mathrm{PCH}C\mathrm{H_3}$). − ^{31}P NMR (162.0 MHz, $\mathrm{CDCl_3}$): $\delta = 47.9$ [s, $J(^{187}\mathrm{Os},^{31}\mathrm{P}) = 168$ Hz]. − $\mathrm{C_{26}H_{49}ClOOsP_2}$ (665.3): calcd. C 46.94, H 7.42; found C 47.34, H 7.42.

3. Preparation of $[\mathrm{OsHCl({=}CHCO_2Et)(CO)(P}i\mathrm{Pr_3)_2}]$ (4): A solution of 105 mg (0.18 mmol) of **1** in 5 mL of toluene was treated with 0.04 mL of $\mathrm{N_2CHCO_2Et}$ at room temperature. An evolution of gas ($\mathrm{N_2}$) occurred which was accompanied by a change of color from orange to dark brown. After the reaction mixture was stirred for 30 min, the solvent was removed in vacuo and the residue was extracted with a mixture of 10 mL of hexane and 0.5 mL of toluene. The extract was filtered and the filtrate was concentrated in vacuo to give an orange solid; yield 98 mg (81%); m.p. 133°C (dec.). − IR (KBr): $\tilde{\nu} = 1923\ \mathrm{cm^{-1}}$ (CO), 1863 (OsH), 1650 ($\mathrm{CO_2Et}$). − ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): $\delta = 17.22$ [dt, $^3J(\mathrm{H,H}) = {}^3J(\mathrm{P,H}) = 3.0$ Hz, 1 H, Os=CH]; 4.23 [q, $^3J(\mathrm{H,H}) = 7.5$ Hz, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$], 2.60 (m, 6 H, $\mathrm{PC}H\mathrm{CH_3}$), 1.17 [t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 3 H, $\mathrm{CH_2C}H_3$], 1.14, 1.06 [both dvt, $N = 14.7$, $^3J(\mathrm{H,H}) = 7.5$ Hz, 18 H each, $\mathrm{PCHC}H_3$], −4.95 [dt, $^3J(\mathrm{H,H}) = 3.0$, $^2J(\mathrm{P,H}) = 31.6$ Hz, 1 H, OsH]. − ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$): $\delta = 267.7$ (br s, $\mathrm{Os{=}}C\mathrm{HCO_2Et}$), 181.5 [t, $^3J(\mathrm{P,C}) = 2.5$ Hz, $C\mathrm{O_2Et}$], 179.3 [t, $^2J(\mathrm{P,C}) = 8.9$ Hz, CO], 59.6 (s, $C\mathrm{H_2CH_3}$), 29.9 (vt, $N = 28.8$ Hz, $\mathrm{P}C\mathrm{HCH_3}$), 18.7 (s, $\mathrm{PCH}C\mathrm{H_3}$), 14.4 (s, $\mathrm{CH_2}C\mathrm{H_3}$). − ^{31}P NMR (81.0 MHz, $\mathrm{CDCl_3}$): $\delta = 56.6$ [s, $J(^{187}\mathrm{Os},^{31}\mathrm{P}) = 165$ Hz]. − $\mathrm{C_{23}H_{49}ClO_3OsP_2}$ (661.3): calcd. C 41.78, H 4.79; found C 41.51, H 7.19.

4. Preparation of $[\mathrm{OsHCl({=}CHSiMe_3)(CO)(P}i\mathrm{Pr_3)_2}]$ (5): A solution of 100 mg (0.17 mmol) of **1** in 5 mL of toluene was treated with 0.15 mL of a 2.0 M solution of $\mathrm{Me_3SiCHN_2}$ in hexane and stirred for 15 h at room temperature. The solvent was evaporated in vacuo, the remaining yellow microcrystalline solid washed twice with 2 mL of hexane and dried in vacuo; yield 91 mg (79%); m.p. 132°C (dec.). − IR (KBr): $\tilde{\nu} = 1938\ \mathrm{cm^{-1}}$ (CO). − ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): $\delta = 19.85$ [dt, $^3J(\mathrm{P,H}) = {}^3J(\mathrm{H,H}) = 2$ Hz, 1 H, $\mathrm{Os{=}C}H\mathrm{SiMe_3}$], 2.53 (m, 6 H, $\mathrm{PC}H\mathrm{CH_3}$) 1.20 [dvt, $N = 14.2$, $^3J(\mathrm{H,H}) = 7.2$ Hz, 18 H, PCHCH_3], 1.08 [dvt, N = 14.7, ^{3}J(H,H) = 7.3 Hz, 18 H, PCHCH_3], 0.16 (s, 9 H, SiCH$_3$), −5.62 [dt, ^{2}J(P,H) = 28.6, ^{3}J(H,H) = 2 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 327.3 (s, Os=CHSiMe$_3$), 182.6 [t, ^{2}J(P,C) = 8.0 Hz, CO], 25.2 (vt, N = 28.6 Hz, PCHCH$_3$), 19.2, 18.8 (both s, PCHCH$_3$), 0.5 (s, SiCH$_3$). − ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 56.5 [s, J(^{187}Os,^{31}P) = 170 Hz]. − C$_{23}$H$_{53}$ClOOsP$_2$Si (661.4): calcd.C 41.77, H 8.08; found C 41.32, H 8.26.

5. Generation of [OsHCl(N$_2$CHSiMe$_3$)(CO)(P*i*Pr$_3$)$_2$] (6): A solution of 35 mg (0.06 mmol) of **1** in 5 mL of toluene was treated at −78 °C with 0.05 mL of a 2.0 M solution of Me$_3$SiCHN$_2$ in hexane. An instant change of color from orange to light yellow occurred which is not accompanied by an evolution of gas. Attempts to isolate the product by low-temperature evaporation of the solvent led always to a mixture of **5** and **6**. Spectroscopic data for **6**: IR (KBr): ṽ = 1890 cm^{-1} (CO), 1933 (OsH or N$_2$). − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.80 (s, 1 H, Me$_3$SiCHN$_2$), 2.62 (m, 6 H, PCHCH$_3$), 1.26 [dvt, N = 13.2, ^{3}J(H,H) = 6.7 Hz, 18 H, PCHCH_3], 1.23 [dvt, N = 13.6, ^{3}J(H,H) = 7.0 Hz, 18 H, PCHCH_3], 0.13 (s, 9 H, SiCH$_3$), −13.70 (br s, 1 H, OsH). − ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 178.8 [t, ^{2}J(P,C) = 8.3 Hz, CO], 33.4 (s, Me$_3$SiCHN$_2$), 24.5 (vt, N = 26.0 Hz, PCHCH$_3$), 19.2, 19.0 (both s, PCHCH$_3$), 0.3 (s, SiCH$_3$). − ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 28.3 [s, J(^{187}Os,^{31}P) = 176 Hz].

6. Preparation of [OsHCl(N$_2$CPh$_2$)(CO)(P*i*Pr$_3$)$_2$] (7): A solution of 51.0 mg (0.09 mmol) of **1** in 2 mL of toluene was treated dropwise at room temperature with a solution of 18.1 mg (0.09 mmol) of Ph$_2$CN$_2$ in 5 mL of toluene. After the reaction mixture was stirred for 2 min, the solvent was removed in vacuo and the residue washed twice with 3 mL of hexane. An off-white solid was obtained which was dried in vacuo; yield 51 mg (75%); m.p. 69 °C (dec.). − IR (KBr): ṽ = 1890 cm^{-1} (CO), 1952 (OsH or N$_2$). − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.32 (m, 8 H, C$_6$H$_5$), 7.15 (m, 2 H, C$_6$H$_5$), 2.60 (m, 6 H, PCHCH$_3$), 1.22 [dvt, N = 13.7, ^{3}J(H,H) = 6.6 Hz, 18 H, PCHCH_3], 1.15 [dvt, N = 13.8, ^{3}J(H,H) = 6.8 Hz, 18 H, PCHCH_3], -11.44 (br s, 1 H, OsH). − ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 179.2 [t, ^{2}J(P,C) = 9.1 Hz, CO], 129.2, 128.6, 127.7, 126.5 (all s, C$_6$H$_5$), 24.6 (vt, N = 25.8 Hz, PCHCH$_3$), 19.4, 19.3 (both s, PCHCH$_3$), signal of Ph$_2$$CN_2$ not observed. − ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 28.0 [s, J(^{187}Os,^{31}P) = 180 Hz]. − C$_{32}$H$_{53}$ClN$_2$OOsP$_2$ (769.4): calcd. C 49.95, H 6.94, N 3.64; found C 49.66, H 6.78, N 3.55.

7. Preparation of [OsHCl(N$_2$C$_5$Cl$_4$)(CO)(P*i*Pr$_3$)$_2$] (8): This compound was prepared analogously as described for **7**, using 50.0 mg (0.09 mmol) of **1** and 23.8 mg (0.10 mmol) of N$_2$C$_5$Cl$_4$ as starting materials. Light brown solid; yield 53 mg (75%); m.p. 73 °C (dec.). − IR (hexane): ṽ = 1904 cm^{-1} (CO), 1941 (OsH or N$_2$). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 2.55 (m, 6 H, PCHCH$_3$), 1.15−1.08 (br m, 36 H, PCHCH_3), −7.06 [t, ^{2}J(P,H) = 22 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 177.3 [t, ^{2}J(P,C) = 7.8 Hz, CO], 113.3, 108.0 (both s, CCl), 82.2 (br s, N$_2$C), 24.9 (vt, N = 27.4 Hz, PCHCH$_3$), 19.9, 19.0 (both s, PCHCH$_3$). − ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 26.3 [s, J(^{187}Os,^{31}P) = 170 Hz]. − C$_{24}$H$_{43}$Cl$_5$N$_2$OOsP$_2$ (805.1): calcd. C 35.81, H 5.38, N 3.48; found C 35.37, H 5.62, N 3.36.

8. Preparation of [OsH(O$_2$CCF$_3$)(=CHPh)(CO)(P*i*Pr$_3$)$_2$] (9): A solution of 120 mg (0.18 mmol) of **3** in 10 mL of toluene was treated with 58 mg (0.18 mmol) of CF$_3$CO$_2$Tl and stirred for 15 h at room temperature. A white solid (TlCl) slowly precipitated. The solution was filtered, the filtrate was concentrated in vacuo and the remaining orange solid dried; yield 121 mg (89%); m.p. 106 °C (dec.). − IR (KBr): ṽ = 1885 cm^{-1} (CO), 1680 (OCO asym), 1425 (OCO sym). − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 17.16 [m, d after ^{31}P decoupling, ^{3}J(H,H) = 4.4 Hz, 1 H, Os=CHPh], 8.15 (m, 2 H, C$_6$H$_5$), 7.54 (m, 1 H; C$_6$H$_5$), 7.35 (m, 2 H, C$_6$H$_5$), 2.43 (m, 6 H, PCHCH$_3$), 1.15 [dvt, N = 14.0, ^{3}J(H,H) = 7.0 Hz, 18 H, PCHCH_3], 1.12 [dvt, N = 13.6, ^{3}J(H,H) = 6.8 Hz, 18 H, PCHCH_3], −2.93 [dt, ^{2}J(P,H) = 29.7, ^{3}J(H,H) = 4.4 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 295.5 (s, Os=CHPh), 185.4 [t, ^{2}J(P,C) = 9.0 Hz, CO], 160.5 [q, ^{2}J(C,F) = 36 Hz, O$_2$$CCF_3$], 156.6 (s, *i*-C$_6H_5$), 132.5, 130.4, 129.6 (all s, C$_6$H$_5$), 115.1 [q, ^{1}J(C,F) = 293 Hz, O$_2$CCF$_3$], 26.4 (br vt, PCHCH$_3$], 18.9, 18.8 (both s, PCHCH$_3$). − ^{31}P NMR (162.0 MHz, CDCl$_3$): δ = 53.0 [s, J(^{187}Os,^{31}P) = 170 Hz]. − ^{19}F NMR (188.0 MHz, CD$_2$Cl$_2$): δ = −75.0 (s). − C$_{28}$H$_{49}$F$_3$O$_3$OsP$_2$ (742.3): calcd. C 45.27, H 6.65; found C 45.04, H 6.32.

9. Preparation of [OsCl$_2$(=CHPh)(CO)(P*i*Pr$_3$)$_2$] (10): A solution of 100 mg (0.15 mmol) of **3** in 5 mL of toluene was treated with 1.80 mL of a ca. 1.0 M solution of HCl in toluene. A rapid change of color from orange to red occurred which was accompanied by the evolution of gas (H$_2$). The solvent was removed, the red air-stable solid was washed twice with 5 mL of pentane and dried; yield 102 mg (98%); m.p. 155 °C. − IR (KBr): ṽ = 1915 cm^{-1} (CO). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 19.04 (s, 1 H, Os=CHPh), 8.28 (br s, 2 H, C$_6$H$_5$), 7.07 (m, 3 H, C$_6$H$_5$), 2.72 (m, 6 H, PCHCH$_3$), 1.25 [dvt, N = 14.0, ^{3}J(H,H) = 7.0 Hz, 18 H, PCHCH_3], 1.08 [dvt, N = 13.6, ^{3}J(H,H) = 6.8 Hz, 18 H, PCHCH_3]. − ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 278.0 (s, Os=CHPh), 181.0 [t, ^{2}J(P,C) = 7.6 Hz, CO], 157.2 (s, *i*-C$_6$H$_5$), 132.9, 132.0, 130.3 (all s, C$_6$H$_5$), 25.6 (vt, N = 28.8 Hz, PCHCH$_3$), 20.1, 19.4 (both s, PCHCH$_3$). − ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 9.3 [s, J(^{187}Os,^{31}P) = 154 Hz]. − C$_{26}$H$_{48}$Cl$_2$OOsP$_2$ (699.8): calcd. C 44.63, H 6.91; found C 44.35, H 6.67.

10. Preparation of [OsCl(=CHPh)(CO)(H$_2$O)(P*i*Pr$_3$)$_2$]BF$_4$ (11): a) A solution of 234 mg (0.35 mmol) of **3** in 5 mL of benzene was treated with 1.0 mL of a 48% solution of HBF$_4$ in water (7.65 mmol) and vigorously stirred for 3 min at room temperature. The aqueous phase was separated and washed four times with 5 mL of benzene each. The organic phase and the benzene washings were combined, and the solution was concentrated to ca. 10 mL in vacuo. Upon standing for 3 h, an orange solid precipitated which was seperated from the mother liquor. The solid was then dissolved in 10 mL of ether and the solution stored for 10 h at −20 °C. Orange-yellow crystals were formed which were filtered, washed twice with 2 mL of ether (0 °C) and dried; yield 184 mg (68%). − b) A solution of 60 mg (0.09 mmol) of **3** in 5 mL of toluene was treated with 30 mg (0.09 mmol) of [CPh$_3$]BF$_4$ and stirred for 15 h at room temperature. The solvent was removed, the orange-yellow solid washed four times with 3 mL of hexane each and dried; yield 44 mg (64%); m.p. 109 °C (dec.). − Λ = 65 cm^{2}Ω^{-1}mol^{-1} (in CH$_3$NO$_2$). − IR (KBr): ṽ = 3375 cm^{-1} (OH), 1936 (CO). − ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, −30 °C): δ = 17.18 (s, 1 H, Os=CHPh), 8.80, 7.97, 7.85 (all m, 1 H each, C$_6$H$_5$), 7.53 (m, 2 H, C$_6$H$_5$), 4.98 (s, 2 H, H$_2$O), 2.55 (m, 6 H, PCHCH$_3$), 1.26 [dvt, N = 14.7, ^{3}J(H,H) = 7.3 Hz, 18 H, PCHCH_3], 1.11 [dvt, N = 13.7, ^{3}J(H,H) = 6.9 Hz, 18 H, PCHCH_3]. − ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$, −30 °C): δ = 274.2 [t, ^{2}J(P,C) ca. 15 Hz, Os=CHPh], 181.2 [t, ^{2}J(P,C) ca. 9 Hz, CO], 134.8, 134.6, 132.5, 130.7, 130.6 (all s, C$_6$H$_5$), 24.1 (vt, N = 25.5 Hz, PCHCH$_3$), 19.2, 18.0 (both s, PCHCH$_3$). − ^{19}F NMR (188.0 MHz, CD$_2$Cl$_2$, −30 °C): δ = −148.7 (s). − ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$, −30 °C): δ = 19.6 (s). − C$_{26}$H$_{51}$BClF$_4$O$_2$OsP$_2$ (770.1): calcd. C 40.55, H 6.68; found C 41.01, H 6.97.

11. Preparation of [Os(CH=CHPh)Cl(=CHPh)(CO)(P*i*Pr$_3$)$_2$] (13): A suspension of 112 mg (0.17 mmol) of **12** in 5 mL of hexane was treated dropwise with 0.30 mL of a 1.4 M solution of $PhCHN_2$ in hexane at room temperature. A red solution was formed from which after stirring for 20 min a red solid precipitated. The mother liquor was decanted, the remaining red solid was washed three times with 3 mL of hexane (0 °C) and dried; yield 104 mg (82%); m.p. 68 °C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 1890 cm^{-1} (CO). − ^1H NMR (400 MHz, C_6D_6): δ = 19.08 (s, 1 H, Os=C*H*Ph), 9.92 [d, ^3J(H,H) = 19.0 Hz, 1 H, CH=C*H*Ph], 8.42, 7.59 (both br s, 2 H each, C_6H_5), 7.38 [dt, ^3J(H,H) = 19.0, ^3J(P,H) ≈ 2 Hz, 1 H, C*H*=CHPh], 7.27, 7.04 (both m, 3 H each, C_6H_5), 2.49 (m, 6 H, PC*H*CH_3), 1.14 [dvt, *N* = 14.0, ^3J(H,H) = 7.1 Hz, 18 H, PCHCH_3], 1.10 [dvt, *N* = 13.6, ^3J(H,H) = 6.8 Hz, 18 H, PCHCH_3]. − ^1H NMR (400 MHz, $CDCl_3$), isomer **A**: δ = 19.31 (s, 1 H, Os=C*H*Ph), 9.15 [d, ^3J(H,H) = 18.7 Hz, 1 H, CH=C*H*Ph], 8.35, 7.59 (both m, 2 H each, C_6H_5), 7.26 (m, C_6H_5), 6.99 (m, 1 H, C*H*=CHPh), 2.49 (m, 6 H, PC*H*CH_3), 1.11 [dvt, *N* = 14.0, ^3J(H,H) = 7.1 Hz, 36 H, PCHCH_3]; isomer **B**: δ = 18.66 (s, 1 H, Os=C*H*Ph), 9.38 [d, ^3J(H,H) = 18.9 Hz, 1 H, CH=C*H*Ph], 8.27, 7.59 (both m, 2 H each, C_6H_5), 7.26 (m, C_6H_5), 6.90 [d, ^3J(H,H) = 18.9 Hz, 1 H, C*H*=CHPh], 2.49 (m, 6 H, PC*H*CH_3), 0.99 [dvt, *N* = 14.0, ^3J(H,H) = 7.1 Hz, 36 H, PCHCH_3]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 302.8 (m, Os=*C*HPh), 184.6 [t, ^2J(P,C) = 9 Hz, CO], 158.3 (s, *i*-C_6H_5), 147.4 [t, ^2J(P,C) = 6 Hz, *C*H=CHPh], 142.5 [t, ^2J(P,C) = 3 Hz, CH=*C*HPh], 133.4, 131.5, 130.2, 125.6, 125.5, 125.4 (all s, C_6H_5), 27.0 (vt, *N* = 28 Hz, P*C*HCH_3), 19.9, 19.7 (both s, PCH*C*H_3). − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 2.1 [s, $J(^{187}Os,^{31}P)$ = 154 Hz]. − ^{31}P NMR (162.0 MHz, $CDCl_3$), isomer **A**: δ = 3.5 (s); isomer **B**: δ = 2.6 (s). − $C_{34}H_{56}ClOOsP_2$ (768.5): calcd. C 53.14, H 7.35; found C 52.73, H 7.16.

12. Generation of [OsCl(η^3-PhCHCHCHPh)(CO)(P*i*Pr_3)$_2$] (14): A solution of 80 mg (0.10 mmol) of **13** in 2 mL of benzene was stirred for 24 h at room temperature. After the solvent was evaporated, a red oil was obtained. The ^1H-NMR spectrum of this material revealed that apart from small amounts of **13** and some unidentified by-products the dominating species (ca. 90%) is compound **14**. Attempts to seperate the by-products from the wanted complex **14** by fractional crystallisation or chromatographic techniques failed. Characteristic NMR data for **14**: ^1H NMR (400 MHz, C_6D_6): δ = 7.63 (br s, 4 H, C_6H_5), 7.20 (m, 6 H, C_6H_5), 6.09 [t, ^3J(H,H) = 11.6 Hz, 1 H, PhCHC*H*CHPh], 4.14 [dd, ^3J(H,H) = 11.6, ^2J(P,H) = 4.8 Hz, 2 H, PhC*H*CHC*H*Ph], 2.47 (m, 6 H, PC*H*CH_3), 1.40, 1.31 (both br m, 36 H, PCHCH_3). − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 180.8 [t, ^2J(P,C) = 10.0 Hz, CO), 96.8 (br s, Ph*C*HCH*C*HPh), 67.0 (br s, PhCH*C*HCHPh), 31.0 (br s, PCHCH_3), 21.1 (br s, PCH*C*H_3), signals of phenyl carbon atoms are very broad and could not be exactly assigned. − ^{31}P NMR (162.0 MHz, C_6D_6): δ = −8.5 (br s).

13. Determination of the X-ray Crystal Structures of Compounds 4, 5, 10, and 11: Single crystals of **4** and **10** were obtained from toluene/hexane at −20 °C, crystals of **5** from hexane at −20 °C, and crystals of **11** from benzene/ether at −20 °C. Data of **4** and **5** were collected on a Stoe−Siemens−Huber diffractometer with CCD area detector, those of **10** and **11** on an Enraf−Nonius CAD4 diffractometer using monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Intensity data were corrected for LP effects. Multi-scan absorption correction was applied for **4** and **5** and a semi-empirical absorption correction was applied for **10** and **11**. The structures of **4**, **10**, and **11** were solved by direct methods and the structure of **5** by Patterson and Fourier methods..[27] All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2,[28] and a riding model was employed in the refinement of the hydrogen atom positions. The hydrogen atoms H19 and H20 of **4** and H10 of **5** were refined freely; H1 of **5** was refined with a distance restraint and by setting the displacement parameter to 120% of the equivalent isotropic U value of C1; H1, H2A, and H2B of **11** were refinded by setting the displacement parameter to 120% of the equivalent isotropic U value of C1 and O2. Two independent molecules (**A** and **B**) of **10** were found in the asymmetric unit. In Figure 3 only molecule **A** is shown. Table 1 contains crystallographic data of the whole asymmetric unit (the chemical formula belongs to one molecule). In the asymmetric unit of **11,** one benzene molecule and two half benzene molecules were found and refined anisotropically with restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-128215 (**4**), -128216 (**5**), -128217 (**10**), and -128218 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. + 44-1223/336−033; E-mail: deposit@ccdc.cam.ac.uk).

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