Vinylidene Transition-Metal Complexes, 50[+]

Carbynehydrido- and Vinylidenehydridoosmium Complexes with $Os(PCy_3)_2$ as a Molecular Unit

Helmut Werner,*[a] Stefan Jung,[a] Birgit Weberndörfer,[a] and Justin Wolf[a]

Dedicated to Professor Christoph Elschenbroich on the occasion of his 60th birthday

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The reaction of $OsCl_3 \cdot 2H_2O$ with PCy_3 leads under reducing conditions either to $[OsH_6(PCy_3)_2]$ (**1**) or $[OsH_2Cl_2(PCy_3)_2]$ (**2**). Treatment of **2** with terminal alkynes $HC\equiv CR$ (R = Ph, $SiMe_3$) affords the carbynehydrido complexes $[OsHCl_2(\equiv CCH_2R)(PCy_3)_2]$ (**4**, **5**), of which **5** (R = $SiMe_3$) is easily converted with traces of water into $[OsHCl_2(\equiv CCH_3)(PCy_3)_2]$ (**6**). Compound **4** (R = Ph) reacts with NaOMe to yield the vinylidenehydridoosmium(II) complex $[OsHCl(=C=CHPh)(PCy_3)_2]$ (**7**) which upon treatment with HBF_4/OEt_2 gives the five-coordinate cationic species $[OsHCl(\equiv CCH_2Ph)(PCy_3)_2]BF_4$ (**8**). The reaction of $[OsH_3Cl(PCy_3)_2]$ (**9**) with $HC\equiv CC(CH_3)_2Cl$ affords a mixture of $[OsHCl_2(\equiv CCH=CMe_2)(PCy_3)_2]$ (**10**) and $[OsCl_2(H_2)(=CHCH=CMe_2)(PCy_3)_2]$ (**11**). Compound **11** is quite labile and by elimination of H_2 gives **10**. The molecular structure of **10** has been determined by X-ray crystallography.

In the course of our continuous studies on the synthesis and reactivity of vinylidenemetal complexes with d^6- and d^8-metal centers,[1] we recently reported that the reaction of the ruthenium(IV) compound $[RuH_2Cl_2(PiPr_3)_2]$ with terminal alkynes $HC\equiv CR$ led, depending on the conditions, to the formation not only of the expected vinylidene complexes $[RuCl_2(=C=CHR)(PiPr_3)_2]$ but also of the related carbene derivatives $[RuCl_2(=CHCH_2R)(PiPr_3)_2]$.[2] Since compounds of this type, in particular with PCy_3 instead of $PiPr_3$ as P-donor ligand, proved to be excellent catalysts for olefin metathesis (including RCM and ROMP),[3] we became interested in studying the formation of carbene complexes $[RuCl_2(=CHCH_2R)(PR'_3)_2]$ from Ru-containing precursors and $HC\equiv CR$ in more detail. As a consequence we developed a convenient and very efficient one-pot synthesis of compounds $[RuCl_2(=CHCH_2R)(PCy_3)_2]$ (R = H, Ph) from ruthenium trichloride, PCy_3, Mg, H_2, water, and terminal alkynes as starting materials.[4] The principal advantage of this method is that it avoids expensive precursors such as $[RuCl_2(PPh_3)_3]$,[5] $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]$,[6] or $[RuH_2(H_2)_2(PCy_3)_2]$,[7] and uses alkynes instead of cyclopropenes, diazoalkanes, vinyl chlorides, or propargylic chlorides as carbene sources.

The aim of the present work was to find out whether the osmium counterparts to the Grubbs-type carbeneruthenium complexes are equally accessible and if so, what their catalytic activity is. Here we report that the preparative routes which for ruthenium give the five-coordinate compounds $[RuCl_2(=CHR)(PCy_3)_2]$ afford the isomeric carbynehydrido complexes $[OsHCl_2(\equiv CR)(PCy_3)_2]$ in good yields in the case of osmium. While these six-coordinate compounds are quite stable and inert towards olefins, the five-coordinate cationic complex $[OsHCl(\equiv CCH_2Ph)(PCy_3)_2]BF_4$ is catalytically active and catalyzes the ring-opening metathesis polymerization (ROMP) of cyclopentene.

Results and Discussion

Dihydrido- and Polyhydridoosmium Complexes

Under the conditions under which $RuCl_3 \cdot 3\,H_2O$ is converted into the hydrido(dihydrogen) complex $[RuHCl(H_2)(PCy_3)_2]$,[4] the reaction of $OsCl_3 \cdot 2\,H_2O$ with activated Mg and PCy_3 under H_2 takes a different course. After the suspension in THF was stirred for 4 h at 65°C, a mixture of products was formed in which, besides two unknown compounds, the dihydridoosmium(IV) complex **2** (Scheme 1) could be identified by ^1H- and ^{31}P-NMR spectroscopy. The trihydrido derivative $[OsH_3Cl(PCy_3)_2]$, the generation of which was anticipated in analogy to that of $[RuHCl(H_2)(PCy_3)_2]$, could not be detected. If the reaction mixture formed from $OsCl_3 \cdot 2\,H_2O$ was continuously stirred under H_2 at 85°C for 19 h, an off-white solid precipitated from which upon extraction with CH_2Cl_2 the hexahydrido complex $[OsH_6(PCy_3)_2]$ (**1**) was isolated. The preparation of this compound was previously reported by Halpern et al.[8] who treated $(NH_4)_2[OsCl_6]$ with PCy_3 and $NaBH_4$ in the presence of ethanol. The new synthetic route described here is more efficient and has the advantage of

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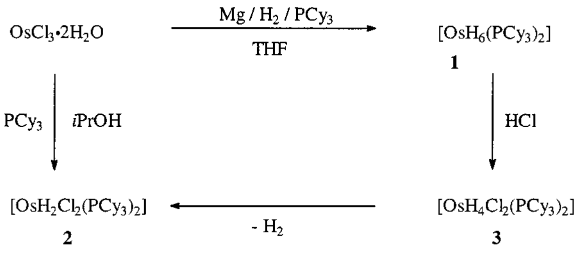
[a] Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

the starting material $OsCl_3 \cdot 2\,H_2O$ instead of the more expensive $(NH_4)_2[OsCl_6]$.



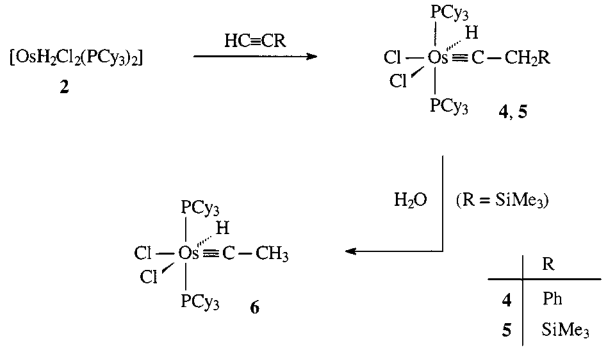
Scheme 1

The above-mentioned dihydridoosmium(IV) complex $[OsH_2Cl_2(PCy_3)_2]$ (**2**) is accessible from $OsCl_3 \cdot 2\,H_2O$ and PCy_3 in 2-propanol under reflux conditions. The same procedure had already been applied in our laboratory to afford the related species $[OsH_2Cl_2(L)_2]$ with L = P*i*Pr$_3$ and P*t*Bu$_2$Me, which represented the first examples of hexacoordinate osmium(IV) dihydrides.[9] Compound **2** was also obtained in almost quantitative yield on treatment of **1** with gaseous HCl in hexane. The most typical spectroscopic features of **2** (which is a red-brown, moderately air-sensitive solid) is the singlet for the two phosphane ligands in the ^{31}P-NMR spectrum at $\delta = 33.6$ and the triplet for the OsH_2 protons in the ^{1}H-NMR spectrum at $\delta = -15.68$. Based on the analogy of these spectroscopic data to those of $[OsH_2Cl_2(PiPr_3)_2]$, we assume that the structure of **2** is similar to that of the bis(triisopropylphosphane) derivative, which is best described as a square antiprism with two missing vertexes.[9]

The reaction of **1** with hydrogen chloride deserves a special comment. If a slow stream of HCl is passed through a suspension of **1** in hexane, almost instantaneously a flocculent white precipitate is formed which, after the reaction mixture is stirred for 10−15 min, is converted into the red-brown compound **2**. When the treatment of the starting material with HCl is stopped after ca. 30 s and the flocculent precipitate separated from the solution, we observed that the color of the off-white solid changed to brown. The ^{31}P-NMR spectrum of the freshly isolated intermediate displayed, besides the signals of **1** and **2** at $\delta = 45.0$ and 33.6, a third singlet at $\delta = 13.1$, which we tentatively assign to the dichlorotetrahydridoosmium(VI) complex **3** (Scheme 1). The ^{1}H-NMR spectrum of the crude product supports this proposal since it shows in the high-field region a signal at $\delta = -10.16$ which due to P-H coupling is split into a triplet. Recently, Berke et al. reported the preparation of the corresponding triisopropylphosphane derivative $[OsH_4Cl_2(PiPr_3)_2]$, the ^{1}H-NMR spectrum of which displays a resonance at $\delta = -10.55$ with a ^2J(PH) coupling constant of 10.1 Hz.[10] We note that even if the ^{1}H-NMR spectrum of the intermediate is measured in CD_2Cl_2 at −78 °C, a slow evolution of gas (H_2) takes place accompanied by the conversion of compound **3** to the more stable dichlorodihydridoosmium(IV) complex **2**.

Carbyne- and Vinylideneosmium Complexes

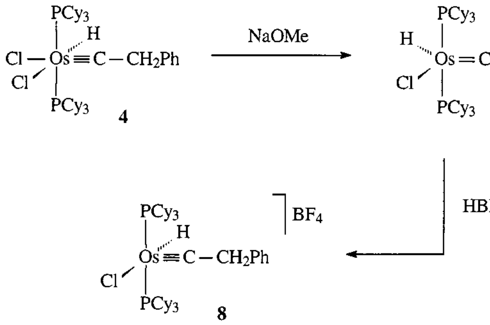
We recently reported that the ruthenium counterpart of compound **2** with the composition $[RuH_2Cl_2(PCy_3)_2]$, which was prepared by Chaudret et al. from $[RuH_2(H_2)_2(PCy_3)_2]$ and aqueous HCl in ether[11] and independently by us from $[RuHCl(H_2)(PCy_3)_2]$,[12] reacts with phenylacetylene to give the five-coordinate vinylidene complex $[RuCl_2(=C=CHPh)(PCy_3)_2]$.[12] In contrast, treatment of **2** with three equivalents of $HC\equiv CPh$ in hexane at 60 °C affords instead of $[OsCl_2(=C=CHPh)(PCy_3)_2]$ the six-coordinate carbynehydrido compound **4** in 63% yield of isolated product. The analogous reaction of **2** with $HC\equiv CSiMe_3$ leads to a mixture of two products **5** and **6**, of which the first is by far the most dominant species (Scheme 2). The ^{31}P-NMR spectrum of the freshly isolated yellow solid displays a rather strong singlet at $\delta = 11.2$ and a weaker resonance at $\delta = 10.8$, which we assign to compounds **5** and **6**, respectively. In the hydride region of the ^{1}H-NMR spectrum of the mixture of **5** and **6** two triplets appear, the chemical shifts and the P-H coupling constants of which are only slightly different. Compound **5** containing the CH_2SiMe_3-substituted carbyne is completely converted into **6** upon addition of two drops of H_2O to a solution in CD_2Cl_2. Therefore, we assume that the small quantities of the carbyne complex **6** formed in the reaction of **2** with $HC\equiv CSiMe_3$ in hexane originate from traces of water in the reaction system. Besides the hydride resonance in the ^{1}H-NMR spectrum, a characteristic spectroscopic feature for **5** and **6** is the signal of the carbyne carbon atom in the ^{13}C-NMR spectrum which appears at $\delta = 267.6$ (**5**) and 265.5 (**6**), respectively. The corresponding resonance for **4** is observed at $\delta = 265.8$.



Scheme 2

With regard to the mechanism of formation of **4** and **5**, we assume that the starting material **2**, containing a metal center with a 16-electron configuration, generates in the initial step of the reaction a 1:1 adduct with the alkyne. It is conceivable that this seven-coordinate species is in equilibrium with the (dihydrogen)osmium(II) compound $[OsCl_2(H_2)(HC\equiv CR)(PCy_3)_2]$, which could first rearrange to the isomeric vinylidene derivative $[OsCl_2(H_2)(=C=CHR)(PCy_3)_2]$ and finally by intramolecular hydrogen transfer to $[OsHCl_2(\equiv CCH_2R)(PCy_3)_2]$. A similar reaction scheme has been proposed by Esteruelas and Oro et al., who prepared analogous carbynehydridoosmium complexes with two triisopropylphosphane ligands from $[OsH_2Cl_2(PiPr_3)_2]$ and $HC{\equiv}CR$.[13] A different synthetic route leading to $[OsHCl_2({\equiv}CCH_2R)(PiPr_3)_2]$ was most recently reported by Caulton and co-workers, who used instead of 1-alkynes the corresponding alkenes $CH_2{=}CHR$ as starting materials.[14] There is ample precedence for this water-assisted conversion of **5** into **6**, as we[15] as well as others[13a,16] observed that upon treatment of various low-valent transition-metal compounds with silylated alkynes or diynes in the presence of traces of H_2O or HX, metal complexes with $C{-}H$ instead of $C{-}SiR_3$ bonds are formed.

The six-coordinate carbynehydrido complex **4** reacts with NaOMe in THF to give the five-coordinate vinylidenehydridoosmium(II) compound **7** in 87% isolated yield. The related bis(triisopropylphosphane) complex had been prepared on a similar route.[13b] The ^{1}H-NMR spectrum of **7** (which is a deep green, moderately air-sensitive solid) exhibits in the high-field region a triplet at $\delta = -16.38$ which is typical for species of this type.[12][13] The presence of the vinylidene ligand is indicated by the ^{13}C-NMR resonances at $\delta = 282.8$ and 107.3, which are assigned to the α- and β-carbon atoms of the $Os{=}C{=}CHR$ chain. Since the ^{31}P-NMR spectrum of **7** displays a singlet at $\delta = 26.6$, we assume, in agreement with theoretical studies by Eisenstein, Caulton et al.[17], that for the five-coordinate hydridovinylidene compound a distorted trigonal-bipyramidal geometry is most likely.

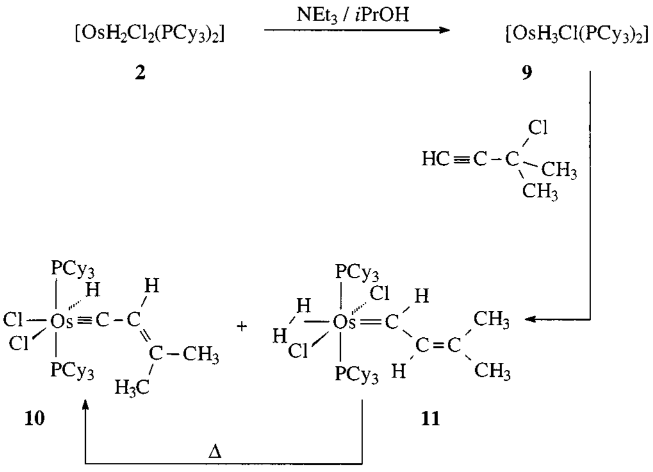


Scheme 3

The reactivity of compound **7** resembles that of the ruthenium counterpart $[RuHCl({=}C{=}CH_2)(PCy_3)_2]$.[18] If HBF_4 is used as the substrate, the attack of the proton does not occur at the metal but at the β-carbon atom of the $Os{=}C{=}CHPh$ unit and thus converts the vinylidene into a carbyne ligand (Scheme 3). In contrast to $[RuHCl({\equiv}CCH_3)(OEt_2)(PCy_3)_2]BF_4$, which is rather labile and decomposes in CH_2Cl_2 at room temperature within 20−30 min,[18] the osmium complex **8** is considerably more stable. In the solid state, it can be stored under argon at 25°C for days, and in solution (CD_2Cl_2) at −18°C it does not decompose within 24 h.

The elemental analysis as well as the ^{1}H-NMR spectrum confirm that in **8**, unlike in $[RuHCl({\equiv}CCH_3)(S)(PCy_3)_2]^+$ ($S = OEt_2$, OH_2)[18] and $[OsHCl({\equiv}CCH_2Ph)(OH_2)(PiPr_3)_2]^+$,[13b] the open coordination site is not occupied by a solvent molecule. By taking the molecular structure of compound **10** (see below) and of the cationic carbyne complex $[OsH\{{\equiv}CCH{=}C(CH_3)_2\}(\kappa^2\text{-}O_2CCH_3)(PiPr_3)_2]^+$ into consideration,[19] we assume that in **8** the coordination around the metal center corresponds to that of a square pyramid with the carbyne moiety in the apical position. In agreement with this proposal, the ^{1}H-NMR spectrum of **8** displays a resonance for the hydrido ligand at $\delta = -8.75$ and the ^{13}C-NMR spectrum exhibits a signal for the carbyne carbon atom at $\delta = 279.6$, the latter of which is split into a triplet due to P-C coupling. For the related bis(triisopropylphosphane) complex $[OsHCl({\equiv}CCH_2Ph)(PiPr_3)_2]^+$, which was most recently isolated by Spivak and Caulton with $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$ as the anion, the chemical shifts for the hydride and the carbyne carbon resonances are $\delta = -9.84$ and 282.6, respectively.[20]

The synthesis of neutral six-coordinate carbynehydridoosmium(II) compounds is also possible by using propargylic chlorides instead of 1-alkynes such as $HC{\equiv}CPh$ or $HC{\equiv}CSiMe_3$ as substrates. In this case, the starting material **2** was first converted into $[OsH_3Cl(PCy_3)_2]$ (**9**), which was obtained from **2** and 2-propanol in the presence of NEt_3 as a brown-yellow air-sensitive solid in almost quantitative yield (Scheme 4). The counterparts of **9** with $PiPr_3$ and $PtBu_2Me$ as phosphane ligands were recently prepared along a similar route.[17][21] Each of the three compounds of the general composition $[OsH_3Cl(PR_3)_2]$ is fluxional in solution. The ^{1}H-NMR spectrum of **9** (in CD_2Cl_2) displays a broad singlet at $\delta = -19.22$ at 25°C, which upon cooling the solution to 0°C is split into a triplet. Below −23°C, a new broadening of the hydride signal is observed which, however, is not resolved even at −60°C. Caulton and coworkers reported that the spectrum of $[OsH_3Cl(PiPr_3)_2]$ shows AB_2 patterns in the hydride region below −80°C.[21a]



Scheme 4

The reaction of **9** with 3-chloro-3-methylbut-1-yne in dichloromethane at −40°C gives a mixture of two products. The more labile component is the carbene(dihydrogen) derivative **11** (see Scheme 4), which could not be separated from the mixture and was therefore characterized by ^{1}H-and ^{13}C-NMR spectroscopy. Compound **11** reacts upon warming to 25 °C to afford the carbynehydrido complex **10**, which was isolated as a pale brownish solid in 53% yield. The most typical spectroscopic features in the ^{1}H-NMR spectrum for **10** are, besides the resonances for the hydrido ligand and the carbyne carbon atom, the signals for the $=$CH proton at $\delta = 4.39$ and for the inequivalent $=$CMe$_2$ methyl protons at $\delta = 2.01$ and 1.50. The resonances for the $=$CH and $=C$Me$_2$ carbon nuclei appear in the ^{13}C-NMR spectrum at $\delta = 135.9$ and 162.1.

The result of the X-ray crystal structure analysis of **10** is shown in Figure 1. The coordination geometry around the osmium center can be described as a distorted octahedron with the two phosphane ligands in the apical positions. The carbyne unit is disposed *trans* to one of the two chlorides. Both the C1−Os−Cl2 and P1−Os−P2 axes are slightly bent, the bond angle P1−Os−P2 [167.95(3)°] in **10** being somewhat larger than in the non-hydride-containing derivative $[OsCl_2(\equiv CCH{=}CPh_2)(\kappa^1\text{-}P\text{-}i\text{Pr}_2PCH_2CO_2Me)\{\kappa^2\text{-}P,O\text{-}i\text{Pr}_2PCH_2C(O)O\}]$ [165.0(1)°], which was recently prepared in our laboratory.[22] The Os−C1 distance in **10** [1.715(4) Å] is nearly identical to that in the above-mentioned carbyne complex [1.72(1) Å][22] as well as in the triisopropylphosphane derivative $[OsHCl_2(\equiv CCH_2Ph)(PiPr_3)_2]$ [1.711(4) Å].[13a] There is, however, a significant difference between the Os−C bond length in **10** and in $[OsCl(\equiv CC_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ [1.78(2) Å][23] which could be explained by the different oxidation state and coordination number of the two compounds. The C1−C2 and C2−C3 bond lengths in **10** are in the expected range and this is true also for the Os−P distances.

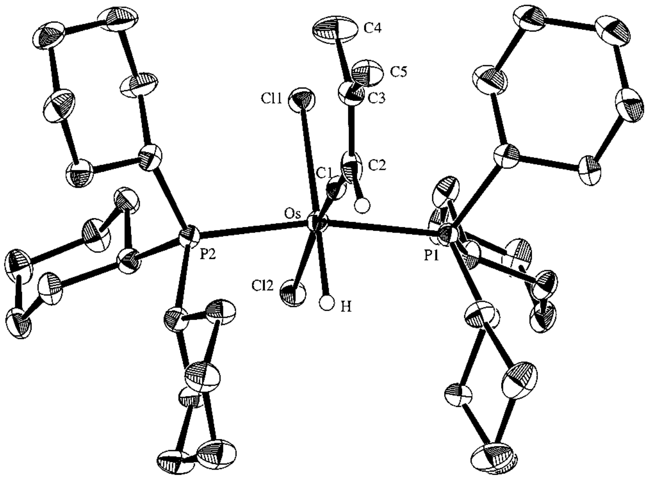


Figure 1. Molecular structure (ORTEP plot) of **10**;[a] the carbon atoms of the cyclohexyl rings are reduced in size for clarity; selected bond lengths [Å] and angles [°]: Os−C1 1.715(4), Os−P1 2.417(1), Os−P2 2.422(1), Os−Cl1 2.515(1), Os−Cl2 2.488(1), C1−C2 1.434(5), C2−C3 1.364(5), C3−C4 1.480(6), C3−C5 1.490(5); P1−Os−P2 167.95(3), P1−Os−C1 90.9(1), P1−Os−Cl1 95.42(3), P1−Os−Cl2 88.24(3), P2−Os−C1 91.0(1), P2−Os−Cl1 95.87(3), P2−Os−Cl2 87.76(3), C1−Os−Cl1 101.0(1), C1−Os−Cl2 170.0(1), Cl1−Os−Cl2 89.02(4), Os−C1−C2 174.4(3), C1−C2−C3 120.6(4), C2−C3−C4 124.1(4), C2−C3−C5 119.5(3), C4−C3−C5 116.3(3)

Catalytic Studies

It was recently found in our laboratory[18] that the cationic carbynehydridoruthenium complexes $[RuHCl(\equiv CCH_3)(S)(PCy_3)_2]BF_4$ (S = OEt$_2$, OH$_2$) are highly efficient catalysts for olefin metathesis. They are not only more active than the Grubbs compound $[RuCl_2({=}CHPh)(PCy_3)_2]$ in the ring-opening metathesis polymerization (ROMP) of cyclooctene but, even more remarkably, they also catalyze the cross-olefin metathesis of cyclopentene with methyl acrylate. By this novel route, a homologous series of multiply unsaturated esters is formed. For the neutral carbyneruthenium complexes $[RuCl(\equiv CR)(CO)(PPh_3)_2]$, prepared by Roper et al.,[24] a similar catalytic activity is unkown.[25]

According to these results, it is not surprising that under standard conditions[5e] neither **4** nor **10** is catalytically active in ROMP of cyclopentene. However, the cationic species **8** reacts rather smoothly in CH$_2$Cl$_2$ with this olefin. After 24 h at room temperature, a highly viscous material was generated from which, after it was dissolved in CHCl$_3$ and the solution poured into methanol, a white powder could be obtained in about 40% yield. The comparison of the ^{1}H- and ^{13}C-NMR data of the polymer with those reported in the literature[25] revealed that 77% of the double bonds are *trans*-configured. The turnover frequency was determined as 154.2 h^{-1} at 25 °C. To the best of our knowledge, compound **8** is the first well-defined osmium complex which catalyzes ROMP of cyclopentene.[25] We note that $OsCl_3 \cdot x\,H_2O$, an adduct of osmium chloride and cycloocta-1,5-diene,[26] and also OsO$_4$[25] were found to be catalytically active in olefin metathesis but as far as we know not in ROMP of cyclopentene.

Experimental Section

All operations were carried out under argon with Schlenk techniques. The alkynes and PCy$_3$ were commercial products from Strem and ABCR. − NMR: Bruker AC 200 and AMX 400 [vt = virtual triplet; $N = {}^1J(PC) + {}^3J(PC)$]. − Melting points determined by DTA.

1. Preparation of $[OsH_6(PCy_3)_2]$ (1): To a slurry of 0.5 g (20.6 mmol) of magnesium turnings, which were activated with 0.50 mL of 1,2-C$_2$H$_4$Cl$_2$, in 25 mL of THF was added stepwise 2.23 g (7.80 mmol) of PCy$_3$ and 557 mg (1.70 mmol) of $OsCl_3 \cdot 2\,H_2O$. The reaction mixture was heated under vigorous stirring under H$_2$ (1 bar) for 90 min at 65 °C and then for 19 h at 85 °C. After the mixture was cooled to room temperature, the solution was separated from the solid (mainly Mg) and the solvent was removed in vacuo. The residue was dissolved in 30 mL of CH$_2$Cl$_2$ and 10 mL of H$_2$O. The organic layer was separated, concentrated to dryness in vacuo, and the residue washed twice with 15-mL portions of 2-propanol and dried. The remaining white solid was identified as **1** by comparison of the ^{1}H- and ^{31}P-NMR data with those reported in the literature;[8] yield 742 mg (58%).

2. Preparation of $[OsH_2Cl_2(PCy_3)_2]$ (2): a) A suspension of 611 mg (1.87 mmol) of $OsCl_3 \cdot 2\,H_2O$ in 2 mL of 2-propanol was treated with a solution of 2.76 g (9.85 mmol) of PCy$_3$ in 20 mL of 2-propanol and then heated for 24 h under reflux. After the reaction mixture was cooled to room temperature, a red-brown solid precipitated. The solid was separated from the mother liquor, washed twice with 10-mL portions of methanol (0°C), twice with 10-mL portions of ether (0°C) and dried in vacuo; yield 1.21 g (79%). − **b)** A slow stream of dry HCl was passed through a suspension of 86 mg (0.11 mmol) of **1** in 8 mL of hexane for 30 s at room temperature. A dark brown solution was formed from which, after it had been stirred for 10 min, a red-brown solid precipitated. The mother liquor was separated and the residue was washed with 5 mL of hexane and dried; yield 90 mg (96%); m.p. 94°C. − ^{1}H NMR (400 MHz, C_6D_6): δ = 2.28−1.15 (m, 66 H, C_6H_{11}), −15.68 [t, *J*(PH) = 35.1 Hz, 2 H, OsH_2]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 39.9 [d, *J*(PC) = 30.5 Hz, *ipso*-C of C_6H_{11}], 30.0 (s, *m*-C of C_6H_{11}), 27.8 [d, *J*(PC) = 10.2 Hz, *o*-C of C_6H_{11}], 26.9 (s, *p*-C of C_6H_{11}). − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 33.6 (s). − $C_{36}H_{68}Cl_2OsP_2$ (824.0): calcd. C 52.48, H 8.32; found C 52.26, H 8.24.

3. Preparation of $[OsHCl_2(\equiv CCH_2Ph)(PCy_3)_2]$ (4): A suspension of 393 mg (0.48 mmol) of **2** in 18 mL of hexane was treated with 156 µL (1.42 mmol) of phenylacetylene and stirred for 24 h at 60°C. A pale brownish solid precipitated. After the reaction mixture was cooled to room temperature, the mother liquor was separated, the solid residue was washed twice with 5-mL portions of hexane and dried; yield 282 mg (63%); m.p. 129°C. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.45−7.25 (m, 5 H, C_6H_5), 2.61 (s, 2 H, CH_2Ph), 2.33−1.04 (m, 66 H, C_6H_{11}), −6.64 [t, *J*(PH) = 16.8 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 265.8 [t, *J*(PC) = 11.5 Hz, Os≡C], 129.5, 129.1, 128.8, 128.1 (all s, C_6H_5), 56.9 (s, CH_2Ph), 36.8 (br. s, *ipso*-C of C_6H_{11}), 29.9, 29.4 (both s, *m*-C of C_6H_{11}), 27.9 (br. s, *o*-C of C_6H_{11}), 27.0 (s, *p*-C of C_6H_{11}). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 8.8 [s, *J*(OsP) = 169.6 Hz]. − $C_{44}H_{74}Cl_2OsP_2$ (926.1): calcd. C 57.06, H 8.05; found C 56.58, H 7.97.

4. Preparation of $[OsHCl_2(\equiv CCH_2SiMe_3)(PCy_3)_2]$ (5): A suspension of 307 mg (0.37 mmol) of **2** in 15 mL of hexane was treated with 156 µL (1.10 mmol) of HC≡CSiMe$_3$ and stirred for 6 h at 60°C. A yellow solid precipitated which was isolated as described for **4**; yield 178 mg. The NMR spectra of the isolated product indicated that besides **5** also small amounts of **6** were already formed. Typical data for **5**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.06 (s, SiMe$_3$), −7.64 [t, *J*(PH) = 17.6 Hz, OsH]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 267.6 (br. s, Os≡C), 30.5 (s, CH_2). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 11.2 (s).

5. Preparation of $[OsHCl_2(\equiv CCH_3)(PCy_3)_2]$ (6): A suspension of 220 mg (0.27 mmol) of **2** in 15 mL of hexane was treated with 112 µL (0.79 mmol) of HC≡CSiMe$_3$ and a few drops of water and then stirred for 24 h at 60°C. A pale brownish solid precipitated, which was isolated as described for **4**; yield 136 mg (60%); m.p. 152°C. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.40−1.30 (m, 66 H, C_6H_{11}), 0.94 (s, 3 H, CH_3), −7.31 [t, *J*(PH) = 16.8 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 265.5 [t, *J*(PC) = 11.5 Hz, Os≡C], 38.6 (s, CH_3), 35.7 (br. s, *ipso*-C of C_6H_{11}), 29.9, 29.5 (both s, *m*-C of C_6H_{11}), 28.1, 27.9 (both vt, *N* = 10.2 Hz, *o*-C of C_6H_{11}), 27.1 (s, *p*-C of C_6H_{11}). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 10.8 [s, *J*(OsP) = 167.9 Hz]. − $C_{38}H_{70}Cl_2OsP_2$ (850.0): calcd. C 53.69, H 8.30; found C 53.62, H 8.38.

6. Preparation of $[OsHCl(=C=CHPh)(PCy_3)_2]$ (7): A suspension of 208 mg (0.23 mmol) of **4** in 35 mL of THF was treated with 14.6 mg (0.27 mmol) of NaOMe and stirred for 2 h at room temperature. After the solvent was removed, the residue was extracted with 20 mL of toluene. The extract was concentrated to dryness in vacuo, and the remaining green solid was washed with small quantities of toluene and pentane (both 0°C) and dried; yield 163 mg (87%); m.p. 131°C. − ^{1}H NMR (400 MHz, C_6D_6): δ = 7.56−6.78 (m, 5 H, C_6H_5), 2.66 (br. s, 1 H, =C*H*Ph), 2.21−1.18 (m, 66 H, C_6H_{11}), −16.38 [t, *J*(PH) = 13.0 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, C_6D_6): δ = 284.1 [t, *J*(PC) = 9.5 Hz, Os=C], 128.3, 128.1, 123.4, 122.8 (all s, C_6H_5), 108.6 (s, Os=C=*C*), 36.1 (vt, *N* = 22.9 Hz, *ipso*-C of C_6H_{11}), 30.9, 30.6 (both s, *m*-C of C_6H_{11}), 28.1, 27.9 (both vt, *N* = 10.2 Hz, *o*-C of C_6H_{11}), 26.9 (s, *p*-C of C_6H_{11}). − ^{31}P NMR (162.0 MHz, C_6D_6): δ = 26.6 [s, *J*(OsP) = 181.4 Hz]. − $C_{44}H_{73}ClOsP_2$ (889.7): calcd. C 59.40, H 8.27; found C 59.07, H 7.87.

7. Preparation of $[OsHCl(\equiv CCH_2Ph)(PCy_3)_2]BF_4$ (8): A solution of 244 mg (0.27 mmol) of **7** in 40 mL of toluene was treated dropwise with 2 mL of a 1.4 M solution (2.8 mmol) of HBF$_4$ in ether. A rapid change of color from deep green to brown-yellow took place. After the reaction mixture had been stirred for 10 min at room temperatuere, a pale brownish solid precipitated which was separated from the mother liquor, washed twice with 8-mL portions of toluene and dried; yield 112 mg (43%); m.p. 134°C (dec.). − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.36−7.05 (m, 5 H, C_6H_5), 3.01 (s, 2 H, CH_2), 2.39−1.17 (m, 66 H, C_6H_{11}), −8.75 (br. s, 1 H, OsH). − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 279.6 [t, *J*(PC) = 10.8 Hz, Os≡C], 130.1, 129.2, 129.0, (all s, C_6H_5), 57.1 (s, CH_2), 36.3 (vt, *N* = 25.4 Hz, *ipso*-C of C_6H_{11}), 30.6, 30.1 (both s, *m*-C of C_6H_{11}), 27.6, 27.4 (both vt, *N* = 10.2 Hz, *o*-C of C_6H_{11}), 26.3 (s, *p*-C of C_6H_{11}). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 46.3 (br. s). − $C_{44}H_{74}BClF_4OsP_2$ (977.5): calcd. C 54.07, H 7.63; found C 53.61, H 7.77.

8. Preparation of $[OsH_3Cl(PCy_3)_2]$ (9): A suspension of 89 mg (0.11 mmol) of **2** in 5 mL of 2-propanol was treated with 38 µL (0.27 mmol) of NEt$_3$ and stirred for 2 h at room temperature. A change of color from red-brown to brown-yellow occurred. The solvent was removed in vacuo and the residue was dissolved in 10 mL of benzene. The solution was filtered and the filtrate was concentrated to dryness in vacuo. The remaining brown-yellow solid was repeatedly washed with methanol and dried; yield 75 mg (86%); m.p. 40°C (dec.). − ^{1}H NMR (400 MHz, C_6D_6, 25°C): δ = 2.31−1.15 (m, 66 H, C_6H_{11}), −19.22 (br. s, 3 H, OsH_3). − ^{1}H NMR (200 MHz, CD_2Cl_2, 0°C): δ = 2.10−1.21 (m, 66 H, C_6H_{11}), −19.74 [t, *J*(PH) = 11.5 Hz, 3 H, OsH_3]. − ^{13}C NMR (100.6 MHz, C_6D_6, 25°C): δ = 37.4 (vt, *N* = 23.4 Hz, *ipso*-C of C_6H_{11}), 31.0 (s, *m*-C of C_6H_{11}), 28.0 (vt, *N* = 10.2 Hz, *o*-C of C_6H_{11}), 27.0 (s, *p*-C of C_6H_{11}). − ^{31}P NMR (162.0 MHz, C_6D_6, 25°C): δ = 41.8 (s). − ^{31}P NMR (81.0 MHz, CD_2Cl_2, 0°C): δ = 41.8 (s). − $C_{36}H_{69}ClOsP_2$ (789.5): calcd. C 54.77, H 8.81; found C 55.22, H 8.64.

9. Reaction of Compound 9 with 3-Chloro-3-methylbut-1-yne: A solution of 57 mg (0.07 mmol) of **9** in 0.5 mL of CD_2Cl_2 was treated at −40°C in an NMR tube with 8.5 µL (0.18 mmol) of HC≡C(CH$_3$)$_2$Cl. The NMR spectra of the solution indicated the formation of a mixture of **10** and **11** which could not be separated by fractional crystallization. Therefore, the more labile component **11** was characterized by NMR spectroscopy. Typical data for **11**: ^{1}H NMR (400 MHz, CD_2Cl_2, −70°C): δ = 16.88 [d, *J*(HH) = 12.7 Hz, 1 H, Os=CH], 7.03 [d, *J*(HH) = 12.7 Hz, 1 H, C*H*=CMe$_2$], 2.95−0.77 (m, 72 H, C_6H_{11} and CH_3], −7.52 [br. s, 2 H, Os(H$_2$)]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2, −70°C): δ = 254.9 (br. s, Os=C). − ^{31}P NMR (162.0 MHz, CD_2Cl_2, −70°C): δ = −1.1 (br. s). − ^{31}P NMR (81.0 MHz, CD_2Cl_2, −40°C): δ = 1.2 (s).

10. Preparation of $[OsHCl_2(\equiv CCH=CMe_2)(PCy_3)_2]$ (10): The solution, obtained from **9** and HC≡C(CH$_3$)$_2$Cl as described above, was stirred after warming for 1 h at room temperature. The solvent was removed, the remaining pale brownish solid was washed with

2 mL of hexane and dried; yield 34 mg (53%); m.p. 122°C. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.39 (s, 1 H, C*H*=CMe$_2$), 2.36−1.15 (m, 66 H, C_6H_{11}), 2.01 (s, 3 H, $CH_{3\ trans}$ to =CH), 1.50 (s, 3 H, $CH_{3\ cis}$ to =CH), −7.17 [t, *J*(PH) = 17.6 Hz, 1 H, OsH]. − ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 256.0 [t, *J*(PC) = 11.4 Hz, Os≡C], 162.1 (s, =*C*Me$_2$), 135.9 (s, =CH), 36.5 (br. vt, *N* = 11.4 Hz, *ipso*-C of C_6H_{11}), 29.6, 29.3 (both s, *m*-C of C_6H_{11}), 28.2, 28.0 (both vt, *N* = 5.1 Hz, *o*-C of C_6H_{11}), 27.1 (s, *p*-C of C_6H_{11}), 26.4, 23.6 (both s, CH_3). − ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 8.2 [s, *J*(OsP) = 169.6 Hz]. − $C_{41}H_{74}Cl_2OsP_2$ (890.1): calcd. C 55.33, H 8.38; found C 55.16, H 8.16.

11. ROMP of Cyclopentene with Compound 8 as Catalyst: A solution of 30 mg (0.03 mmol) of **8** in 1 mL of CH_2Cl_2 was treated with 10 mL (0.11 mol) of cyclopentene and stirred for 24 h at room temperature. The highly viscous reaction mixture was dissolved in 40 mL of $CHCl_3$ and the solution was poured into 100 mL of methanol. The white material was filtered and, after it was dried in vacuo, characterized by ^{1}H- and ^{13}C-NMR spectroscopy. The comparison of the NMR data with those reported in the literature[25] revealed a *trans*/*cis* ratio of the configuration at the double bonds of 77:23; yield 4.19 g.

12. Determination of the X-ray Crystal Structure of 10:[27] Single crystals of **10** were grown from CH_2Cl_2. Crystal data (from 5000 reflections, $4.26° < \Theta < 54.06°$): monoclinic; space group *I*2/*a* (No. 15); *a* = 25.655(5), *b* = 9.527(2), *c* = 39.988(8) Å, β = 107.26(3)°; *V* = 9333(3) Å^3; *Z* = 8; $d_{calcd.}$ = 1.448 gcm^{-3}; μ(Mo-K_α) = 3.115 mm^{-1}; crystal size 0.13 × 0.12 × 0.10 mm; STOE (IPDS), Mo-K_α radiation (0.71073 Å), graphite monochromator; *T* = 173(2) K; ψ-scans, max. 2Θ = 54.06°; 82743 reflections measured, 10147 independent ($R_{int.}$ = 0.0303), 7230 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86).[28] Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93).[29] The positions of all hydrogen atoms, except of metal-bound H, were calculated according to ideal geometry and refined by using the riding method. The position of H could be located in a final difference Fourier synthesis and was refined with fixed U_{eq}. The asymmetric unit includes one and a half molecules of CH_2Cl_2 which were refined anisotropically. Two alternative positions for CH_2Cl_2 consisting of C91, Cl5, and Cl6 were found and refined with the occupancy factors 0.54:0.46 with restraints. Conventional *R* = 0.0313 [for 7230 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.0682 for all 10137 located reflections; reflection/parameter ratio 21.12; residual electron density +2.401/−1.213 eÅ^{-3}.

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[27] 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-114480. 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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