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Reactions of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ with unsaturated organic molecules

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Abstract

The 1-butene ligand of the dihydrido complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**) can be readily displaced by cyclopentadiene to yield $OsH_2(\eta^2\text{-}C_5H_6)(CO)(P^iPr_3)_2$ (**2**). Complex **1** selectively hydrogenates the carbon–carbon triple bond of 2-methyl-1-hexen-3-yne to give the methylhexadiene derivative $Os\{\eta^4\text{-}CH_2{=}C(CH_3)CH{=}CHCH_2CH_3\}(CO)(P^iPr_3)_2$ (**3**). Treatment of **1** with phenylacetylene in a 1:10 molar ratio leads to the diphenylbutenynyl complex $Os(C_2Ph)\{\eta^3\text{-}C(C{\equiv}CPh){=}CHPh\}(CO)(P^iPr_3)_2$ (**5a**) containing the carbonyl ligand *trans* disposed to the carbon–carbon triple bond of the butenynyl unit. In benzene-d_6 at 60°C, **5a** affords a new isomer **5b**, where the carbonyl group is disposed *trans* to the OsC= carbon atom of the diphenylbutenynyl ligand. Isomer **5a** reacts with $HBF_4 \cdot H_2O$ to give $Os(CH_2Ph)(FBF_3)(CO)_2(P^iPr_3)_2$ (**6**), which by reaction with NaCl yields $Os(CH_2Ph)Cl(CO)_2(P^iPr_3)_2$ (**7**). The reactions of **1** with dicyclohexyl-carbodiimide, phenylisocyanate, phenylisothiocyanate and methylisothiocyanate lead to the corresponding insertion products $OsH\{\kappa^2\text{-}N(Cy)CHN(Cy)\}(CO)(P^iPr_3)_2$ (**8**), $OsH\{\kappa^2\text{-}N(Ph)CHO\}(CO)(P^iPr_3)_2$ (**9**), $OsH\{\kappa^2\text{-}N(Ph)CHS\}(CO)(P^iPr_3)_2$ (**10**) and $OsH\{\kappa^2\text{-}N(CH_3)CHS\}(CO)(P^iPr_3)_2$ (**11**). Complex **1** also reacts with benzophenone imine, in this case the reaction product is $\overline{OsH\{NH{=}C(Ph)}C_6H_4\}(Co)(PiPr_3)_2$ (**12**). The protonation of **12** with $HBF_4 \cdot OEt_2$ gives the five-coordinate complex $[OsH(CO)(NH{=}CPh_2)(P^iPr_3)_2]BF_4$ (**13**), which by reaction with carbon monoxide and trimethylphosphite affords $[OsH(CO)_2(NH{=}CPh_2)(P^iPr_3)_2]BF_4$ (**14**), and $[OsH(CO)(NH{=}CPh_2)(P(OMe)_3)(P^iPr_3)_2]BF_4$ (**15**), respectively. © 1997 Elsevier Science S.A.

1. Introduction

The chemistry of hydrido complexes of transition metals has received increasing attention in recent years [1–6], owing to the possibilities offered by these compounds for the design of homogeneous catalysts [7], and the preparation of other types of complexes [8].

As a part of our study of the chemical properties of the five-coordinate complex $OsHCl(CO)(P^iPr_3)_2$ [9], we have previously reported the synthesis of the dihydrido-butene derivative $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**) and studied its reactivity towards some potentially useful molecules in catalysis (Scheme 1) [10–13]. Thus, it has been observed that complex **1** reacts with $H\text{–}ER_3$ to give the corresponding $OsH_3(ER_3)(CO)(P^iPr_3)_2$ (E = Si, Ge, Sn), which can be formulated as derivatives of osmium (IV) with a weak H–E agostic interaction [11]. Complex **1** also reacts with CS_2 to give the dithioformato compound $OsH(\kappa^2\text{-}S_2CH)(CO)(P^iPr_3)_2$. The protonation of this complex with $HBF_4 \cdot OEt_2$ leads to two different derivatives depending upon the nature of the solvent used. The dihydrogen compound $[Os(\kappa^2\text{-}S_2CH)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2]BF_4$ is formed in dichloromethane-d_2, while the methanedithiolate complex $[OsH(\kappa^2\text{-}S_2CH_2)(CO)(P^iPr_3)_2]BF_4$ is obtained in diethyl ether [10]. Similarly to CS_2, CO_2 undergoes an insertion reaction into one of the hydrido ligands of **1** to give the formato complex $OsH(\kappa^2\text{-}O_2CH)(CO)(P^iPr_3)_2$ [12,13], which was parallel-prepared by Werner, as a result of the treatment of $OsHCl(CO)(P^iPr_3)_2$ with KOH in methanol under CO_2-atmosphere [14,15].

Continuing our study on the reactivity of **1**, we have now investigated the reactions of this compound with cyclopentadiene, 2-methyl-1-hexen-3-yne, phenylacetylene, heteroallenes and benzophenone imine. in this paper, we report the results from this study.

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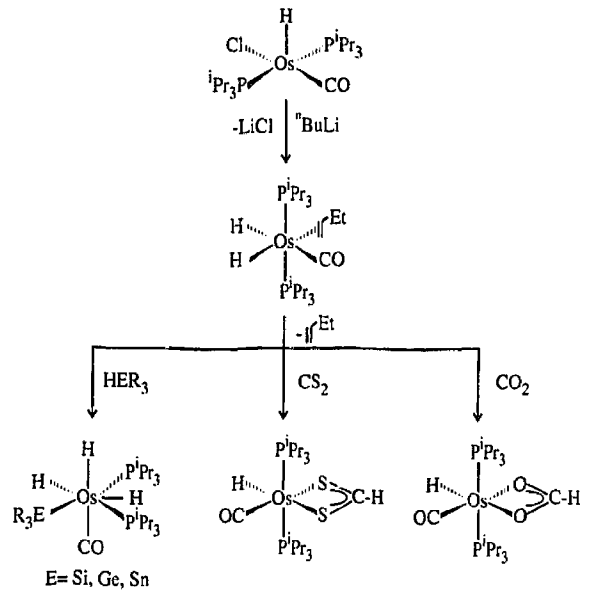
2. Results and discussion

2.1. Reactions of $OsH_2(\eta^2\text{-}CH_2=CHEt)(CO)(P^iPr_3)_2$ with cyclopentadiene and 2-methyl-1-hexen-3-yne

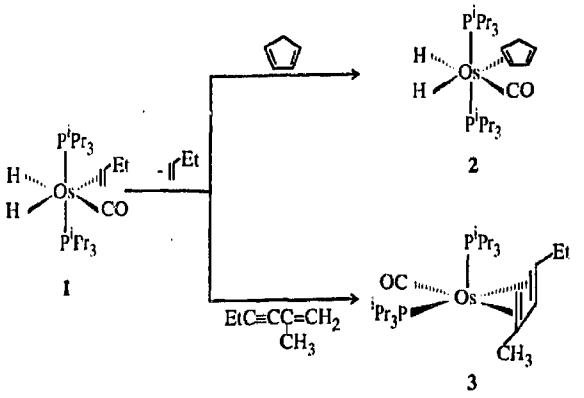
The 1-butene ligand of **1** can be readily displaced by cyclopentadiene to yield $OsH_2(\eta^2\text{-}C_5H_6)(CO)(P^iPr_3)_2$ (**2**, in Scheme 2). The reaction was carried out in hexane as solvent, at room temperature, and using an excess of cyclopentadiene. Complex **2** was isolated as a white solid in 55% yield, and characterized by elemental analysis, IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

The IR spectrum in Nujol shows a strong absorption at 1990 cm^{-1}, attributable to ν(Os–H), in agreement with a *cis* arrangement for these ligands. In addition, it should be mentioned the ν(CO) band, which is observed at 1875 cm^{-1}. The ^1H NMR spectrum in benzene-d_6 agrees well with the IR spectrum. Thus, it contains in the high field region two double triplets at −9.78 and −11.99 ppm for the hydrido ligands. The values of the *H–H* (4.0 Hz) and *P–H* (30.0 and 21.9 Hz, respectively) coupling constants strongly support the structure proposed for **2** in Scheme 2. The six protons of the cyclopentadiene diolefin give rise to six multiplets between 3.36 and 2.42 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows at 30.7 ppm a singlet that is split under off-resonance conditions into a double doublet, as a result of the coupling with two chemically inequivalent hydrido ligands.

Although the two hydrido ligands and the coordinated C=C bond of cyclopentadiene are in a meridional arrangement around the metal center, which should lead to the rapid hydrogenation of the olefin [7], complex **2** does not evolve by hydrogenation of one of the two



Scheme 1.



Scheme 2.

carbon–carbon double bonds of the diene, even at 60°C. However, complex **1** in pentane at room temperature is capable of selectively hydrogenating the carbon–carbon triple bond of 2-methyl-1-hexen-3-yne to afford the methylhexadiene complex $Os\{\eta^4\text{-}CH_2=C(CH_3)CH=CHCH_2CH_3\}(CO)(P^iPr_3)_2$ (**3**, in Scheme 2), which was isolated as colorless crystals in 72%.

The structure of **3** is proposed on the basis of its ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra. Fig. 1 shows the ^1H COSY NMR spectrum. The olefinic protons of the hexadiene display four resonances at 4.73, 1.88, 1.66 and 0.77 (partially hidden under the CH_2 resonance of the ethyl group) ppm. The resonance at lower field was assigned to the internal proton H_c, while the resonance at higher field was assigned to H_a, and the resonances at 1.88 and 1.66 to H_d and H_b, respectively. The chemical shifts of these protons agree well with those previously reported for the complexes $Os(\eta^4\text{-}C_4H_6)(CO)_3$ [16] and $Os(\eta^4\text{-}C_4H_5R)(CO)(P^iPr_3)_2$ (R=H; Ph) [17]. In addition, it should be mentioned the values of the $J(H_cH_d)$ (7.3 Hz) and $J(H_bH_a)$ (2.7 Hz), obtained from the $^1H\{^{31}P\}$ NMR spectrum. These values are similar to those reported for the phenylbutadiene complex $Os(\eta^4\text{-}C_4H_5R)(CO)(P^iPr_3)_2$, where a significant contribution of the resonance form $\sigma^2\text{–}\pi$ to the Os-butadiene bond has been proposed, on the basis of an X-ray diffraction study [17]. From this X-ray diffraction study an arrangement of ligand around the osmium atom, similar to that shown for **3** in Scheme 2, was also found. This is in agreement with the coupling between the olefinic protons and the phosphorous nuclei. Thus, the values of $J(H\text{–}P)$ are 2.2 and 3.9 Hz (H_c), 3.6 and 4.5 Hz (H_d), 2.2 and 2.7 Hz (H_b), and 1 Hz for both $H_a\text{–}P$ coupling constants. In the $^{13}C\{^1H\}$ NMR spectrum the resonances of the sp^2-carbon atoms disposed *trans* to the triisopropylphosphine ligand appear at 74.4 (=CH) and 27.8 (=CHEt) ppm. The first resonance as a doublet with a $C\text{–}P$ coupling constant of 5 Hz, and the second resonance as a double doublet with $C\text{–}P$ cou-

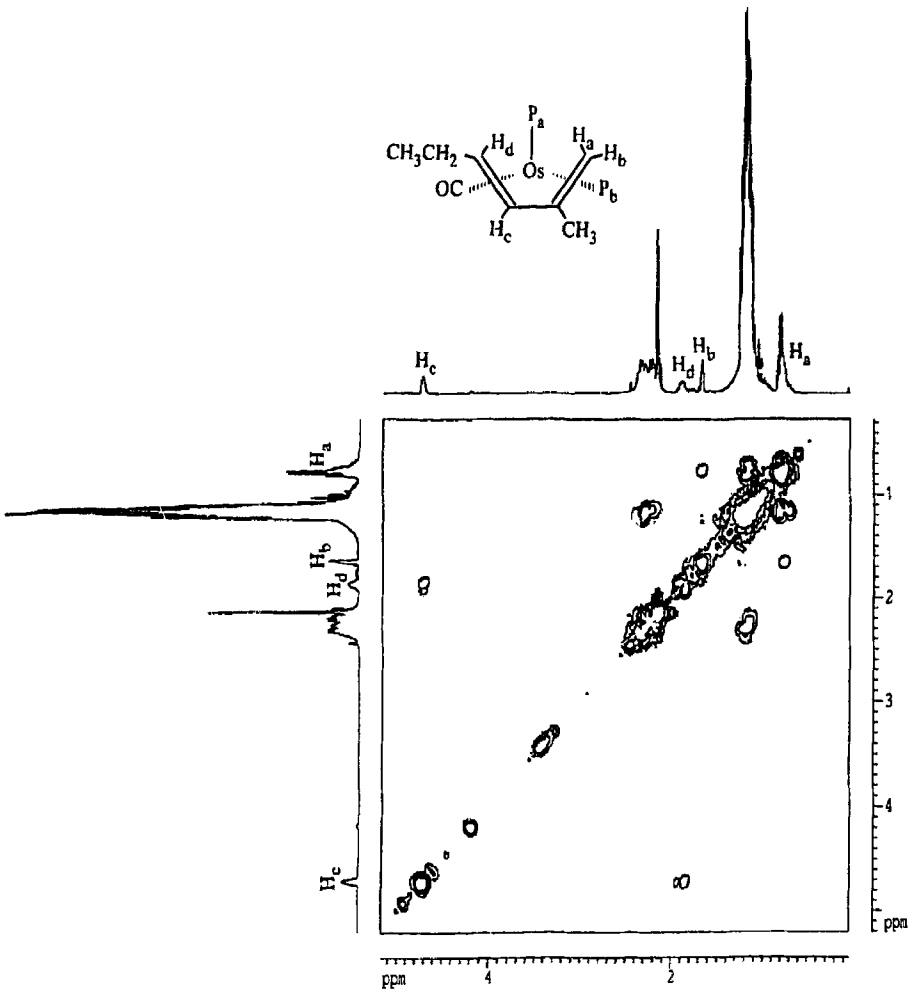
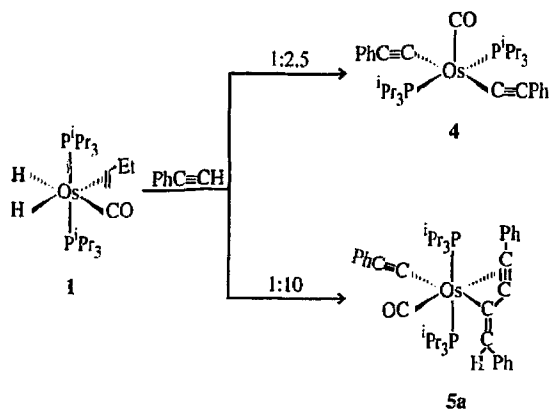


Fig. 1. ^{1}H COSY NMR of the complex Os{η^3-CH_2=C(CH_3)CH=$CHCH_2CH_3$}(CO)(P^iPr_3)$_2$ (3).

pling constants of 9 and 5 Hz. The resonances of the sp^2-carbon atoms disposed *trans* to the carbonyl group give rise to a singlet at 94.2 (=C(CH_3)) ppm and a doublet with a *C–P* coupling constants of 6 Hz, at 28.2 (=CH_2) ppm. The resonance of the carbonyl ligand is observed at 192.1, as a double doublet with *C–P* coupling constants of 10 and 2 Hz. The ^{31}P{^{1}H} NMR spectrum of **3** contains two doublets at 18.6 and 2.3 ppm with a *P–P* coupling constants of 5 Hz.



Scheme 3.

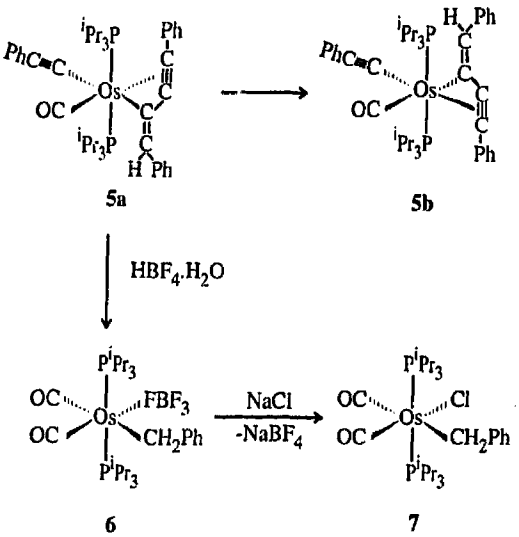
2.2. Reactions of $OsH_2(\eta^2$-CH_2=CHEt)(CO)(P^iPr_3)$_2$ with phenylacetylene

Treatment of **1** with phenylacetylene in a 1:2.5 molar ratio in pentane leads to the well-known bis-alkynyl complex Os(C_2Ph)$_2$(CO)(P^iPr_3)$_2$ (**4**) [18–21] in nearly quantitative yield. The reaction most probably involves the dissociation of the 1-butene ligand from **1** and the H–C(sp) activation of the alkyne to afford the alkynyl-hydrido-dihydrogen intermediate OsH(C_2Ph)(η^2-H_2)(CO)(P^iPr_3)$_2$, which subsequently reacts with a second molecule of alkyne to give **4** [18–21]. Under the same conditions, treatment of **1** with phenylacetylene in a 1:10 molar ratio affords the diphenylbutenynyl complex Os(C_2Ph){η^3-C(C≡CPh)=CHPh}(CO)(P^iPr_3)$_2$ (**5a**, in Scheme 3), which was isolated as a yellow solid in 65% yield. According to the observations of other

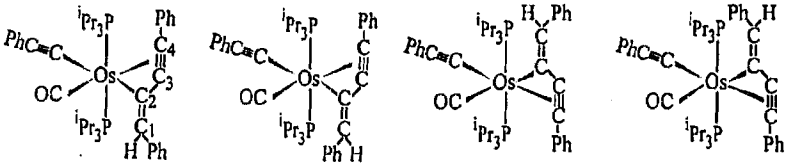
groups [22–33], the formation of **5a** could proceed via a bis-alkynyl-vinylidene intermediate, which evolves by migratory insertion of the vinylidene into a σ-osmium–alkynyl bond.

The IR spectrum of **5a** in Nujol shows the $\nu(C{\equiv}C)$ band of the alkynyl ligand at 2089 cm^{-1} and the $\nu(CO)$ band at 1905 cm^{-1}. The presence of an η^3-butenynyl ligand in **5a** is unambiguously demonstrated by the ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectrum in benzene-d_6 contains a singlet at 8.13 ppm, which was assigned to the vinyl hydrogen of the PhC_3CHPh ligand. From the analysis of the $^{13}C\{^1H\}$ and ^{13}C-DEPT, resonances at 141.2, 110.3 and 60.3 ppm were assigned to the OsC=, –C≡ and ≡C(Ph) carbon atoms of the butenynyl group, respectively. The resonance at lower field appears as a triplet with a *C–P* coupling constant of 5 Hz, in agreement with the mutually *cis*-disposition of the OsC= carbon atom and the two equivalent phosphine ligands. The resonance of the C_α carbon atom of the alkynynyl group appears at 93.8 ppm as a triplet with a *C–P* coupling constant of 12 Hz, while the C_β carbon atom display a singlet at 120.2 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −0.6 ppm.

In benzene-d_6 at 60°C, complex **5a** isomerizes into a new diphenylbutenynyl derivative (**5b**, Scheme 4), and both decompose at this temperature by loss of *cis*-PhC≡CCH=CHPh. For **5a** and **5b**, four isomeric structures (I–IV) may be drawn out:



Scheme 4.



Structure I differs from structure II only in the stereochemistry of the butenynyl ligand (Z vs. E). Structures, III and IV contain (Z)- and (E)-butenynyl ligands, respectively, which, however, are anchored to the $Os(C_2Ph)(CO)(P^iPr_3)_2$ moiety in a different fashion (C_4 is *trans* to the alkynyl ligand, whereas it is *trans* to the carbonyl group in structures I and II). The exclusive formation of *cis*-PhC≡CCH=CHPh as a result of the decomposition of the butenynyl complexes suggests that the butenynyl ligand of both isomers has a Z-stereochemistry. Furthermore, as a consequence of the high π-acceptor power of the carbonyl group, one should expect that structure III, with the carbonyl group *trans* to C_2, is thermodynamically more favored than structure I, which shows the carbonyl group *trans* to C_4. So we assume that the butenynyl isomer **5a** (product of kinetic control) has the structure I, while the isomer **5b** (product of thermodynamic control) has the structure III. This seems to be in agreement with the $^{13}C\{^1H\}$ NMR spectra. The spectrum of **5b**, which shows the resonance due to C_4 at 61.5 ppm, shifted 1.2 ppm toward lower field when compared with that of **5a**. Thus, the increase of the donor power of the ligand disposed *trans* to C_4 produces a light decrease of the acetylenic character of this atom. The resonances corresponding to C_2 and C_3 are observed at 142.7 and 104.4 ppm. As for **5a**, the resonance at lower field appears as a triplet, in this case, with a *C–P* coupling constant of 4 Hz. The $^{13}C\{^1H\}$ NMR spectrum also shows a triplet with a *C–P* coupling constant of 12 Hz at 94.1 ppm, corresponding to the C_α carbon atom of the alkynyl ligand and a singlet at 120.3 ppm due to the C_β carbon atom of the same ligand. In addition, it should be noted that, although lightly, the resonance corresponding to the C_α carbon atom of the alkynyl ligand of **5b** slides toward lower field when compared with that of **5a**, which again agrees well with our structural proposal. The $^{31}P\{^1H\}$ NMR spectrum of **5b** contains a singlet at −0.3 ppm. The presence of a singlet in the $^{31}P\{^1H\}$ NMR spectra of both isomers suggests that the butenynyl ligands of **5a** and **5b** lie in the plane, which is perpendicular to the P–Os–P plane.

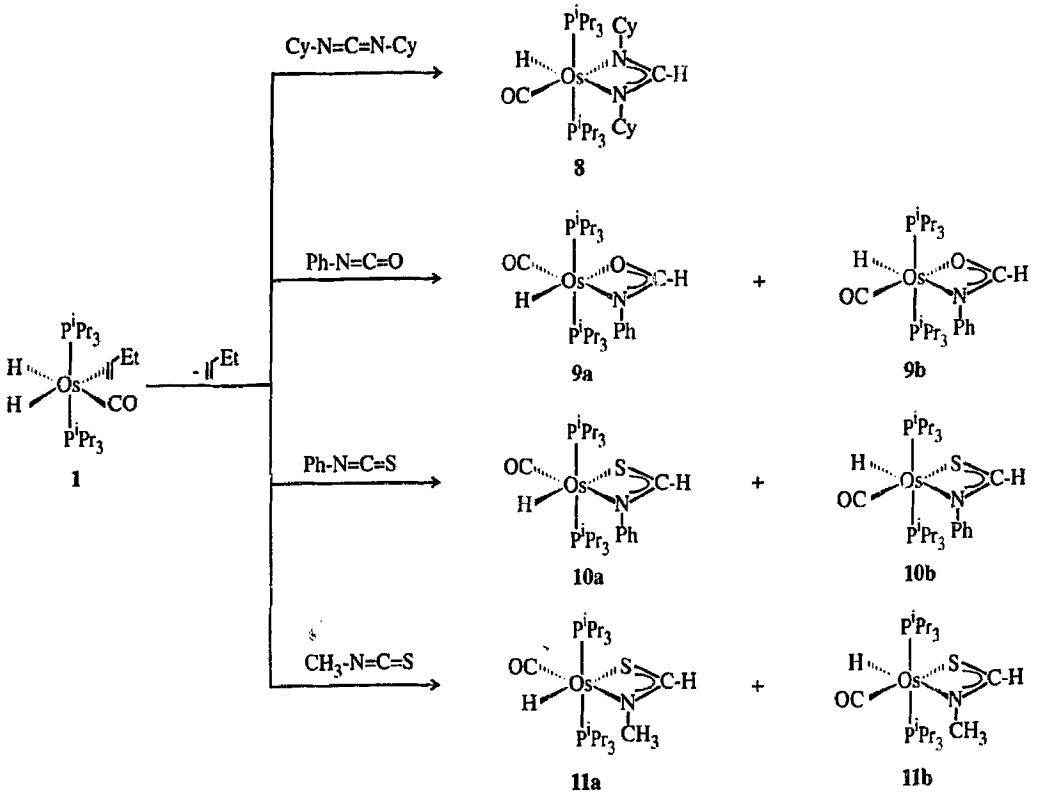
(Z)-1,4-diphenylbut-1-en-3-yne is also formed by treatment of **5a** with 1 equivalent of $HBF_4 \cdot H_2O$ in acetone at room temperature. Under these conditions the metallic fragment evolves into the benzyl complex

$Os(CH_2Ph)(FBF_3)(CO)_2(P^iPr_3)_2$ (**6**, in Scheme 4), which was isolated as a yellow solid in 36% yield. There are precedents for this metal-promoted hydration-desproportionation reaction. Thus, we have recently observed that in 2-propanol as solvent the C-C triple bond of one of the two alkynyl ligands of 4 can be selectively broken by reaction with water, to afford $Os(C_2Ph)(CH_2Ph)(CO)_2(P^iPr_3)_2$ [34]. In the same sense, Werner has reported that the reaction of $[OsI(\eta^6\text{-}C_6H_6)(=C=CHR)(PMetBu_2)]PF_6$ (R=H, Me) with water gives the carbonyl-osmium compound $[OsI(\eta^6\text{-}C_6H_6)(CO)(PMe^tBu_2)]PF_6$ [35]. The reaction is quite general for cationic vinylidene complexes, which afford alkynyl-carbonyl derivatives in the presence of water [36–39] and for octahedral complexes of ruthenium(II) and osmium(II) with one labile halide ligand such as a *cis*-$RuCl_2(bpy)_2$ (bpy = 2,2′-bipyridine), *cis*-$[RuCl(trpy)(bpy)]PF_6$ (trpy = 2,2′,2″-terpyridine), and *cis*-$OsCl_2(phen)\{1,2\text{-bis(diphenyl-phosphino)benzene}\}$ (phen = 1,10-phenantroline), which react with terminal alkynes and water to give the corresponding monocarbonyl derivatives and alkane [40,41].

In the solid state, the presence of a coordinated $[FBF_3]^-$ anion in **6** was inferred from its IR spectrum in Nujol, which contains three strong bands at 1133, 1030 and 950 cm^{-1}, a characteristic pattern for a coordinated $[FBF_3]^-$ anion with C_{3v} symmetry [42]. The IR spectrum also shows two ν(CO) bands at 2015 and 1937 cm^{-1}, in agreement with the *cis*-dicarbonyl formulation. The $^{13}C\{^1H\}$ NMR spectrum in chloroform-*d* also supports this proposal showing two triplets at 181.3 ppm ($J(CP) = 7$ Hz), and at 179.8 ppm ($J(CP) = 8$ Hz) attributable to the carbonyl ligands. The spectrum also contains the expected resonances for the benzyl ligand. The resonance due to the $-CH_2-$ carbon atom appears at 17.7 ppm, as a triplet with a *C–P* coupling constant of 6 Hz. In the ^1H NMR spectrum the $-CH_2-$ protons of this ligand display at 2.88 ppm a triplet with an *H–P* coupling constant of 7.5 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 7.7 ppm.

The absence of *C–F* coupling suggest that in solution **6** dissociates the $[BF_4]^-$ anion, which can be easily displaced by chloride. Thus, the treatment of **6** with NaCl in a 1:1 molar ratio in methanol leads to a white solid in 56% yield after 90 min, which was characterized as the chloro-benzyl complex $Os(CH_2Ph)Cl(CO)_2(P^iPr_3)_2$ (**7**, in Scheme 4).

The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum in Nujol, which shows two strong ν(CO) bands at 1989 and 1914 cm^{-1}. In agreement with the IR spectrum, the $^{13}C\{^1H\}$ NMR contains two triplets, at 181.8 and 180.8 ppm, with *C–P* coupling constants of 7 and 8 Hz, respectively, for the carbonyl ligands. The resonance of the $-CH_2-$ carbon



Scheme 5.

atom of the benzyl group is observed at 14.5 ppm, also as a triplet with a *C–P* coupling constant of 6 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −1.2 ppm.

2.3. Reactions of $OsH_2(\eta^2\text{-}CH_2=CHEt)(CO)(P^iPr_3)_2$ with heteroallenes

The 1-butene ligand of **1** can also be displaced by heteroallenes. These unsaturated molecules behave as electrophiles. Their δ^+ charged central carbon atom can be attacked not only by conventional nucleophiles (e.g. OR^-, SR^-, NHR^-, etc.) but also by metallic bases to form $M(\eta^2\text{-}C_{heteroallene})$ [43]. The stability of these intermediates is mainly determined by the energetics of subsequent reactions. For example, when the metal center binds a hydrido ligand, the transfer of the hydrido ligand from the metal to the central carbon atom of the heteroallene is generally observed [44]. In agreement with this, the reactions of **1** with dicyclohexylcarbodiimide, phenylisocyanate, phenylisothiocyanate and methylisothiocyanate lead to the corresponding insertion products (Scheme 5).

The formamidinato complex $OsH\{\kappa^2\text{-}N(Cy)CHN(Cy)\}(CO)(P^iPr_3)_2$ (**8**) was isolated as a white solid in 77% yield. In the ^1H NMR spectrum in benzene-d_6, the most noticeable resonances are a triplet at −16.38 ppm with an *H–P* coupling constant of 20.5 Hz, corresponding to the hydrido ligand, and in the low field region an unresolved triplet ($J(HP) < 1$ Hz) at 8.89 due to the –CH- proton of the formamidinato ligand. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 25.6 ppm, which under off-resonance condition is split into a doublet as a result of the *P–H* coupling with a hydrido ligand.

We note that related *p*-tolyl-formamidinato complexes of ruthenium (II) and osmium (II) have been previously prepared by fragmentation of at least two *p*-tolyl-isocyanate moieties in the presence of the hydrido derivatives $RuH_2(PPh_3)_4$ and $OsH_4(PPh_3)_3$ [45–48].

The reaction of **1** with phenylisocyanate produces the formamido complex $OsH\{\kappa^2\text{-}N(Ph)CHO\}(CO)(P^iPr_3)_2$ (**9**), which was isolated as a white solid in 85% yield. The IR spectrum of the solid in Nujol shows the bands corresponding to the ν(OsH) and ν(CO) vibrations at 2140 and 1910 cm^{-1}, respectively. Furthermore, the spectrum contains two bands at 1555 and 1270 cm^{-1} attributable to the formamidene ligand in agreement with a κ^2-coordination bonding mode [45–48]. In solution, at room temperature, complex **9** exists as a 1:2 mixture of the isomer **9a** and **9b** (Scheme 5). In the ^1H NMR spectrum, the characteristic resonances of isomer **9a**, with the oxygen atom of the chelate ligand *trans* disposed to the hydrido, are a triplet at −21.54 ppm with an *H–P* coupling constant of 16.1 Hz for the hydrido ligand, and an unresolved triplet ($J(HP) < 1$ Hz) at 9.32 for the –CH- proton. The hydrido resonance of isomer **9b**, with the hydrido ligand *trans* disposed to the nitrogen atom, appears at a similar field to that of the hydrido of **8** (−15.19 ppm), also as a triplet, but with an *H–P* coupling constant of 18.8 Hz. The resonance of the –CH- proton is observed at 9.04 ppm, as an unresolved triplet ($J(HP) < 1$ Hz). In the $^{31}P\{^1H\}$ NMR spectrum both isomers display singlets at 30.6 (**9a**) and 34.7 (**9b**) ppm. Under off resonance conditions, they are split into doublets.

From the reaction of **1** with phenylisothiocyanate and methylisothiocyanate the thioformamidinato complexes $OsH\{\kappa^2\text{-}N(Ph)CHS\}(CO)(P^iPr_3)_2$ (**10**) and $OsH\{\kappa^2\text{-}N(CH_3)CHS\}(CO)(P^iPr_3)_2$ (**11**) were isolated as yellow solid in 60% and 69% yield, respectively.

The IR spectrum of **10** in Nujol shows two bands at 2120 and 1840 cm^{-1} corresponding to the ν(OsH) and ν(CO) vibrations, respectively, along with three bands due to chelate ligand at 1550, 1255 and 880 cm^{-1}, which agree well with those previously reported for related ruthenium, osmium and iridium compounds, where a κ^2-coordination bonding mode for the thioformamido group has been also proposed [49]. In solution, at room temperature, complex **10** also exists as a 4:1 mixture of the isomers **10a** and **10b** (Scheme 5). In the ^1H NMR spectrum of the mixture the characteristic resonances of the isomer **10a** are a triplet at −14.31 ppm with an *H–P* coupling constant of 18.9 Hz for the hydrido ligand, and an unresolved triplet ($J(PH) < 1$ Hz) at 10.62 ppm due to the –CH- proton. In the same spectrum, the isomer **10b** gives a triplet, with an *H–P* coupling constant of 23.4 Hz, at −15.20 ppm, corresponding to the hydrido ligand; and an unresolved triplet ($J(HP) < 1$ Hz) due to the –CH- proton at 10.35 ppm. The chemical shift of the hydrido ligand of **10a** agrees well with that of the hydrido of the dithioformato complex $OsH(\kappa^2\text{-}S_2CH)(CO)(P^iPr_3)_2$ [10], while the chemical shift of the hydrido ligand of **10b** agrees well with those of the hydrido ligands of **8** and **9b**. In the $^{31}P\{^1H\}$ NMR spectrum of the mixture both isomers display singlets at 21.6 (**10a**) and 27.0 (**10b**). Under off-resonance conditions, they are split into doublets.

In solution at room temperature, complex **11** also exists as a mixture of the **11a** and **11b** isomers. In this case, the **11a**:**11b** molar ratio is 1:2. In the ^1H NMR spectrum of the mixture, characteristic resonances of **11a** are a double triplet with *H–H* and *H–P* coupling constants of 1.8 and 20.7 Hz, respectively, at −14.82 ppm for the hydrido ligand; and an unresolved triplet for the –CH- proton at 9.37 ppm. In the same spectrum, the related resonances of **11b** appear at −15.10 ppm (t, $J(HP) = 18.0$ Hz), and 9.37 (br t, $J(HP) < 1$ Hz). These chemical shifts are in agreement with those above mentioned for **10a** and **10b**. The $^{31}P\{^1H\}$ NMR spectrum of the mixture shows two singlets at 29.1 (**11a**)

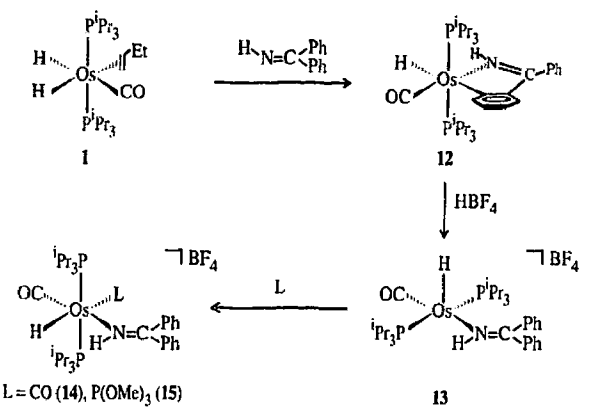
and 26.6 (**11b**). As expected, under off-resonance conditions, both singlets are split into doublets.

2.4. Reactions of $OsH_2(\eta^2\text{-}CH_2=CHEt)(CO)(P^iPr_3)_2$ with benzophenone imine

Treatment of complex **1** with benzophenone imine in a 1:1 molar ratio in hexane at room temperature leads to the previously reported orthometallated compound $OsH\{NH=C(Ph)C_6H_4\}(CO)(PiPr_3)_2$ (**12**, in Scheme 6) [50], which was isolated in 85% yield.

Complex **12** reacts with 1 equivalent of $HBF_4 \cdot OEt_2$ in dichloromethane to afford the five-coordinate cationic complex $[OsH(CO)(NH=CPh_2)(P^iPr_3)_2]BF_4$ (**13**), which was isolated as a white solid in 78% yield. The non-coordination of the $[BF_4]^-$ anion to the osmium atom is strongly supported by the IR spectrum of **13** in Nujol, which contains the characteristic band of this anion with T_d symmetry centered at 1075 cm^{-1}. In the ^1H NMR spectrum, the most noticeable resonances are a broad signal at 10.63 ppm, corresponding to the NH proton, and a triplet at −15.03 ppm with an *H–P* coupling constant of 18.1 Hz due to the hydrido ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 28.0 ppm. Under off-resonance conditions, this singlet is split into a doublet as a result of the *P–H* coupling with a hydrido ligand.

Although monodentate nitrogen-bonded imine complexes are rare as a consequence of the weak Lewis basicity of the imine nitrogen atom [51–56], complex **13** is relatively stable in the solid state and in solution under argon, and it is a useful starting material to prepare six-coordinate osmium-imine compounds. The coordination number six for the osmium can be achieved by reaction with carbon monoxide and trimethylphosphite. By passing a slow stream of this gas though a dichloromethane solution of **13**, the *cis*-dicarbonyl complex $[OsH(CO)_2(NH=CPh_2)(P^iPr_3)_2]BF_4$ (**14**) is formed. Similarly, the addition of 1 equivalent of trimethylphosphite to **13** in dichloromethane yields $[OsH(CO)(NH=CPh_2)\{P(OMe)_3\}(P^iPr_3)_2]BF_4$ (**15**).



Scheme 6.

Complex **14** was isolated as a white solid in 85% yield. The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum, which shows, along with the ν(NH) and ν(OsH) bands at 3120 and 2060 cm^{-1}, two strong ν(CO) absorptions at 1995 and 1940 cm^{-1}. In the ^1H NMR spectrum, the NH resonance appears at 9.81 ppm, whereas the hydrido ligand gives rise to a triplet at −4.94 ppm with an *H–P* coupling constant of 20.5 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 29.1 ppm. Under off-resonance conditions, it is split into a doublet.

Complex **15** was isolated as a white solid in 70% yield. The $^{31}P\{^1H\}$ NMR spectrum of this compound consists of a triplet at 101.0 ppm and a doublet at 20.2 ppm. In agreement with a phosphite ligand *cis*-disposed to two equivalent phosphine ligands, the value of the *P–P* coupling constant is 17 Hz. The proposed *trans* disposition of hydrido and phosphite ligands is supported by the ^1H NMR spectrum, which contains a doublet ($J(HP) = 137.7$ Hz) of triplets ($J(HP) = 22.5$ Hz) at −7.34 ppm. In the low field region, the most noticeable resonance is that due to the NH proton, which is observed at 10.68 ppm.

3. Conclusion

The results reported in this paper, as well as in previous ones, reveal that the dihydrido-1-butene complex $OsH_2(\eta^2\text{-}CH_2=CHEt)(CO)(P^iPr_3)_2$ has a high tendency to release the olefin ligand. At the time the resulting unsaturated fragment $OsH_2(CO)(P^iPr_3)_2$ shows a relatively strong Lewis base character. Thus, it reacts by oxidative addition with group 14 element hydrido compounds, to afford the corresponding trihydrido-silyl, trihydrido-stannyl and trihydridogermyl derivatives of osmium (IV) [11], and coordinates π-acid ligands such as cyclopentadiene. This diolefin is coordinated in an η^2-bonding mode with the coordinated carbon–carbon double bond coplanar to the hydrido ligands. Although this arrangement should lead to a rapid hydrogenation of the carbon–carbon double bond, the complex does not evolve by hydrogenation even at 60°C. However, the fragment $OsH_2(CO)(P^iPr_3)_2$ is capable of selectively hydrogenating the carbon–carbon triple bond of 2-methyl-1-hexen-3-yne to give the methylhexadiene derivative $Os\{\eta^4\text{-}CH_2=C(CH_3)\text{-}CH=CHCH_2CH_3\}(CO)(P^iPr_3)_2$. The carbon–carbon triple bond of phenylacetylene is not hydrogenated either. The reactions of complex $OsH_2(\eta^2\text{-}CH_2=CHEt)\text{-}(CO)(P^iPr_3)_2$ with this alkyne lead to either $Os(C_2Ph)_2\text{-}(CO)(P^iPr_3)_2$ or $Os(C_2Ph)\{\eta^3\text{-}C(C\equiv CPh)=CHPh\}$ depending upon the excess of alkyne used. Heteroallenes undergo insertion reactions into one of the two hydrido

ligands of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$, while benzophenone imine affords the orthometallated complex $OsH\{NH{=}C(Ph)C_6H_4\}$.

In summary, we report overwhelming evidence showing the versatility of the chemistry of the complex $OsH_2(\eta^2\text{-}CH{=}CHEt)(CO)(P^iPr_3)_2$.

4. Experimental details

All reactions were carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**) was prepared by a published method [10].

NMR spectra were recorded on a Varian UNITY 300 or on a Bruker ARX 300 spectrometer at room temperature unless stated. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ (^1H, $^{13}C\{^1H\}$) and 85% H_3PO_4 ($^{31}P\{^1H\}$ NMR spectra). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^1H, and $N = J(CP) + J(CP')$ for ^{13}C) are given in hertz. Infrared spectra were recorded on a Nicolet 550 spectrometer using Nujol mulls on polyethylene sheets. C, H, and N analyses were carried out on a Perkin Elmer 240C microanalyzer.

4.1. Preparation of $OsH_2(\eta^2\text{-}C_5H_6)(CO)(P^iPr_3)_2$ (2)

A solution of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**) (ca. 200 mg, 0.35 mmol) in 6 ml of hexane was treated with an excess of freshly distilled cyclopentadiene (0.5 ml, 7 mmol). The mixture was stirred for 75 min at room temperature. The mixture was filtered through Kieselguhr and then the solution was stored at −78°C for 12 h to yield a white solid. The orange solution was decanted, and the solid washed with pentane and dried in vacuo. Yield: 107 mg (55%). Anal. Found: C, 51.74; H, 9.60. $C_{24}H_{50}OOsP_2$ Calc.: C, 51.81; H, 9.06. IR (Nujol, cm^{-1}): ν(Os–H) 1990(s); ν(CO) 1875(vs). ^1H NMR (300 MHz, C_6D_6): 3.36, 3.17, 2.93, 2.70 (all m, 1H each, C*H*=), 2.53, 2.42 (both m, 1H each, CH_2), 2.32 (m, 6H, PC*H*CH_3), 1.19 (dvt, 18H, $J_{H-H} = 6.6$ Hz, $N = 13.2$ Hz, PCHCH_3), 1.18 (dvt, 18H, $J_{H-H} = 6.6$ Hz, $N = 13.7$ Hz, PCCH_3), −9.78 (td, 1H, $J_{H-H} = 4.0$ Hz, $J_{H-P} = 30.0$ Hz, Os–*H*), −11.99 (dt, 1H, $J_{H-H} = 4.0$ Hz, $J_{H-P} = 21.9$ Hz, Os–*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 830.7(s).

4.2. Preparation of $Os[\eta^4\text{-}CH_2 = C(CH_3)CH = CHCH_2CH_3](CO)(P^iPr_3)_2$ (3)

A solution of $OsH_2(CO)(\eta^2\text{-}CH{=}CHEt)(P^iPr_3)_2$ (*1*) (ca. 300 mg, 0.522 mmol) in 6 ml of pentane was treated with $CH_3CH_2C{\equiv}CC(CH_3){=}CH_2$ (195 μl, 1.56 mmol). The mixture was stirred for 3 h at room temperature. The resulting yellow solution was concentrated to dryness leaving a yellow oil. The residue was treated with 5 ml of methanol to yield a white solid. The orange solution was decanted, and the solid washed with methanol and dried in vacuo. After recrystallization from a saturated solution of **3** in acetone at −20°C colorless crystals were obtained. Yield: 238.6 mg (72%). Anal. Found: C, 49.41; H, 8.33. $C_{26}H_{54}OOsP_2$ Calc.: C, 49.18; H, 8.57. IR (Nujol, cm^{-1}): ν(CO) 1874(vs). ^1H NMR (300 MHz, C_6D_6, labelling scheme in Fig. 1): δ 4.73 (m, 1H, $J_{H_c-H_d} = 7.3$ Hz, $J_{H_c-P_a} = 2.2$ Hz, $J_{H_c-P_b} = 3.9$ Hz, H_c), 2.38 (m, 3H, PC*H*CH_3), 2.24 (m, 3H, PC*H*CH_3), 2.15 (s br, 3H, $J_{H-P_b} < 1$ Hz, CH_3), 1.88 (m, 1H, $J_{H_d-H_c} = 7.3$ Hz, $J_{H_d-P_a} = 3.6$ Hz, $J_{H_d-P_b} = 4.5$ Hz, H_d), 1.66 (m, 1H, $J_{H_b-H_a} = 2.7$ Hz, $J_{H_b-P_a} = 2.2$ Hz, $J_{H_b-P_b} = 2.6$ Hz, H_b), 1.21 (m, 3H, $J_{H-H} = 6.3$ Hz, CH_2CH_3), 1.17 (dd, 18H, $J_{H-P} = 12.1$ Hz, $J_{H-H} = 7.4$ Hz, PCHCH_3), 1.15 (dd, 18H, $J_{H-P} = 11.7$ Hz, $J_{H-H} = 7.3$ Hz, PCHCH_3), 0.80 (q, 2H, $J_{H-H} = 5.9$ Hz, CH_2CH$_3$); 0.77 (m, 1H, $J_{H_a-H_b} = 2.7$ Hz, $J_{H_a-P_a} = J_{H_a-P_b} = 1$ Hz, H_a). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 192.1 (dd, $J_{C-P} = 10$ Hz, $J_{C-P} = 2$ Hz, *C*O), 94.2 (s, $CH_3CH_2CH{=}CHCCH_3{=}CH_2$), 74.4 (d, $J_{C-P} = 5$ Hz, $CH_3CH_2CH{=}CHCCH_3{=}CH_2$), 29.8 (d, $J_{C-P} = 22$ Hz, P*C*HCH$_3$), 28.8 (d, $J_{C-P} = 20$ Hz, P*C*HCH$_3$), 28.2 (d, $J_{C-P} = 6$ Hz, $CH_3CH_2CH{=}CHCCH_3{=}CH_2$), 27.8 (dd, $J_{C-P} = 9$ Hz, $J_{C-P} = 5$ Hz, $CH_3CH_2CH{=}CH{-}CCH_3{=}CH_2$), 22.5 (s, $CH_3CH_2CH{=}CHCCH_3{=}CH_2$), 21.8 (s, *C*H$_3CH_2$CH=CHCCH$_3$=CH$_2$), 21.2 (s, PCH*C*H$_3$), 20.3 (s, PCH*C*H$_3$), 18.4 (s, $CH_3CH_2CH{=}CHCCH_3{=}CH_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 18.6 (d, $J_{P-P} = 5$ Hz); 2.3 (d, $J_{P-P} = 5$ Hz).

4.3. Preparation of $Os(C_2Ph)[\eta^3\text{-}C(C{\equiv}CPh){=}CHPh](CO)(P^iPr_3)_2$ (5a)

A solution of $OsH_2(CO)(\eta^2\text{-}CH_2{=}CHEt)(P^iPr_3)_2$ (**1**) (ca. 250 mg, 0.43 mmol) in 6 ml of pentane was treated with excess of PhC≡CH (439 μl, 4.3 mmol). The mixture was stirred for 5 h at room temperature. A yellow solid was formed. The solution was decanted, and the solid washed with pentane and dried in vacuo. Yield: 240 mg (65%). Anal. Found: C, 61.65; H, 7.15. $C_{43}H_{58}OOsP_2$ Calc.: C, 61.26; H, 6.93. IR (Nujol, cm^{-1}): ν(C≡C) 2089 (m); ν(CO) 1905 (vs); $\nu(C_6H_5)$ 1594 (w). ^1H NMR (300 MHz, C_6D_6): δ 8.55 (m, 2H), 8.32 (m, 2H), 8.13 (s, 1H, =C*H*Ph), 7.68 (m, 2H), 7.43 (m, 2H), 7.29 (m, 2H), 7.20 (m, 3H), 7.04 (m, 2H) [C_6H_5]; 2.51 (m, 6H, PC*H*CH_3), 1.23 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 13.2$ Hz, PCHC*H*3), 1.08 (dvt, 18H, $J_{H-H} = 6.6$ Hz, $N = 12.9$ Hz, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 187.7 (t, $J_{P-C} = 10$ Hz, *C*O),

141.2 (t, J_{P-C} = 5 Hz, C_α =), 139.6 (s, C_{ipso}), 139.1 (s, C_{ipso}), 132.7, 130.8, 129.5, 129.3, 128.9, 128.5, 126.1, 125.8, 124.4 (all s, C_6H_5 and $=C_\beta$), 120.2 (s, Os–C≡C_β), 110.3 (s, C(C≡CPh)), 93.8 (t, J_{P-C} = 12 Hz, Os–C_α≡C), 60.3 (s, C(C≡CPh)), 25.1 (vt, N = 24 Hz, PCHCH$_3$), 20.0 (s, PCHCH$_3$), 19.4 (s, PCHCH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ −0.6 (s).

4.4. Isomerization of Os(C$_2$Ph){η^3-C(C≡CPh)=CHPh}(CO)(P^{i}Pr$_3$)$_2$ (5b)

A solution of **5a** (40 mg, 0.07 mmol) in 0.5 ml of C_6D_6 contained in a NMR tube was heated at 60°C. After 24 h the ^{1}H and ^{31}P{^{1}H} NMR spectra showed the presence of a mixture of **5a** and **5b** in a 1:1 molar ratio. Spectroscopy data for **5b**. ^{1}H NMR (300 MHz, C_6D_6): δ 8.65 (m, 2H), 7.77 (m, 2H), 7.72 (m, 2H), 7.43 (m, 2H), 7.31–7.18 (m), 7.07–6.99(m) [C_6H_5], 2.46 (m, 6H, PCHCH$_3$), 1.25 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 12.8 Hz, PCHCH_3), 1.09 (dvt, 18H, J_{H-H} = 6.3 Hz, N = 12.2 Hz, PCHCH_3). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 188.8 (t, J_{P-C} = 10 Hz, CO), 142.7 (t, J_{P-C} = 4 Hz, C_α =), 139.9 (s, C_{ipso}), 139.6 (s, C_{ipso}), 132.2, 130.7, 130.6, 128.7, 128.6, 127.4, 127.2, 125.8, 124.6 (all s, C_6H_5 and $=C_\beta$), 120.3 (s, Os–C≡C_β), 104.4 (s, C(C≡CPh)), 94.1 (t, J_{P-C} = 12 Hz Os–C_α≡C), 61.5 (s, C(C≡CPh)), 25.9 (vt, N = 24 Hz, PCHCH$_3$), 20.0 (s, PCHCH$_3$), 19.3 (s, PCHCH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ −0.3(s).

4.5. Preparation of Os(CH$_2$Ph)(FBF$_3$)(CO)$_2$(P^{i}Pr$_3$)$_2$ (6)

A suspension of Os(C$_2$Ph){C(C≡CPh)=CHPh}(CO)P^{i}Pr$_3$)$_2$ (**5a**) (302 mg, 0.36 mmol) in 5 ml of acetone was treated with $HBF_4 \cdot H_2O$ (49 μl, 0.36 mmol). Immediately a pale brown solution was observed. The mixture was stirred for 90 min at room temperature. The resulting solution was concentrated to ca. 0.5 ml, and the addition of diethyl ether caused the precipitation of a yellow solid. The solution was decanted, and the solid washed with diethyl ether and dried in vacuo. Yield: 100 mg (36%). Anal. Found: C, 43.51; H, 6.56. $C_{27}H_{49}BF_4O_2OsP_2$ Calc.: C, 43.55; H, 6.63. IR (Nujol, cm^{-1}): ν(CO) 2015, 1937(s); ν(C_6H_6) 1596(m); ν(BF_4) 1133(s) 1030(s) 950(s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (br, 5H, C_6H_5), 2.88 (t, 2H, J_{H-P} = 7.5 Hz, CH_2), 2.77 (m, 6H, PCHCH$_3$), 1.39 (dvt, 18H, J_{H-H} = 7.3 Hz, N = 13.9 Hz, PCHCH_3), 1.31 (dvt, 18H, J_{H-H} = 6.4 Hz, N = 13.5 Hz, PCHCH_3). ^{13}C{^{1}H} NMR (75.43 MHz, $CDCl_3$): δ 181.3 (t, J_{C-P} = 7 Hz, CO), 179.8 (t, J_{P-C} = 8 Hz, CO), 149.7 (s, $C_{ipso\text{-Ph}}$), 129.4 (s, $CH_{ortho\text{-Ph}}$), 128.0 (s, $CH_{meta\text{-Ph}}$), 123.6 (s, $CH_{para\text{-Ph}}$), 25.3 (vt, J_{C-P} = 25 Hz, PCHCH$_3$), 19.5 (s, PCHCH$_3$), 19.3 (s, PCHCH$_3$), 17.7 (t, J_{C-P} = 6 Hz, CH_2). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): 7.7(s).

4.6. Preparation of Os(CH$_2$Ph)Cl(CO)$_2$(P^{i}Pr$_3$)$_2$ (7)

A solution of Os(CH$_2$Ph)(FBF$_3$)(CO)$_2$(P^{i}Pr$_3$)$_2$ (**6**) (100 mg, 0.13 mmol) in 8 ml of methanol was treated with NaCl (7.7 mg, 0.13 mmol). The mixture was stirred for 90 min at room temperature. A white solid was formed. The solution was decanted, the solid washed with methanol and dried in vacuo. Yield: 50 mg (56%). Anal. Found: C, 46.35; H, 7.25. $C_{27}H_{49}ClO_2OsP_2$ Calc.: C, 46.78; H, 7.12. IR (Nujol, cm^{-1}): ν(CO) 1989, 1914 (vs); ν(C_6H_6) 1596 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 2H, o-C_6H_5), 7.09 (m, 2H, m-C_6H_5), 6.87 (m, 1H, p-C_6H_5), 2.83–2.73 (m, 8H, the signal for CH_2 are overlapped with the signal of PCHCH$_3$), 1.41 (dvt, 18H, J_{H-H} = 7.1 Hz, N = 13.8 Hz, PCHCH_3), 1.23 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 12.9 Hz, PCHCH_3). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 181.8 (t, J_{C-P} = 7 Hz, CO), 180.8 (t, J_{C-P} = 8 Hz, CO), 153.8 (s, $C_{ipso\text{-Ph}}$), 130.0 (s, C_6H_5), 122.6 (s, C_6H_5), 24.8 (vt, N = 24 Hz, PCHCH$_3$), 20.2 (s, PCHCH$_3$), 19.1 (s, PCHCH$_3$), 14.5 (t, J_{C-P} = 6 Hz, CH2). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ −1.2(s).

4.7. Preparation of OsH{κ^2-N(Cy)CHN(Cy)}(CO)(P^{i}Pr$_3$)$_2$ (8)

A solution of OsH$_2$(CO)(η^2-CH$_2$=CHEt)(PiPr$_3$)$_2$ (**1**) (ca. 121 mg, 0.21 mmol) in 6 ml of pentane was treated with 1,3-dicyclohexyl-carbodiimide (47.75 mg, 0.23 mmol). The mixture was stirred for 5 min at room temperature. The solution was concentrated to dryness, and the residue was treated with 5 ml of methanol to yield a white solid. The solution was decanted, and the solid washed with methanol and dried in vacuo. Yield: 121 mg (77%). Anal. Found: C, 51.38; H, 10.08; N, 3.57. $C_{32}H_{66}ON_2OsP_2$ Calc.: C, 51.45; H, 8.90; N, 3.75. IR (Nujol, cm^{-1}): ν(Os–H) 2130 (s); ν(CO) 1882 (s); ν(CyNCHNCy) 1575 (m) 1235 (m) 885 (w). ^{1}H NMR (300 MHz, C_6D_6): δ 8.89 (br, 1H, CyNCH-NCy), 3.30 (m, 1H, CHN, Cy); 2.84 (m, 1H, CHN, Cy); 2.32–1.65 (m, 15H, CH_2, Cy); 2.40 (m, 6H, PCHCH$_3$), 1.32 (dvt, 18H, J_{H-H} = 6.4 Hz, N = 13.2 Hz, PCHCH_3), 1.18–0.94 (m, 5H, CH_2, Cy); 1.27 (dvt, 18H, J_{H-H} = 6.7 Hz, N = 13.3 Hz, PCHCH_3), −16.38 (t, 1H, J_{H-P} = 20.5 Hz, Os–H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 25.6 (s).

4.8. Preparation of OsH{κ^2-OCHN(Ph)}(CO)(P^{i}Pr$_3$)$_2$ (9)

A solution of OsH$_2$(CO)(η^2-CH$_2$=CHEt) (P^{i}Pr$_3$)$_2$ (**1**) (ca. 95.5 mg, 0.16 mmol) in 6 ml of pentane was treated with phenylisocyanate (14.11 μl, 0.176 mmol). The mixture was stirred for 5 min at room temperature. The solution was concentrated to dryness, and the residue was treated with 5 ml of methanol to yield a

white solid. The solution was decanted, and the solid washed with methanol and dried in vacuo. The solid obtained was a mixture of two isomers **9a**:**9b** in a 1:2 molar ratio. Yield: 89 mg (85%). Anal. Found: C, 47.40; H, 7.36, N, 2.62. $C_{26}H_{49}O_2NOsP_2$ Calc.: C, 47.33; H, 7.48; N, 2.12. IR (Nujol, cm^{-1}): ν(Os–H) 2140(s); ν(CO) 1910 (s); ν(PhNCHO) 1555 (m) 1270 (w). Spectroscopy data for **9a**: ^{1}H NMR (300 MHz, C_6D_6): δ 9.32 (br, 1H, PhNC*H*O), 6.91 (br, 5H, C_6H_5), 2.10 (m, 6H, PC*H*CH$_3$), 1.03 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.3 Hz, PCHCH_3), 0.93 (dvt, 18H, J_{H-H} = 6.9 Hz N = 13.1 Hz, PCHCH_3), −21.54 (t, 1H, J_{H-P} = 16.1 Hz, Os–*H*. ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 30.6(s). Spectroscopy data for **9b**: ^{1}H NMR (300 MHz, C_6D_6): δ 9.04 (br, 1H, PhNC*H*O), 6.91 (br, 5H, C_6H_5), 2.10 (m, 6H, PC*H*CH$_3$), 1.03 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.3 Hz, PCHCH_3), 0.93 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.1 Hz, PCHCH_3), −15.19 (t, 1H, J_{H-P} = 18.8 Hz, Os–*H*). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 34.7(s).

4.9. Preparation of OsH{κ²-N(Ph)CHS}(CO)(PiPr₃)₂ (10)

A solution of $OsH_2(CO)(\eta^2$-CH_2=CHEt)(P^{i}Pr$_3$)$_2$ (**1**) (ca. 91.9 mg, 0.15 mmol) in 6 ml of pentane was treated with phenylisothiocyanate (20.35 μl, 0.17 mmol). Immediately an orange solution was obtained. The mixture was stirred for 5 min at room temperature. A yellow solid was formed. The solution was decanted, and the solid washed with pentane and dried in vacuo. The solid obtained was a mixture of two isomers **10a**:**10b** in a 4:1 molar ratio. Yield: 62 mg (60%). Anal. Found: C, 46.08; H, 8.02; N, 1.98. $C_{26}H_{49}ONOsP_2S$ Calc.: C, 46.20; H, 7.31, N, 2.07. IR (Nujol, cm^{-1}): ν(Os–H) 2120(s); ν(CO) 1840 (s); ν(PhNCHS) 1550 (w) 1255 (w) 880 (w). Spectroscopy data for **10a**: ^{1}H NMR (300 MHz, C_6D_6): δ 10.62 (br, 1H, PhNC*H*S); 7.10 (br, 5H, C_6H_5), 2.30 (m, 6H, PC*H*CH$_3$), 1.27 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.5 Hz, PCHCH_3), 1.21 (dvt, 18H, J_{H-H} = 6.6 Hz, N = 13.8 Hz, PCHCH_3), −14.31 (t, 1H, J_{H-P} = 18.9 Hz, Os–*H*). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 21.6 (s). Spectroscopy data for **10b**: ^{1}H NMR (300 MHz, C_6D_6): δ 10.35 (br, 1H, PhNC*H*S), 6.91 (br, 5H, C_6H_5), 2.70 (m, 6H, PC*H*CH$_3$), 1.03 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.3 Hz, PCHCH_3), 0.93 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.1 Hz, PCHCH_3), −15.20 (t, 1H, J_{H-P} = 23.4 Hz, Os–*H*). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 27.0 (s).

4.10. Preparation of OsH{κ²-N(CH₃)CHS}(CO)(P^{i}Pr₃)₂ (11)

A solution of $OsH_2(CO)(\eta^2$-CH_2=CHEt)(P^{i}Pr$_3$)$_2$ (**1**) (ca. 111.6 mg, 0.19 mmol) in 6 ml of pentane was treated with methylisothiocyanate (15 mg, 0.21 mmol). The solution was concentrated to dryness, and the residue was treated with 5 ml of methanol to yield a pale yellow solid. The solution was decanted, and the solid washed with methanol and dried in vacuo. The solid obtained was a mixture of two isomers **11a**:**11b** in a 1:2 molar ratio. Yield: 79 mg (69%). Anal. Found: C, 41.57 H, 8.63; N, 2.21. $C_{21}H_{47}ONOsP_2S$ Calc.: C, 41.09; H, 7.72; N, 2.28. IR (Nujol, cm^{-1}): ν(Os–H) 2130 (m) 2100 (m); ν(CO) 1885 (s); ν(MeNCS) 1550, 1540 (w) 1245 (w) 880 (w). Spectroscopy data for **11a**: ^{1}H NMR (300 MHz, C_6D_6): δ 9.37 (br, 1H, CH$_3$NC*H*S), 3.24 (s, 3H, CH_3), 2.77 (m, 6H, PC*H*CH$_3$), 1.23 (dvt, 36H, J_{H-H} = 7.2 Hz, N = 12.6 Hz, PCHCH_3), −14.82 (td, 1H, J_{H-H} = 1.8 Hz, J_{H-P} = 20.7 Hz, Os–*H*). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 29.1 (s). Spectroscopy data for **11b**: ^{1}H NMR (300 MHz, C_6D_6): δ 9.61 (br, 1H, CH$_3$NC*H*S), 2.66 (s, 3H, CH_3), 2.35 (m, 6H, PC*H*CH$_3$), 1.30 (dvt, 36H, J_{H-H} = 6.9 Hz, N = 13.2 Hz, PCHCH_3), −15.10 (t, 1H, J_{H-P} = 18.0 Hz, Os–*H*). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 26.6 (s).

4.11. Preparation of OsH{NH=C(Ph)C₆H₄} (CO)(P^{i}Pr₃)₂ (12)

A solution of $OsH_2(CO)(\eta^2$-CH_2=CHEt)(P^{i}Pr$_3$)$_2$ (**1**) (ca. 162 mg, 0.28 mmol) in 6 ml of hexane was treated with the stoichiometric amount of NH=CPh$_2$ (47.3 μl, 0.28 mmol). Immediately a red solution was observed. The mixture was stirred for 60 min at room temperature. The resulting dark red solution was concentrated to dryness, and the residue was treated with 5 ml of methanol to yield an orange solid. The orange solution was decanted, and the solid washed with methanol and dried in vacuo. Yield: 171 mg (85%). Anal. Found: C, 53.30; H, 7.42; N, 1.94. $C_{32}H_{55}ONOsP_2$: Calc.: C, 53.88; H, 8.22; N, 2.01. IR (Nujol, cm^{-1}): ν(NH) 3325 (s); ν(OsH) 2080 (m); ν(CO) 1875 (s). ^{1}H NMR (300 MHz, C_6D_6): δ 10.35 (s, br, 1H, N*H*), 8.36 (m, 2H), 7.66 (m, 1H), 7.48 (m, 2H), 7.18 (m, 2H), 7.48 (m, 2H) [C_6H_4 and C_6H_5], 2.14 (m, 6H, PC*H*CH$_3$), 1.21 (dvt, 18H, J_{H-H} = 6.7 Hz, N = 12.9 Hz, PCHCH_3), 0.93 (dvt, 18H, J_{H-H} = 6.6 Hz, N = 12.8 Hz, PCHCH_3), −11.55 (t, 1H, J_{H-P} = 23.8 Hz, Os–*H*). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 192.4 (t, J_{C-P} = 10 Hz, Os–*C*), 187.0 (t, J_{C-P} = 10 Hz, *C*O), 181.2 (s, N = *C*), 146.8, 144.1, 140.4, 129.7, 128.9, 128.8, 128.4, 128.3, 128.1, 127.7, 120.5 (all s, C_6H_4 and C_6H_5), 27.4 (vt, N = 25 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$), 19.3 (s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ 22.2 (s).

4.12. Preparation of [OsH(NH=CPh₂)(CO)(P^{i}Pr₃)₂]BF₄ (13)

A solution of OsH{NH=C(Ph)C$_6$H$_4$} (CO)(P^{i}Pr$_3$)$_2$ (**12**) (80 mg, 0.11 mmol) in 5 ml of CH_2Cl_2 was treated

with $HBF_4 \cdot OEt_2$ (18.2 μl, 0.13 mmol). Immediately the solution changed from orange to yellow. The resulting solution was concentrated to ca. 0.5 ml, and the addition of diethyl ether caused the precipitation of a white solid. The solution was decanted, and the solid washed with diethyl ether and dried in vacuo. Yield: 80 mg (78%). Anal. Found: C, 47.71; H, 7.44; N, 1.63. $C_{32}H_{54}BF_4NOOsP_2$ Calc.: C, 47.58; H, 6.74; N, 1.73. IR (Nujol, cm^{-1}): ν(NH) 3260 (s) ν(OsH) 2210 (m); ν(CO) 1940 (s); ν(BF_4) 1075 (br). ^1H NMR (300 MHz, $CDCl_3$): δ 10.63 (s br, 1H, N*H*), 7.59–7.41 (m, 10H, C_6H_5), 2.06 (m, 6H, PC*H*CH_3), 1.12 (dvt, 18H, J_{H-H} = 6.3 Hz, N = 12.6 Hz, PCHC*H*$_3$), 0.91 (dvt, 18H, J_{H-H} = 6.1 Hz, N = 12.4 Hz, PCHC*H*$_3$), −15.03 (t, 1H, J_{H-P} = 18.1 Hz, Os–*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 28.0 (s).

4.13. Preparation of $[OsH(NH=CPh_2)(CO)_2(P^iPr_3)_2]BF_4$ (14)

Carbon monoxide was bubbled through a pale yellow solution of $[OsH(NH{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ (**13**) (150 mg, 0.19 mmol) in 5 ml of CH_2Cl_2 for 15 min. The resulting yellow solution was concentrated to ca. 0.5 ml, and the addition of diethyl ether caused the precipitation of a white solid. The solution was decanted and the solid washed with diethyl ether and dried in vacuo. Yield: 135 mg (85%). Anal. Found: C, 47.54; H, 6.89; N, 1.53. $C_{33}H_{54}BF_4NO_2OsP_2$ Calc.: C, 47.43; H, 6.51; N, 1.67. IR (Nujol, cm^{-1}): ν(NH) 3120 (s), ν(OsH) 2060 (m); ν(CO) 1995, 1940 (s); ν(BF_4) 1065 (br). ^1H NMR (300 MHz, $CDCl_3$): δ 9.81 (s, br, 1H, N*H*), 7.66–7.18 (m, 10H, C_6H_5), 2.27 (m, 6H, PC*H*CH_3), 1.29 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.4 Hz, PCHC*H*$_3$), 1.23 (dvt, 18H, J_{H-H} = 6.6 Hz, N = 13.5 Hz, PCHC*H*$_3$), −4.94 (t, 1H, J_{H-P} = 20.5 Hz, Os–*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 29.1 (s).

4.14. Preparation of $[OsH(NH=CPh_2)(CO)\{P(OMe)_3\}(P^iPr_3)_2]BF_4$ (15)

A solution of $[OsH(NH{=}CPh_2)(CO)(P^iPr_3)_2]BF_4$ (**12**) (100 mg, 0.12 mmol) in 5 ml of CH_2Cl_2 was treated with $P(OMe)_3$ (17.5 μl, 0.15 mmol). The mixture was stirred for 1 h at room temperature. The resulting yellow solution was concentrated to ca. 0.5 ml, and the addition of diethyl ether caused the precipitation of a white solid. The solution was decanted and the solid washed with diethyl ether and dried in vacuo. Yield: 124 mg (70%). Anal. Found: C, 45.01; H, 7.53; N, 1.48. $C_{35}H_{63}BF_4NO_4OsP_3$ Calc.: C, 45.11; H, 6.81; N, 1.50. IR (Nujol, cm^{-1}): ν(NH) 3260 (s); ν(OsH) 2040 (m); ν(CO) 1935 (s); ν(BF_4) 1080 (br). ^1H NMR (300 MHz, $CDCl_3$): δ 10.68 (s, br, 1H, N*H*), 7.80–7.19 (m, 10H, C_6H_5), 4.01 (d, 9H, J_{H-P} = 10.16 Hz, OC*H*$_3$), 2.23 (m, 6H, PC*H*CH_3), 1.13 (dvt, 18H, J_{H-H} = 6.9 Hz, N = 13.7 Hz, PCHC*H*$_3$), 1.07 (dvt, 18H, J_{H-H} = 6.3 Hz, N = 12.1 Hz, PCHC*H*$_3$), −7.34 (dt, 1H, J_{H-P} = 137.7 Hz, J_{H-P} = 22.5 Hz, Os–*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 101.0 (t, J_{P-P} = 17 Hz, $P(OMe)_3$); 20.2 (d, J_{P-P} = 17 Hz, P^iPr_3).

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