DALTON

# Synthesis and reactivity of [OsH{$C_6H_4$(CH=CHH)}(CO)($PPr^i_3$)$_2$] and the formato compounds [Os{(*E*)-CH=CHPh}($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] and [OsH($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$]*

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The complex [OsH{$C_6H_4$(CH=CHH)}(CO)($PPr^i_3$)$_2$] has been prepared by reaction of the five-co-ordinate [Os{(*E*)-CH=CHPh}Cl(CO)($PPr^i_3$)$_2$] with LiBu$^n$ in hexane. It reacts with $P(OMe)_3$ and CO to give [OsH{(*E*)-CH=CHPh}(CO){$P(OMe)_3$}($PPr^i_3$)$_2$] and [OsH{(*E*)-CH=CHPh}$(CO)_2$($PPr^i_3$)$_2$], while under a $CO_2$ atmosphere the formato derivative [Os{(*E*)-CH=CHPh}($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] is obtained. Carbonylation of the latter leads to the monodentate formato complex [Os{(*E*)-CH=CHPh}{$\eta^1$-OC(O)H}$(CO)_2$($PPr^i_3$)$_2$] and under a hydrogen atmosphere it affords styrene and [OsH($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$], which can be also prepared by reaction of [$OsH_2$($\eta^2$-$CH_2$=CHEt)(CO)($PPr^i_3$)$_2$] with $CO_2$. The complex [OsH($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] reacts with CO, $P(OMe)_3$ and $MeO_2CC{\equiv}CCO_2Me$ to give [OsH{$\eta^1$-OC(O)H}(CO)L($PPr^i_3$)$_2$] [L = CO, $P(OMe)_3$ or $MeO_2CC{\equiv}CCO_2Me$]; the carbon atom of its formate ligand is attacked by $NEt_2H$ leading to the carbamato compound [OsH($\eta^2$-$O_2CNEt_2$)(CO)($PPr^i_3$)$_2$] and molecular hydrogen. Similarly treatment of [Os{(*E*)-CH=CHPh}-($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] with $NEt_2H$ afforded [Os{(*E*)-CH=CHPh}($\eta^2$-$O_2CNEt_2$)(CO)($PPr^i_3$)$_2$]. The former complex also reacts with $HBF_4{\cdot}OEt_2$, giving two different derivatives depending upon the conditions: in diethyl ether as solvent and in the presence of acetonitrile the vinyl complex [Os{(*E*)-CH=CHPh}(CO)$(MeCN)_2$-($PPr^i_3$)$_2$]$BF_4$ is formed, while the carbene derivative [Os($\eta^2$-$O_2$CH)(=$CHCH_2$Ph)(CO)($PPr^i_3$)$_2$]$BF_4$ is obtained in chloroform. The products formed by reaction of [OsH($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] with $HBF_4{\cdot}OEt_2$ also depend upon the reaction conditions: in diethyl ether and in the presence of MeCN the hydrido compound [OsH(CO)-$(MeCN)_2$($PPr^i_3$)$_2$]$BF_4$ is obtained; however a mixture of products, mainly dihydrogen derivatives, is formed in $CDCl_3$. On the basis of theoretical calculations and $T_1$ measurements, the nature and structure of these dihydrogen compounds are discussed.

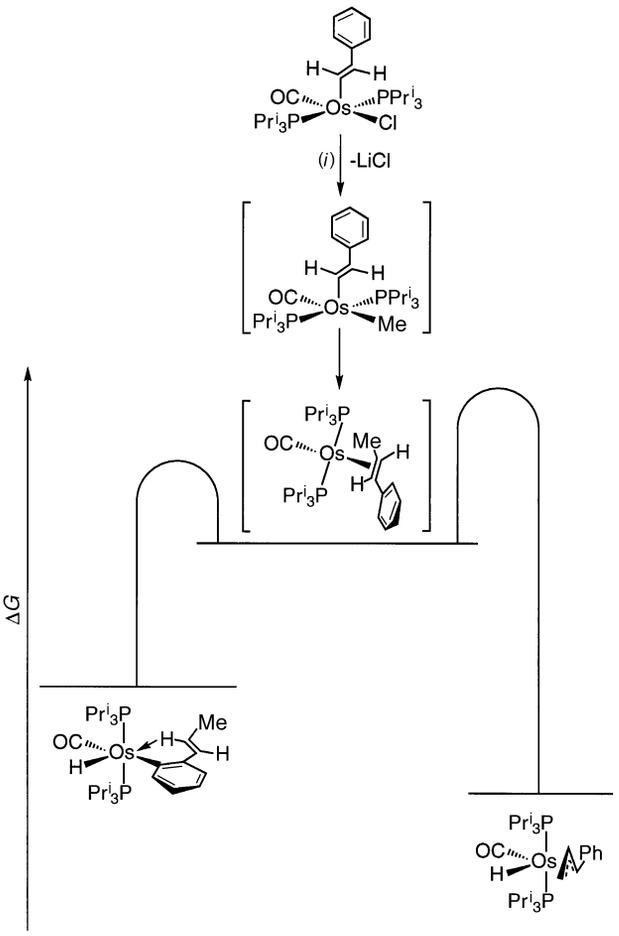
In the search for homogeneous transition-metal systems effective in the synthesis of functionalized organic molecules from basic hydrocarbons, we have recently observed that treatment of the alkenylosmium(II) complexes [Os{(*E*)-CH=CHR}-Cl(CO)($PPr^i_3$)$_2$] (R = H or Ph) with main-group organometallic compounds leads to osmium(0) species containing olefin ligands. As shown in Scheme 1 for LiMe, these transformations involve replacement of the $Cl^-$ anion by the organic fragments of the main-group organometallic compounds, and subsequent reductive carbon–carbon coupling of the $\eta^1$-carbon ligands.†,[1,2]

For butadiene and phenylbutadiene the osmium(0) species are stable, and do not undergo subsequent transformation.[1] However, for *trans*-stilbene and *trans*-methylstyrene, the metallic centre is capable of activating a C–H bond of the substituents of the co-ordinated olefin to afford hydridoosmium(II) derivatives.[2] The C–H activation products depend upon the substituents present at the alkene ligand, and can be rationalized in the light of thermodynamic and kinetic considerations. Thus, when the alkene ligand is *trans*-methylstyrene, the activation of an *ortho* position of the phenyl ring is kinetically favoured. The product of this activation, which shows an agostic interaction between the osmium centre and one of the olefinic C–H bonds, evolves to the more favoured thermodynamic product [OsH($\eta^3$-$CH_2$CHCHPh)(CO)($PPr^i_3$)$_2$] (Scheme 1).[2]

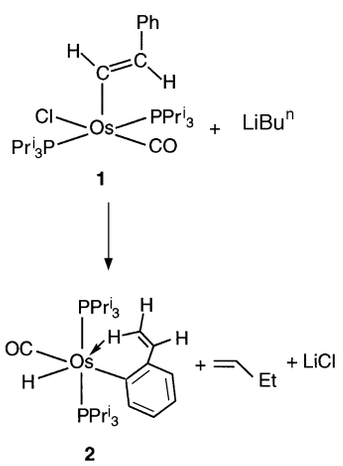
Products from the oxidative addition of the olefinic C–H bonds of *trans*-methylstyrene were not observed. This does not necessarily imply that the olefinic C–H activation in [Os($\eta^2$-MeCH=CHPh)(CO)($PPr^i_3$)$_2$] is kinetically disfavoured with regard to C–H activation of the phenyl ring. At first glance, low activation barriers should be expected for all the possible intramolecular C–H activations in osmium(0) intermediates like [Os($\eta^2$-MeCH=CHPh)(CO)($PPr^i_3$)$_2$], in view of the mild isomerization conditions and the values of the activation enthalpies reported for this kind of reaction.[3] So, the non-observation of hydridoalkenyl complexes could probably be a consequence of their lower thermodynamic stability compared to the hydridophenyl derivative [OsH{$C_6H_4$[(*E*)-CH=CHMe]-2}(CO)($PPr^i_3$)$_2$].

As a continuation of our work in this field, and with the idea of casting some light on olefinic C–H activation compared to C–H activation of the *ortho* position of the phenyl ring in osmium(0)–phenyl–olefin species, we have now studied the reaction of [Os{(*E*)-CH=CHPh}Cl(CO)($PPr^i_3$)$_2$] with LiBu$^n$. In this paper, we also report the synthesis and characterization of [OsH{$C_6H_4$(CH=CHH)}(CO)($PPr^i_3$)$_2$], [Os{(*E*)-CH=CHPh}-($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] and [OsH($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$], and the reactivity of the formato compounds towards CO, $P(OMe)_3$, $H_2$, $NEt_2H$, alkynes and $HBF_4$. On the basis of

† *Non-SI unit employed*: cal = 4.184 J.




**Scheme 1** (*i*) LiMe



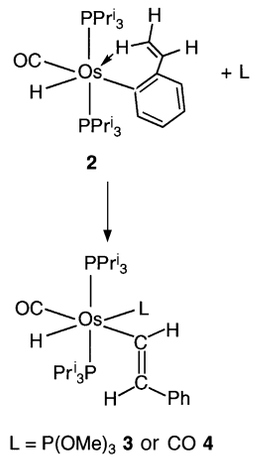
**Scheme 2**

spectroscopic data and theoretical calculations, the nature of the compounds formed by addition of $HBF_4$ to $[OsH(\eta^2\text{-}O_2CH)(CO)(PPr^i_3)_2]$ is also discussed.

## Results and Discussion

### Reaction of [Os{(*E*)-CH=CHPh}Cl(CO)(PPr$^i_3$)$_2$] with LiBu$^n$

Reaction of the five-co-ordinate alkenyl complex $[Os\{(E)\text{-}CH{=}CHPh\}Cl(CO)(PPr^i_3)_2]$ **1** with LiBu$^n$ in hexane at room temperature gives a yellow solution from which the hydridoaryl derivative $[OsH\{C_6H_4(CH{=}CHH)\}(CO)(PPr^i_3)_2]$ **2** (Scheme 2) was isolated as a colourless oil in quantitative yield. In the presence of a trace of water this compound evolves into the previously reported $[OsH_2(\eta^2\text{-}CH_2{=}CHPh)(CO)(PPr^i_3)_2]$.[4]

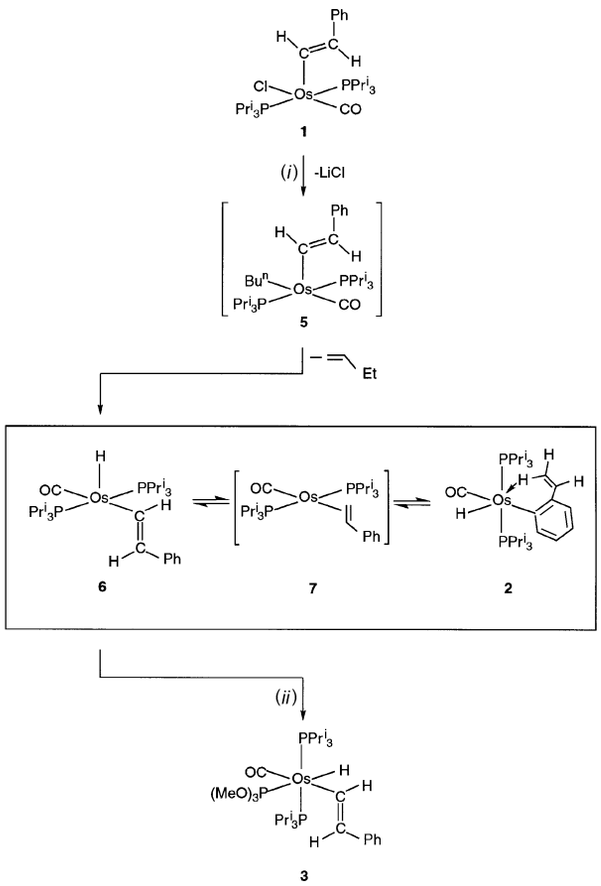



**Scheme 3**

The $^1$H NMR spectrum in $C_6D_6$ shows in the hydrido region a triplet at δ −8.01 with a P–H coupling constant of 27.3 Hz. The low-field region contains the expected resonances for the 2-vinylphenyl ligand. The PhC*H*= proton appears at δ 4.95 as a doublet of doublets with H–H coupling constants of 9.0 and 7.7 Hz. The olefinic proton disposed *cis* to this appears at δ 2.74 as a doublet while that disposed *trans*, consistent with the agostic interaction, displays a doublet of triplets with a P–H coupling constant of 5.7 Hz. In the $^{13}$C-{$^1$H} NMR spectrum the olefinic carbon atoms gave rise to two broad signals at δ 50.5 and 46.3. The aryl carbon atom linked to the metal is observed at δ 138.6 as a triplet with a P–C coupling constant of 10.0 Hz. The $^{31}$P-{$^1$H} NMR spectrum has a singlet at δ 16.7 indicating that both phosphine ligands are equivalent and mutually *trans* disposed. These spectroscopic data agree well with those previously reported for the related complexes $[OsH\{C_6H_4[(E)\text{-}CH{=}CHR]\text{-}2\}(CO)(PPr^i_3)_2]$ where a Os···H agostic interaction has been confirmed by X-ray diffraction.[2]

Complex **2** reacts with trimethyl phosphite and carbon monoxide in hexane at room temperature to give the six-co-ordinate hydridostyryl derivatives $[OsH\{(E)\text{-}CH{=}CHPh\}(CO)L(PPr^i_3)_2]$ [L = $P(OMe)_3$ **3** or CO **4**] (Scheme 3) which were isolated as white solids in good yields [85 (**3**), 72% (**4**)]. The IR spectrum of **3** in Nujol shows two absorptions at 2050 and 1910 cm$^{-1}$, which were assigned to the ν(Os–H) and ν(CO) vibrations, respectively. The $^{31}$P-{$^1$H} NMR spectrum contains a triplet at δ 102.4 [$P(OMe)_3$] and a doublet at δ 17.5 ($PPr^i_3$) with a P–P coupling constant of 18.6 Hz, consistent with two equivalent $PPr^i_3$ ligands both *cis* disposed to the trimethyl phosphite group. The relative *trans* position of the hydride and phosphite ligands was inferred from the hydrido signal in the $^1$H NMR spectrum, which appears as a doublet ($J_{P-H}$ = 134.4 Hz) of triplets ($J_{P-H}$ = 24.5 Hz) of doublets ($J_{H-H}$ = 1.6 Hz) at δ −8.94. In the low-field region the most noticeable resonances are those corresponding to the vinyl protons of the styryl ligand, which appear at δ 8.78 (OsCH=) and 7.03 (=CHPh). The *trans* stereochemistry of the two hydrogen atoms at the C=C double bond is supported by the value of the H–H coupling constant (18.3 Hz), which is typical for this arrangement.[5] In the $^{13}$C-{$^1$H} NMR spectrum the $C_\alpha$ carbon atom of the styryl ligand appears at δ 143.3 as a virtual quartet with a P–C coupling constant of 13.4 Hz, while the $C_\beta$ carbon atom displays at δ 144.4 a doublet of triplets with P–C coupling constants of 10.1 and 4.2 Hz.

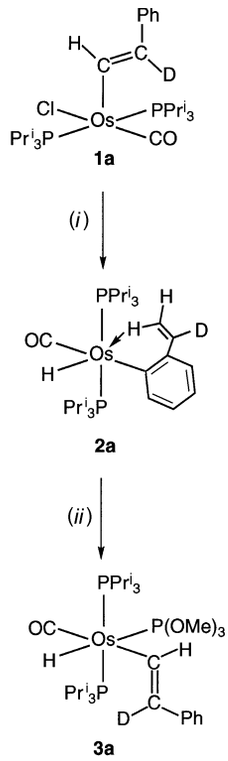
The spectroscopic data obtained for complex **4** also support the structure proposed in Scheme 3. The *cis* relative position of the carbonyl ligands was inferred from the IR spectrum in Nujol, which shows, together with the ν(Os–H) band at 1990 cm$^{-1}$, two strong ν(CO) absorptions at 1945 and 1865 cm$^{-1}$, typical for mononuclear *cis*-dicarbonyl complexes. The



**Scheme 4** (*i*) LiBu$^n$; (*ii*) P(OMe)$_3$

$^{13}$C-{$^1$H} NMR spectrum also supports this proposal, showing two triplets at δ 190.4 ($J_{P-C}$ = 5.5) and 185.5 ($J_{P-C}$ = 7.8 Hz) attributable to the carbonyl ligands. It also contains the expected resonances for the vinylic carbon atoms of the styryl ligand, which appear at δ 142.5 ($C_\beta$) and 135.2 ($C_\alpha$) as triplets with P–C coupling constants of 3.7 and 12.9 Hz, respectively. The CH groups of the phosphine ligands give a virtual triplet at δ 26.2 ($N$ = 27.6 Hz), which is characteristic of the two equivalent phosphine ligands in a *trans* relative position. This is consistent with the singlet at δ 19.0 found in the $^{31}$P-{$^1$H} NMR spectrum. The $^1$H NMR spectrum shows the hydrido resonance at δ −7.13 as a triplet ($J_{P-H}$ = 22.0 Hz) of doublets ($J_{H-H}$ = 5.0 Hz). The vinylic protons of the styryl ligand appear at δ 8.34 (OsCH=) and 7.20 (=CHPh). The value of the $H_\alpha$–$H_\beta$ coupling constant (16.1 Hz) is also in agreement with the proposed *E* stereochemistry at the C=C double bond.

On the basis of our previous reports[1,2,6] the reactions shown in Schemes 2 and 3 can be rationalized according to Scheme 4. The reaction of **1** with LiBu$^n$ to give **2** most probably involves replacement of the $Cl^-$ anion by a butyl group to afford the intermediate **5**, which by subsequent hydrogen β elimination could give **6**. In this context, it should be mentioned that the reaction of the five-co-ordinate complex [OsH(Cl)(CO)-($PPr^i_3$)$_2$] with LiBu$^n$ affords [$OsH_2(\eta^2$-$CH_2$=CHEt)(CO)-($PPr^i_3$)$_2$].[6] The reductive elimination of styrene from **6** followed by the C–H activation of the *o*-aryl proton should lead to **2** *via* the styreneosmium(0) intermediate **7**. In spite of the fact that **2** is the only species detected in solution, the formation of **3** and **4** from **2** (Scheme 3) suggests that in solution complex **2** is in equilibrium with no detectable concentrations of **6**. This implies that **7** is easily accessible and can give rise to activation reactions at both the olefinic and the *ortho* phenyl C–H bonds of the co-ordinated styrene. Although **2** is more stable than **6**, the latter is more substitution labile. In addition, it should be pointed out that the olefinic C–H activation is selective, thus



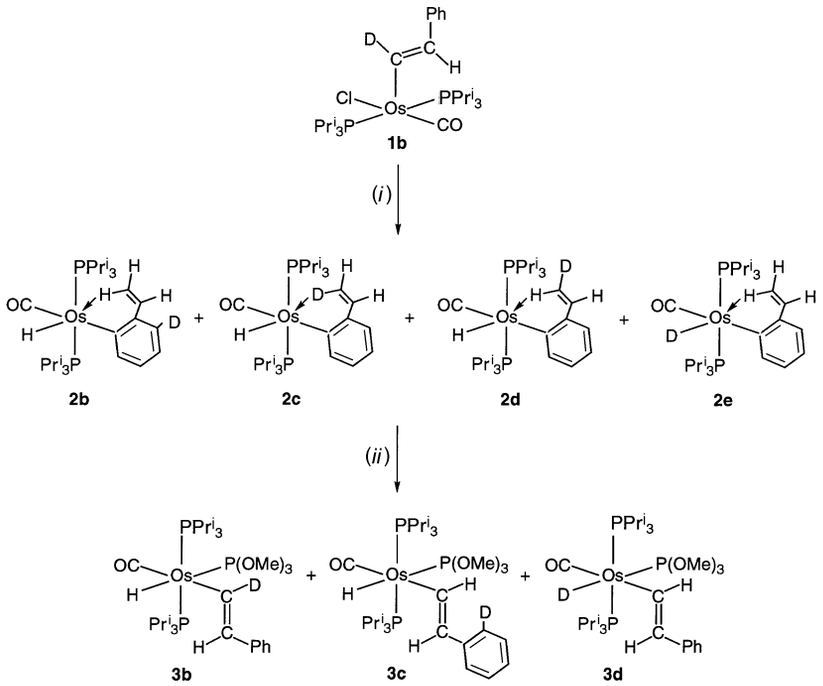
**Scheme 5** (*i*) LiBu$^n$; (*ii*) P(OMe)$_3$

only the C–H bond disposed *trans* to the phenyl group is activated.

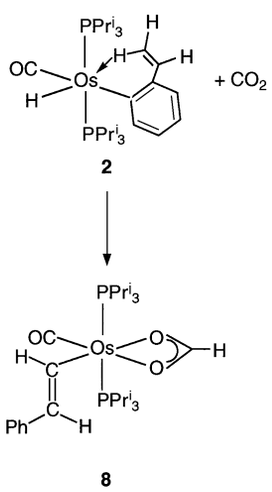
Consistent with the high selectivity observed for the olefinic C–H activation, the reaction of the deuteriated complex [Os{(*E*)-CH=CDPh}Cl(CO)($PPr^i_3$)$_2$] **1a** with LiBu$^n$ leads to [OsH{$C_6H_4$(CD=CHH)}(CO)($PPr^i_3$)$_2$] **2a**, and the addition of trimethyl phosphite to **2a** affords [OsH{(*E*)-CH=CDPh}-(CO){P(OMe)$_3$}($PPr^i_3$)$_2$] **3a** containing the deuterium atom at the $C_\beta$ carbon atom of the styryl ligand (Scheme 5). The position of the deuterium atoms in these compounds was inferred from the $^2$H NMR spectra, which contain resonances at δ 5.03 (**2a**) and 7.01 (**3a**).

The reaction of the $C_\alpha$-deuteriated complex [Os{(*E*)-CD=CHPh}Cl(CO)($PPr^i_3$)$_2$] (**1b**) with LiBu$^n$, in contrast to that of $C_\beta$-deuteriated **1a**, produces a mixture of four deuteriated derivatives in approximately 1:1:1:1 molar ratio, as shown by the $^2$H NMR spectrum which contains four resonances with the same intensity at δ 6.52, 3.68, 2.65 and −8.02. According to the $^1$H NMR spectrum of **2**, these resonances were respectively assigned to the complexes **2b**, **2c**, **2d** and **2e** of Scheme 6. The presence of **2b**, **2d** and **2e** in the mixture suggests that in **2** the terminal olefinic carbon atom interacts with the hydride ligand, thus the migration of the hydride onto the olefinic terminal carbon atom and subsequent hydrogen extraction from the resulting methyl group could explain the deuterium distribution. Direct migration of the hydride from the osmium atom onto the terminal olefinic carbon atom does not seem likely in view of the mutually *trans* disposition of the hydride and the agostic interaction. Hence it could be proposed that the exchange process proceeds by a five-co-ordinate aryl intermediate, resulting from cleavage of the agostic interaction. Although this intermediate has not been detected by NMR spectroscopy, even at −80 °C, one should assume it, giving that at high temperatures important amounts of the relative five-co-ordinate aryl derivatives [OsH{$C_6H_4$(CH=CHR)}(CO)-($PPr^i_3$)$_2$] are in equilibrium with the six-co-ordinate complexes [OsH{$C_6H_4$(CH=CHR)}(CO)($PPr^i_3$)$_2$] (R = Me or Ph).[2]

The $^2$H NMR spectrum of the solution formed by addition of *ca*. 1 equivalent of trimethyl phosphite to the mixture of



**Scheme 6** (*i*) $LiBu^n$; (*ii*) $P(OMe)_3$



**Scheme 7**

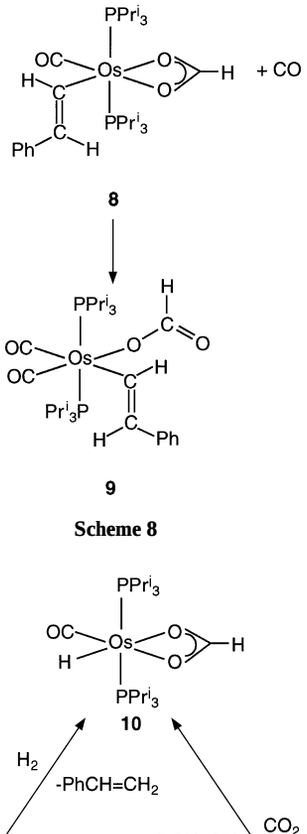
complexes **2b**–**2e** in benzene shows two broad singlets at δ 8.81 and 7.46 and a doublet at δ −8.88, with a P–D coupling constant of 20.2 Hz. According to the $^1$H NMR spectrum of **3**, the singlets correspond to complexes **3b** and **3c** of Scheme 6, respectively, while the doublet is due to the derivative **3d**. The formation of these compounds is new evidence in favour of the equilibrium between **2** and **6** (Scheme 4). Thus complex **3b** is the product of the reaction of **2c** with $P(OMe)_3$, **3c** is formed from **2b** and **2e** in the presence of the phosphite, while **3d** is a result of the addition of the ligand to **2d**.

### Synthesis and reactivity of [Os{(*E*)-CH=CHPh}(η$^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] and [OsH(η$^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$]

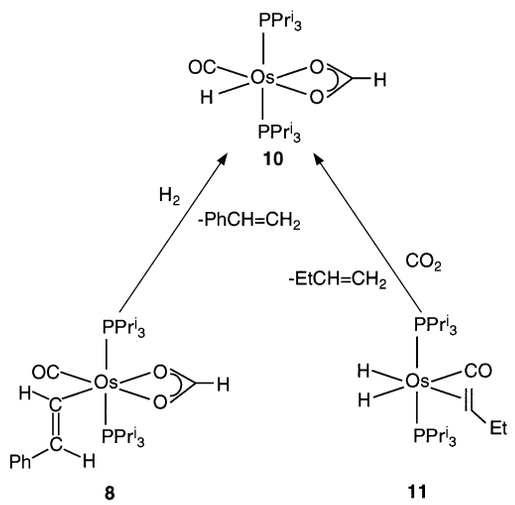
Passing a slow stream of carbon dioxide through a hexane solution of complex **2** affords the formato complex [Os{(*E*)-CH=CHPh}(η$^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] **8** (Scheme 7). This compound was isolated at −78 °C as a microcrystalline solid in 75% yield. The formation of **8** from the reaction of **2** with $CO_2$ is consistent with the proposal that in solution **2** is in equilibrium with no detectable concentrations of **6** (Scheme 4). Thus, the reaction can be easily rationalized as the transfer of the hydride ligand from **6** to the carbon atom of the $CO_2$ molecule.

The η$^2$ co-ordination mode of the formate ligand in complex **8** is indicated by the IR spectrum in Nujol, which contains bands at 1300 and 1560 cm$^{-1}$ assignable to the symmetric and asymmetric (OCO) stretching frequencies, respectively.[7] The value of the asymmetric ν(OCO) stretching is very similar to that of 1565 cm$^{-1}$ for [RuH(η$^2$-$O_2$CH)($PPh_3$)$_3$], which contains a chelating formate ligand as confirmed by X-ray diffraction.[8] This value is also in agreement with those previously reported for the complexes [MoH(η$^2$-$O_2$CH)(dppe)$_2$] (dppe = $Ph_2P$-$CH_2CH_2PPh_2$; 1550 cm$^{-1}$)[9] and [RuH(η$^2$-$O_2$CH){PhP[$CH_2CH_2$-$CH_2P(C_6H_{11})_2]_2$}] (1575 cm$^{-1}$).[10] Other characteristic bands are observed at 1900 and 1540 cm$^{-1}$ and were assigned to the ν(CO) and ν(C=C) stretchings, respectively. The $^1$H NMR spectrum in $C_6D_6$ shows resonances due to the triisopropylphosphine ligands and the phenyl group, along with a doublet at δ 9.09 ($J_{H-H}$ = 15.6 Hz), a triplet at δ 8.63 ($J_{P-H}$ = 1.9 Hz) and a doublet of triplets at δ 6.46 ($J_{H-H}$ = 15.6, $J_{P-H}$ < 1 Hz), which were assigned to the Os–CH=, $O_2$CH and =CHPh protons, respectively. The most noticeable signals in the $^{13}$C-{$^1$H} NMR spectrum are three triplets at δ 174.4 ($J_{P-C}$ = 1.4), 137.0 ($J_{P-C}$ = 9.7 Hz) and 132.8 ($J_{P-C}$ = 2.7 Hz). The triplet at δ 174.4 was assigned to the carbon atom of the formato group by comparison of this spectrum with that previously reported for the complex [Re(η$^2$-$O_2$CH)(dppe)$_2$] (δ 171.9).[11] The other two triplets were assigned to the $C_\alpha$ and $C_\beta$ carbon atoms of the vinyl ligand. The $^{31}$P-{$^1$H} NMR spectrum has a singlet at δ 15.6, indicating that the two phosphine ligands are equivalent and are mutually *trans* disposed.

Carbonylation of the bidentate formato complex **8** leads to formation of the monodentate formato derivative **9** (Scheme 8). The reaction was carried out in hexane, and complex **9** was isolated as a white solid in 83% yield. In agreement with the mutually *cis* disposition of the two carbonyl ligands, the IR spectrum in Nujol shows two ν(CO) absorptions at 2020 and 1940 cm$^{-1}$. Furthermore, the carboxylato region reflects the conversion of the formato group from bi- to mono-dentate. Thus the symmetric and asymmetric ν(OCO) stretchings appear at 1295 and 1625 cm$^{-1}$ in agreement with those of other monodentate formato species.[12] In the $^1$H NMR spectrum the




**Scheme 8**

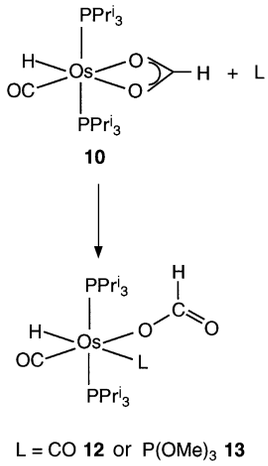



**Scheme 9**

formato proton gives a singlet at δ 8.11. The α-vinyl proton appears at δ 8.68 as a doublet of triplets with a H–H coupling constant of 17.0 Hz and a P–H coupling constant <1 Hz, whereas the proton in β position is masked by the $C_6D_6$ signal. In the $^{13}$C-{$^1$H} NMR spectrum the carbon atom of the formate ligand appears at δ 168.4 as a singlet, while the $C_\beta$ and $C_\alpha$ carbon atoms of the styryl ligand display triplets, at δ 143.2 ($J_{P-C}$ = 2.3) and 140.0 ($J_{P-C}$ = 4.6 Hz), respectively. The $^{31}$P-{$^1$H} NMR spectrum shows a singlet at δ 9.3.

Under a hydrogen atmosphere complex **8** quantitatively yields styrene and the hydridoformato complex [OsH(η$^2$-$O_2$CH)(CO)(PPr$^i_3$)$_2$] **10**,[13] which can be also prepared in 82% yield by bubbling carbon dioxide through a hexane solution of the dihydrido complex [$OsH_2$(η$^2$-$CH_2$=CHEt)(CO)(PPr$^i_3$)$_2$] **11** (Scheme 9). As for **8**, the bidentate formate ligand of **10** is converted into a monodentate group by carbonylation. Thus, the reaction of **10** with carbon monoxide affords [OsH{η$^1$-OC(O)H}$(CO)_2$(PPr$^i_3$)$_2$] **12**. Similarly, the addition of a stoichiometric amount of $P(OMe)_3$ to a hexane solution of **10** yields [OsH{η$^1$-OC(O)H}(CO)}(CO){P(OMe)$_3$}(PPr$^i_3$)$_2$] **13** (Scheme 10). The behaviour of **10** towards carbon monoxide contrasts to that previously reported for the related ruthenium compound [RuH(η$^2$-$O_2$CH)$(PPh_3)_3$], which reacts with CO to give [$RuH_2$(CO)$(PPh_3)_3$] and $CO_2$.[8]

Complex **12** was isolated as a white solid in 82% yield. The monohapto nature of the formate ligand is supported by the values of the symmetric and asymmetric ν(OCO) stretchings, in the IR spectrum in Nujol, which appear at 1370 and 1643 cm$^{-1}$ respectively. In the 2000 cm$^{-1}$ region the spectrum shows three



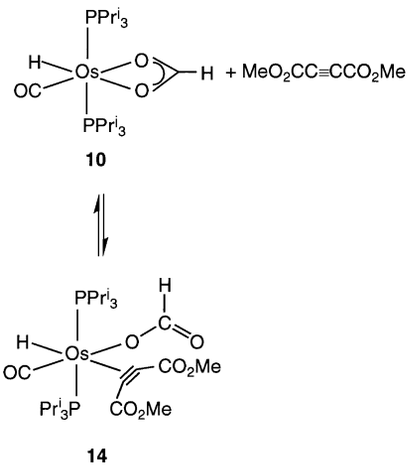

**Scheme 10**

bands, at 2050, 1975 and 1915 cm$^{-1}$. The first band was assigned to the ν(Os–H) absorption, and the other two to ν(CO) absorptions, in agreement with a *cis* arrangement of these ligands. In the $^1$H NMR spectrum in $C_6D_6$ the hydride ligand appears at δ −4.29 as a triplet with a P–H coupling constant of 21.0 Hz. The chemical shift of this signal is very close to that previously reported for the hydride ligand disposed *trans* to a carbonyl group in the complex [OsH(Cl)$(CO)_2$(PPr$^i_3$)$_2$] (δ −4.70).[14] The proton of the formato group gives rise to a singlet at δ 7.88. The $^{31}$P-{$^1$H} NMR spectrum shows a singlet at δ 29.1.

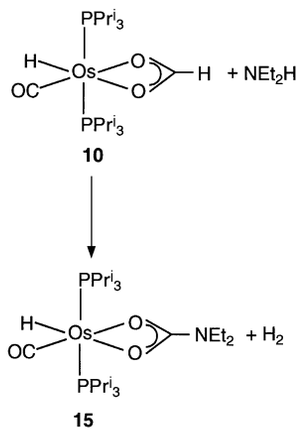
Complex **13** was isolated as a white solid in 80% yield. The IR spectrum in Nujol shows the symmetric and asymmetric ν(OCO) stretchings at 1380 and 1650 cm$^{-1}$. The $^{31}$P-{$^1$H} NMR contains a triplet at δ 102.9 [$P(OMe)_3$] and a doublet at δ 20.8 (PPr$^i_3$). The value of the P–P coupling constant is 17.9 Hz. The proposed *trans* disposition of hydride and phosphite ligands is supported by the $^1$H NMR spectrum in $C_6D_6$, which contains a doublet of triplets at δ −6.30, with P–H coupling constants of 149.0 and 23.8 Hz. The proton of the formato group appears at δ 8.37 as a singlet.

Attempts to prepare complex **8** by reaction of **10** with phenylacetylene were unsuccessful. Complex **10** is not only inert towards phenylacetylene but also towards cyclohexylacetylene and methyl propiolate. However, addition of the stoichiometric amount of methyl acetylenedicarboxylate to a hexane suspension of **10** leads to a white solid in 80% yield, which was characterized as the π-alkyne compound [OsH{η$^1$-OC(O)H}(η$^2$-$MeO_2CC{\equiv}CCO_2Me$)(CO)(PPr$^i_3$)$_2$] **14**. The π co-ordination of the alkyne is strongly supported by the IR spectrum of **14** in Nujol which shows a strong absorption at 1880 cm$^{-1}$, characteristic of a ν(C≡C) vibration.[15] Furthermore, the spectrum contains bands at 2040, 1955 and 1710 cm$^{-1}$, which were assigned to ν(Os–H), ν(CO) (carbonyl ligand) and ν(CO) ($CO_2$Me groups of the alkyne), along with the asymmetric and symmetric ν(OCO) vibrations of the monodentate formate ligand, at 1620 and 1375 cm$^{-1}$ respectively.

According to the $^1$H, $^{13}$C-{$^1$H} and $^{31}$P-{$^1$H} NMR spectra of complex **14**, in solution, this compound partially dissociates the alkyne (Scheme 11). At room temperature in $C_6D_6$ the **14**:**10** molar ratio is 1:1. Characteristic signals for **14** in the $^1$H NMR spectrum are two singlets at δ 7.63 and 3.74, and a triplet with a P–H coupling constant of 28.3 Hz at δ −2.28. The singlets were assigned to the $O_2$CH and $CO_2CH_3$ protons, respectively, and the triplet to the hydride ligand. The chemical shift of this ligand agrees well with that previously reported for the complex [OsH(Cl)(η$^2$-$MeO_2CC{\equiv}CCO_2Me$)(CO)(PPr$^i_3$)$_2$] (δ −2.80), where a *trans* disposition of the hydride and π-alkyne ligands has also been proposed.[16] In contrast to the behaviour of the related chloro-derivative, insertion of the alkyne into the osmium–hydride bond of **14** is not observed. In the $^{13}$C-{$^1$H}




**Scheme 11**

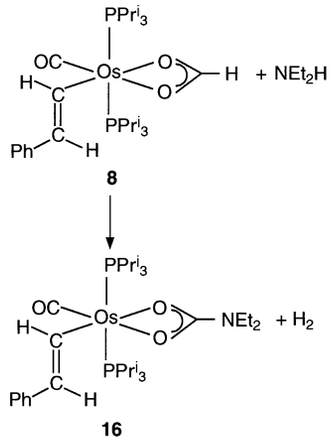



**Scheme 12**

NMR spectrum the acetylenic carbon atoms appear at δ 107.3 as a triplet with a P–C coupling constant of 3.3 Hz. The resonance due to the carbon atom of the formato group is observed at δ 166.2, as a triplet with a P–C coupling constant of 5.3 Hz. A singlet at δ 30.8 in the $^{31}$P-{$^1$H} NMR spectrum is also characteristic of **14**.

The carbon atom of the formate ligand of complex **10** is an electrophilic centre susceptible to attack by nucleophiles. Addition of 1 equivalent of diethylamine to a NMR tube containing a $C_6D_6$ solution of **10** yields, after 1 h at 60 °C, the carbamato derivative [OsH(η$^2$-O$_2$CNEt$_2$)(CO)(PPr$^i_3$)$_2$] **15** in quantitative yield, (Scheme 12). The $^1$H NMR spectrum of **15** exhibits two quartets at δ 3.14 and 3.02 and two triplets at δ 0.95 and 0.91, corresponding to two inequivalent ethyl groups. The inequivalence of the ethyl groups of the carbamate ligand indicates that the molecule has no mirror plane of symmetry containing the P–Os–P unit, in agreement with the structure shown. The hydride ligand appears at δ −20.37 as a triplet with a P–H coupling constant of 16.2 Hz. In the $^{13}$C-{$^1$H} NMR spectrum the ethyl groups display four singlets, two for the $CH_2$ carbon atom at δ 39.3 and 39.0 and two for the $CH_3$ carbon atoms at δ 14.2 and 14.2. The central carbon atom of the carbamato group appears at δ 165.4. The chemical shift of this resonance compares well with those previously reported for related compounds (δ 170–160).[17] The $^{31}$P-{$^1$H} NMR spectrum shows a singlet at δ 38.4.

The $^1$H, $^{13}$C-{$^1$H} and $^{31}$P-{$^1$H} NMR spectra of the solution formed by addition of *ca*. 1 equivalent of diethylamine to complex **8** in $C_6D_6$ show, after 3 h at room temperature, the presence of styrene and resonances that were assigned to the complexes **8**(41), **10**(10), **15**(12) and the styrylcarbamato derivative [Os{(*E*)-CH=CHPh}(η$^2$-O$_2$CNEt$_2$)(CO)(PPr$^i_3$)$_2$] **16** (37%), by comparison of these spectra with those recorded for **8**, **10** and **15**. After 24 h at room temperature the composition consists of only **15**(60) and **16**(40%). Bubbling molecular hydrogen through this solution does not affect the **15**:**16** molar ratio, even after 6 h. These results can be rationalized according to schemes 9, 12 and 13. As for **10**, the carbon atom of the formate ligand of **8** is susceptible to attack by nucleophiles. Thus, the reaction of this complex with diethylamine leads to the styrylcarbamato derivative **16** (Scheme 13). The molecular hydrogen generated from the nucleophilic substitution reacts with **8** to give **10** and styrene (Scheme 9). Complex **10** then reacts further with the amine to afford **15** and molecular hydrogen (Scheme 12).



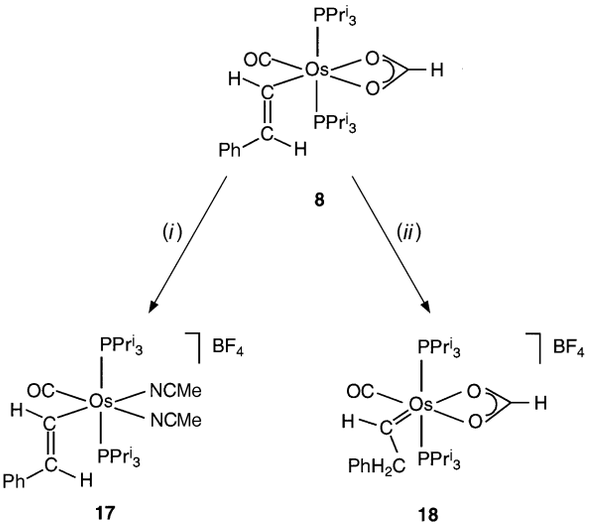

**Scheme 13**

In the $^1$H NMR spectrum the most noticeable signals for complex **16** are those corresponding to the styryl and carbamate ligands. The vinyl protons of the styryl ligand display a doublet at δ 9.37 with a H–H coupling constants of 15.6 Hz, and a doublet of triplets at δ 6.57 with a P–H coupling constant < 1 Hz, assigned to the α- and β-proton respectively. Similarly to **15**, the ethyl protons of the carbamate ligand appear as two quartets at δ 3.14 and 3.04 and two triplets at δ 0.93 and 0.91. In the $^{13}$C-{$^1$H} NMR spectrum the central carbon atom of the carbamato group appears as a singlet at δ 165.0, the α-carbon atom of the styryl ligand appears at δ 138.7 as a triplet with a P–C coupling constant of 7.7 Hz, and the β-carbon atom gives rise to a broad singlet at δ 132.3. A singlet at δ 16.1 in the $^{31}$P-{$^1$H} NMR spectrum is also characteristic of **16**.

### Protonation of complexes 8 and 10

Complex **8** also reacts with HBF$_4$·OEt$_2$, leading to different derivatives depending upon the conditions. In diethyl ether as solvent one of the two oxygen atoms of the formate ligand undergoes electrophilic attack of the proton of the acid to give the unsaturated [Os{(*E*)-CH=CHPh}(CO)(PPr$^i_3$)$_2$]$^+$ fragment, which can be trapped as [Os{(*E*)-CH=CHPh}(CO)(MeCN)$_2$-(PPr$^i_3$)$_2$]BF$_4$ **17** in the presence of acetonitrile. While, in chloroform as solvent, electrophilic attack of the proton takes place at the β-carbon atom of the styryl ligand. In this case the compound formed is the carbene derivative [Os(η$^2$-O$_2$CH)-(=CHCH$_2$Ph)(CO)(PPr$^i_3$)$_2$]BF$_4$ **18** (Scheme 14).

Complex **17** was isolated as a white solid in 80% yield. The IR spectrum in Nujol shows the absorption due to the [BF$_4$]$^-$ anion with $T_d$ symmetry, at about 1100 cm$^{-1}$ indicating that this anion is not co-ordinated to the metal. Consistent with the mutually *cis* disposition of the acetonitrile ligands, the $^1$H NMR spectrum shows two singlets for their protons, at δ 2.68 and 2.57. The α-vinylic proton of the styryl group appears at δ 8.28 as a doublet with a H–H coupling constant of 17.3 Hz, while the β-vinylic proton appears at δ 6.42 as a doublet of triplets with a P–H coupling constant 1 Hz. In the $^{13}$C-{$^1$H} NMR spectrum the acetonitrile ligands also give rise to two singlets at δ 126.0 and 125.5. The $C_\alpha$ and $C_\beta$ atoms of the vinyl




**Scheme 14** (*i*) $HBF_4$, MeCN, $Et_2O$; (*ii*) $HBF_4$, $CHCl_3$

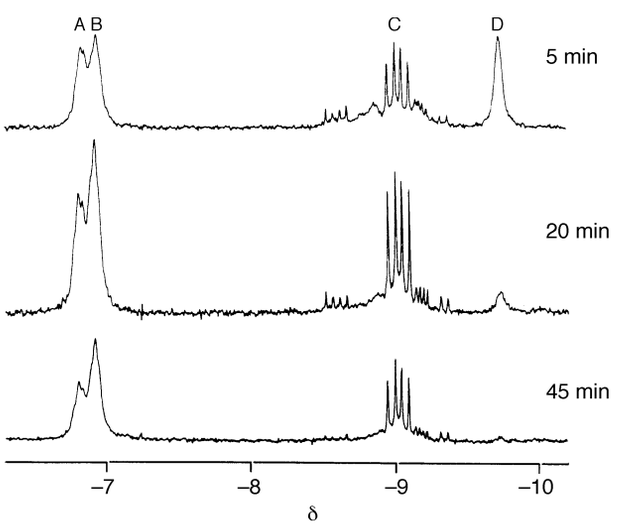



**Fig. 1** Proton NMR spectrum ($CDCl_3$) of the mixture resulting from the reaction of [OsH(η$^2$-$O_2$CH)(CO)(PPr$^i_3$)$_2$] **10** with $HBF_4$·$OEt_2$ in the hydrido region, at different reaction times

ligand display triplets at δ 132.7 and 136.2, with P–C coupling constants of 8.9 and 3.0 Hz, respectively. The $^{31}$P-{$^1$H} NMR spectrum contains a singlet at δ 3.1.

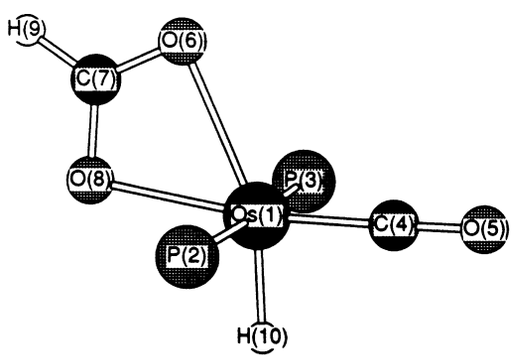
Complex **18** was isolated as a green oil in quantitative yield, and was characterized in solution by IR, $^1$H, $^{13}$C-{$^1$H} and $^{31}$P-{$^1$H} NMR spectroscopy. The IR spectrum in dichloromethane shows two bands at 1560 and 1355 cm$^{-1}$, supporting the bidentate co-ordination of the formato group. The presence of a carbene ligand was inferred from the $^1$H and $^{13}$C-{$^1$H} NMR spectra in $CDCl_3$. The $^1$H NMR spectrum contains at δ 17.63 a triplet with a H–H coupling constant of 6.1, and at δ 3.52 a doublet with the same H–H coupling constant. These resonances were assigned to the Os=CH and C*H*$_2$Ph protons, respectively. The proton of the formato group appears at δ 9.19, as a singlet. In the $^{13}$C-{$^1$H} spectrum the $C_\alpha$ carbon atom of the carbene ligand appears at δ 290.8 as a broad signal. The carbon atom of the formato group gives rise to a singlet at δ 168.7. The $^{31}$P-{$^1$H} NMR spectrum contains a singlet at δ 38.3.

The reaction of complex **10** with $HBF_4$·$OEt_2$ also leads to different derivatives depending upon the conditions. Similarly to **8**, in diethyl ether as solvent, the reaction produces a very unsaturated [OsH(CO)(PPr$^i_3$)$_2$]$^+$ fragment, which can be trapped with acetonitrile to afford the previously reported compound [OsH(CO)(MeCN)$_2$(PPr$^i_3$)$_2$]$BF_4$ **19**.[18] However, in $CDCl_3$ the electrophilic attack of the proton occurs at the hydride ligand and/or at the metal to give a mixture of products. Fig. 1 shows the high-field region of the $^1$H NMR spectrum at different reaction times. After 5 min the spectrum mainly contains four signals A–D. After 45 min signal D disappears, and the B : A intensity ratio increases. A variable-temperature 300 MHz $T_1$ study of the peaks A–C gave $T_{1(min)}$ values of 17, 21 and 260 ms, respectively, suggesting that A and B correspond to dihydrogen compounds, while C is due to a dihydrido derivative. The correlation of the spectra shown in Fig. 1 with the $^{31}$P-{$^1$H} NMR spectra registered at the same reaction times (5, 20 and 45 min) indicates that the signals A and B are related with singlets at δ 25.6 and 41.8, respectively, while the D may be related with a broad resonance centred at δ 35.6. The signal C could not be clearly correlated.

In order to cast light on the nature and structure of the products of the reaction of complex **10** with $HBF_4$·$OEt_2$ in $CDCl_3$, *ab initio* theoretical calculations have been carried out. They were performed at the Møller–Plesset Perturbatia (MP)2 and 4 levels using $PH_3$ in place of the triisopropylphosphine ligand. The geometry optimizations were carried out at the MP2 level. Fig. 2 shows a plot of the optimized structure for the complex [OsH(η$^2$-$O_2$CH)(CO)(PH$_3$)$_2$] **10a**. The most significant parameters are included in Table 1. As expected the co-

**Table 1** Selected geometrical parameters (Å and °) of the MP2 optimized structures. The atom numbering is that defined in Figs. 2 and 3; X corresponds to a point at the centre of the straight line between H(10) and H(11)

| | Structure | | | | |
|---|---|---|---|---|---|
| | **10a** | **20a** | **21a** | **22a** | **23a** |
| Os(1)–P(2) | 2.404 | 2.460 | 2.482 | 2.484 | 2.489 |
| Os(1)–P(3) | 2.404 | 2.460 | 2.476 | 2.502 | 2.495 |
| Os(1)–C(4) | 1.837 | 1.876 | 1.839 | 1.936 | 1.889 |
| Os(1)–O(6) | 2.419 | 2.156 | 1.979 | 1.987 | 2.000 |
| Os(1)–O(8) | 2.253 | 2.244 | 3.390 | 3.463 | 3.460 |
| Os(1)–H(10) | 1.588 | 1.688 | 1.728 | 1.594 | 1.603 |
| Os(1)–H(11) | — | 1.688 | 1.729 | 1.594 | 1.592 |
| Os(1)–X | — | 1.623 | 1.669 | 0.810 | 1.400 |
| H(10)–H(11) | — | 0.930 | 0.894 | 2.745 | 1.534 |
| P(2)–Os(1)–P(3) | 172.4 | 169.3 | 170.1 | 170.3 | 165.2 |
| P(2)–Os(1)–C(4) | 93.6 | 93.0 | 90.8 | 103.6 | 98.2 |
| P(2)–Os(1)–O(6) | 89.9 | 84.9 | 89.9 | 93.9 | 90.6 |
| P(2)–Os(1)–X | — | 94.5 | 93.8 | 53.3 | 96.7 |
| C(4)–Os(1)–O(6) | 114.1 | 104.8 | 110.6 | 162.5 | 150.9 |
| C(4)–Os(1)–X | — | 94.5 | 93.8 | 53.3 | 96.7 |
| C(4)–Os(1)–O(6) | 114.1 | 104.8 | 110.6 | 162.5 | 150.9 |
| C(4)–Os(1)–X | — | 89.0 | 88.2 | 50.3 | 81.9 |
| O(6)–Os(1)–X | — | 166.2 | 160.8 | 147.2 | 127.0 |
| H(10)–Os(1)–H(11) | — | 32.0 | 30.0 | 118.9 | 57.4 |




**10a**

**Fig. 2** The MP2 optimized geometry of the reactant species [OsH(η$^2$-$O_2$CH)(CO)(PH$_3$)$_2$] **10a**. Hydrogen atoms of phosphine ligands are omitted for clarity

**Table 2** The MP2 and MP4 relative energies (kcal $mol^{-1}$) of different isomers of $[OsH_2(O_2CH)(CO)(PH_3)_2]^+$. Geometries are optimized at the MP2 level

| | Geometry | | | |
|---|---|---|---|---|
| | **20a** | **21a** | **22a** | **23a** |
| MP2 | 0.00 | 15.97 | 12.00 | 11.87 |
| MP4 | 0.00 | 15.91 | 12.42 | 12.36 |

ordination geometry around the metal is distorted octahedral. The distortion is due to the small angle of the bidentate formato group [O(6)–Os(1)–O(8) 57.9°].

Since protonation of complex **10** leads a mixture of products containing dihydrogen and dihydride ligands, all the reasonable dihydrogen and dihydrido structures containing the formate ligand co-ordinated in mono- or di-hapto manner, and with the phosphine ligands mutually *trans* disposed, were considered.* The MP2 optimizations lead to the species **20a**–**23a**, presented in Fig. 3. The most significant geometrical parameters are collected in Table 1, with MP2 and MP4 relative energies in Table 2.

The theoretical calculations suggest that two dihydrogen and two dihydrido derivatives are possible. Thermodynamically, the most stable complex is the six-co-ordinated $\eta^2$-formato (dihydrogen) **20a**, where the two hydrogen atoms of the dihydrogen ligand are separated by 0.930 Å. Its stability is in agreement with its nature as a $d^6$ $ML_6$ complex. According to Fig. 1, the most stable species displays signal B, which shows a $T_{1(min)}$ value of 21 ms at 300 MHz. This value corresponds to a hydrogen–hydrogen distance of 0.94 Å (fast spinning).† So we propose that signal B is characteristic of the $\eta^2$-formato (dihydrogen) cation $[Os(\eta^2\text{-}O_2CH)(\eta^2\text{-}H_2)(CO)(PPr^i_3)_2]^+$ **20**.

Signal A is also characteristic of a dihydrogen derivative, its $T_{1(min)}$ value (17 ms at 300 MHz) corresponding to a hydrogen–hydrogen distance of 0.90 Å (fast spinning). Species **21a** has a square-pyramidal structure (Fig. 3) with a larger distortion corresponding to the C(4)–Os(1)–O(6) angle (110.6°, Table 1). It is a dihydrogen complex [H(10)–H(11) 0.894 Å], and its nature as a monodentate formate compound is indisputable [Os(1)···O(8) 3.390 Å]. Thus, at first glance, one could propose that signal A corresponds to a five-co-ordinate $\eta^1$-formato (dihydrogen) derivative with the carbonyl group in the apical position. However, it should be noted that (*i*) **20a** is 15.91 kcal $mol^{-1}$ more stable than **21a** and (*ii*) a high kinetic barrier would not be expected for the $\eta^1$-formato ⟶ $\eta^2$-formato transformation. Hence, we believe that this signal corresponds to a six-co-ordinate $\eta^1$-formato (dihydrogen) species, stabilized by co-ordination of a diethyl ether molecule (**21**), originating from the $HBF_4{\cdot}OEt_2$ solution used in the reaction. The co-ordination of the ether molecule *cis* to the dihydrogen ligand should increase the kinetic barrier for the $\eta^1$-formato ⟶ $\eta^2$-formato transformation without affecting the metal–dihydrogen interaction and, therefore, the hydrogen–hydrogen separation.

Signal C is characteristic of a dihydrido derivative containing non-equivalent phosphine ligands. The $T_{1(min)}$ value for this signal is 260 ms at 300 MHz. Complex **22a** is not octahedral [H(10)–Os(1)–H(11) 118.9°] but a bicapped tetrahedron, a co-ordination polyhedron characteristic for $d^4$ $ML_6$ complexes.[21,22] The bicapped tetrahedron **22a** contains non-equivalent phosphine ligands [Os(1)–P(2) 2.484, Os(1)–P(3) 2.502 Å], and they

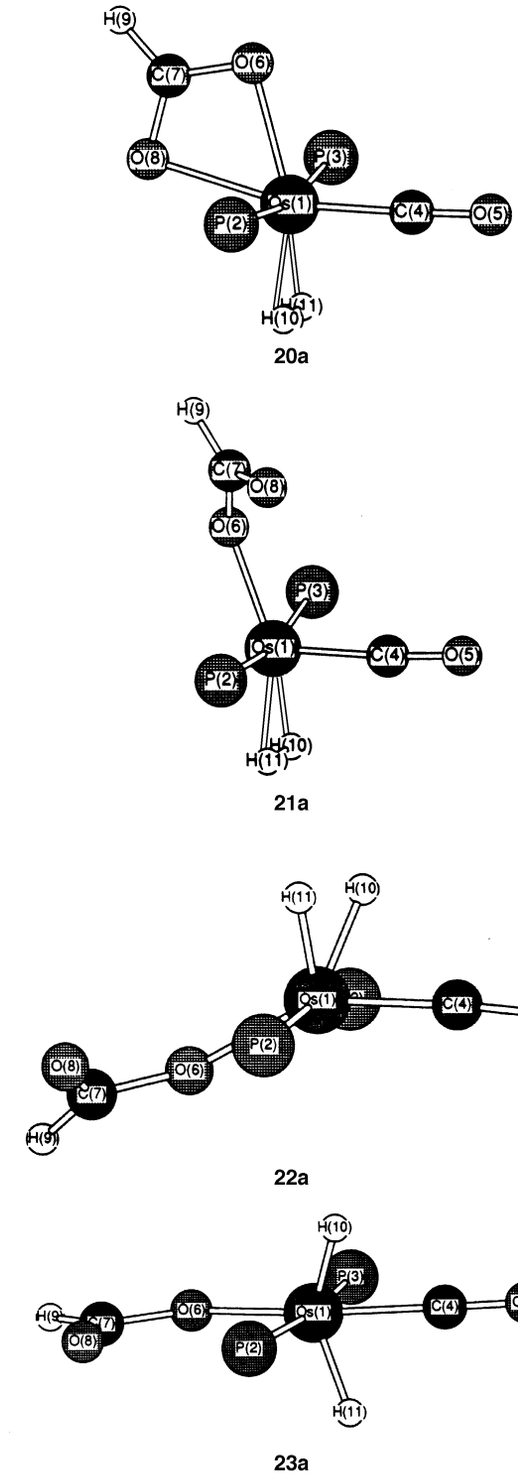


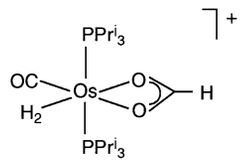

**Fig. 3** The MP2 optimized geometries of the dihydrogen complexes $[Os(\eta^2\text{-}O_2CH)(\eta^2\text{-}H_2)(CO)(PH_3)_2]^+$ **20a** and $[Os\{\eta^1\text{-}OC(O)H\}(\eta^2\text{-}H_2)(CO)(PH_3)_2]^+$ **21a** and of the dihydrido complexes $[OsH_2\{\eta^1\text{-}OC(O)H\}(CO)(PH_3)_2]^+$ **22a** and **23a**. Hydrogen atoms of phosphine ligands are omitted for clarity

cannot be interconverted through reorientation of the formate ligand. The hydrogen–hydrogen separation in **22a** is 2.745 Å. For this distance a $T_{1(min)}$ value of 224 ms at 300 MHz‡ is expected. The experimental properties of signal C seem well suited to that inferred for **22a** from the theoretical calculations. So, we correlate it to the derivative $[OsH_2\{\eta^1\text{-}OC(O)$-

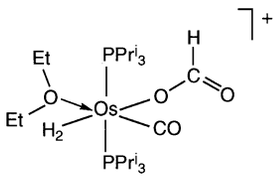
* The mutually *trans* disposition for the phosphine ligands is a reasonable assumption in the view of the steric demands of the $PPr^i_3$ ligand. Trigonal-bipyramidal geometries were not considered because they are not likely in $d^6$ $ML_5$ species like this one.[19]

† At the temperature of minimum $T_1$, $\tau = 0.62/2\pi\nu$, and the equation for dipolar relaxation simplifies to $r_{H-H} = 4.611\ (T_{1min}/\nu)^{\frac{1}{6}}$ for rapid rotation ($\nu$/MHz, $T_1$/s).[20]

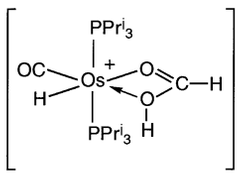
‡ It has been recently shown that, for polyhydrido complexes, $T_{1(min)}$ can be calculated by using internuclear distances obtained from neutron, X-ray diffraction[23a] and theoretical studies.[23b]



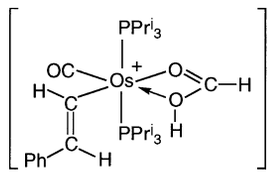
**20**



**21**



**24**



**25**

H}(CO)($PPr^i_3$)$_2$]$^+$ **22**, which may have the structure shown in Fig. 3.

Signal D rapidly disappears, and it cannot be studied. It may be assigned to species **23a**.

The reactions of complex **10** with $HBF_4$·$OEt_2$ to give **19**, and **20**, and **21**, as well as the protonations of **8** to afford **17** and **18**, can be rationalized *via* the intermediates **24** and **25**. The electrophilic attack of the proton could initially take place at one of the two oxygen atoms of the formate ligands of both **10** and **8**. Thus, in the presence of acetonitrile the displacement of the resulting formic acid by the nitrogen-donor ligand should yield **19** and **17**, while in the absence of this ligand the transfer of the proton from the oxygen atom to the hydride and vinyl ligands could afford the thermodynamically more stable compounds **21** and **18**.

## Conclusion

This study has shown that the reaction of the five-co-ordinate compound [Os{(*E*)-CH=CHPh}Cl(CO)($PPr^i_3$)$_2$] **1** with $LiBu^n$ leads to [OsH{$C_6H_4$(CH=CH)}(CO)($PPr^i_3$)$_2$] **2** in equilibrium with the co-ordinatively unsaturated complex [OsH{(*E*)-CH=CHPh}(CO)($PPr^i_3$)$_2$] **6**. Complexes **2** and **6** are connected by the osmium(0) intermediate [Os($\eta^2$-$CH_2$=CHPh)(CO)($PPr^i_3$)$_2$] **7**, which gives rise to C–H activation reactions in the terminal olefinic and the *ortho*-phenyl C–H bonds of the co-ordinated styrene. Complex **6** cannot be detected in solution, most probably due to the higher stability of its 18-electron isomer **2**. However, the reactivity of **2** can easily be understood as a result of the reactions of the more labile isomer **6**. Thus, the formato complex [Os{(*E*)-CH=CHPh}($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] **8**, formed by passing a slow stream of carbon dioxide through a hexane solution of **2**, can be rationalized from the insertion of the $CO_2$ molecule into the Os–H bond of **6**. Hydrogenation of **8** gives styrene and the hydrido complex [OsH($\eta^2$-$O_2$CH)(CO)($PPr^i_3$)$_2$] **10**.

The reactivity of complexes **8** and **10** towards CO, $NEt_2H$ and $HBF_4$ has been also studied. By carbonylation, the bidentate formate ligand of these compounds becomes monodentate. In the presence of diethylamine, the central carbon atoms of the bidentate formato groups undergo nucleophilic attack affording the carbamato derivatives [OsR($\eta^2$-$O_2CNEt_2$)(CO)($PPr^i_3$)$_2$] (R = H **15** or CH=CHPh **16**). The reactions of **8** and **10** with $HBF_4$ lead to different derivatives depending upon the conditions. In diethyl ether as solvent the formato groups of both compounds undergo electrophilic attack by protons to give fragments of the type [OsR(CO)($PPr^i_3$)$_2$]$^+$ (R = H or CH=CHPh), which can be trapped in the presence of acetonitrile. In chloroform, complex **8** leads to the carbene [Os($\eta^2$-$O_2$CH)(=CHC$H_2$Ph)(CO)($PPr^i_3$)$_2$]$^+$ **18**, and **10** gives a mixture of products, mainly dihydrogen derivatives. On the basis of theoretical calculations and $T_1$ measurements, we propose that these derivatives could be the cations [Os($\eta^2$-$O_2$-CH)($\eta^2$-$H_2$)(CO)($PPr^i_3$)$_2$]$^+$ **20** and [Os{$\eta^1$-OC(O)H}($\eta^2$-$H_2$)-($Et_2O$)(CO)($PPr^i_3$)$_2$]$^+$ **21**.

## Experimental

All reactions were carried out with rigorous exclusion of air by using Schlenk-tube techniques. Solvents were dried by known procedures and distilled under argon prior to use.

### Physical measurements

Infrared spectra were recorded as Nujol mulls on polyethylene sheets or NaCl cell windows using a Perkin-Elmer 883 or a Nicolet 550 spectrometer, NMR spectra on a Varian UNITY 300 or Brucker 300 AXR spectrometer. Proton and $^{13}$C-{$^1$H} chemical shifts were measured relative to partially deuteriated solvent peaks but are reported relative to tetramethylsilane, $^{31}$P-{$^1$H} chemical shifts relative to external 85% $H_3PO_4$. Coupling constants $J$ and $N$ [= $J$(PH) + $J$(P′H) for $^1$H, $J$(PC) + $J$(P′C) for $^{13}$C] are given in Hz. The C, H and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyser. The starting materials [Os{(*E*)-CH=CHPh}Cl(CO)($PPr^i_3$)$_2$] **1** and [$OsH_2$($\eta^2$-$CH_2$=CHEt)(CO)($PPr^i_3$)$_2$] **11** were prepared by published methods.[5,6] The deuteriated complexes [Os{(*E*)-CH=CDPh}Cl(CO)($PPr^i_3$)$_2$] **1a** and [Os{(*E*)-CD=CHPh}Cl(CO)-($PPr^i_3$)$_2$] **1b** were prepared by reaction of [OsD(Cl)(CO)($PPr^i_3$)$_2$] with PhC≡CH and [OsH(Cl)(CO)($PPr^i_3$)$_2$] with PhC≡CD, respectively.

### Preparations

**[OsH{$C_6H_4$(CH=CH)}(CO)($PPr^i_3$)$_2$] 2.** A solution of [Os{(*E*)-CH=CHPh}Cl(CO)($PPr^i_3$)$_2$] **1** (100 mg, 0.15 mmol) in hexane (5 cm$^3$) was treated with $LiBu^n$ (0.01 cm$^3$, 1.6 mol dm$^{-3}$ solution in hexane) and stirred during *ca*. 5 min at room temperature. The mixture changed from dark blue to pale yellow. The resulting suspension was filtered through Kieselguhr and the filtrate was dried *in vacuo* to give a colourless oil. NMR ($C_6D_6$, 20 °C): $^1$H, δ 7.26 (d, $J_{H-H}$ = 7.1, 1 H, $H_{Ph}$), 7.03 (t, $J_{H-H}$ = 7.1, 1 H, $H_{Ph}$), 6.90 (t, $J_{H-H}$ = 7.1, 1 H, $H_{Ph}$), 6.56 (d, $J_{H-H}$ = 7.1, 1 H, $H_{Ph}$), 4.95 (dd, $J_{H-H}$ = 9.0, *J* 7.7, 1 H, CH=), 3.71 (dt, $J_{H-H}$ = 9.0, $J_{P-H}$ = 5.7, 1 H, =$CH_2$), 2.74 (d, $J_{H-H}$ = 7.7, 1 H, =$CH_2$), 2.15 (m, 6 H, PC*H*$CH_3$), 1.05 (dvt, *N* = 13.5, $J_{H-H}$ = 6.3, 36 H, PCHC$H_3$) and −8.01 (t, $J_{P-H}$ = 27.3, 1 H, OsH); $^{13}$C-{$^1$H}, d 187.9 (t, $J_{P-C}$ = 8.0, CO), 152.2 (t, $J_{P-C}$ = 2.0, $C_{Ph}$), 138.6 (t, $J_{P-C}$ = 10.0, $C_{Ph}$), 135.8 (br, $CH_{Ph}$), 126.1 (br, $CH_{Ph}$), 122.9 (br, $CH_{Ph}$), 121.0 (br, $CH_{Ph}$), 50.5 (br, CH=), 46.3 (br, =$CH_2$), 26.6 (vt, *N* = 26.4 Hz, P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$) and 20.0 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 16.7 (s).

**[OsH{(*E*)-CH=CHPh}(CO){P(OMe)$_3$}($PPr^i_3$)$_2$] 3.** A solution of complex **1** (100 mg, 0.15 mmol) in hexane (5 cm$^3$) was treated with $LiBu^n$ (0.01 cm$^3$, 1.6 mol dm$^{-3}$ solution in hexane) and stirred during *ca*. 5 min at room temperature. The resulting suspension was filtered through Kieselguhr and treated with $P(OMe)_3$ (17 μl, 0.15 mmol). After 30 min of reaction a white solid was formed, decanted, washed with hexane and dried *in vacuo*. Yield 95.7 mg (85%) (Found: C, 47.5; H, 8.2. Calc. for $C_{30}H_{59}O_4OsP_3$: C, 47.0; H, 7.75%). IR (Nujol, cm$^{-1}$): ν(Os–H) 2050s, ν(CO) 1910s, ν(C=C) 1540m. NMR ($C_6D_6$, 20 °C): $^1$H, δ 8.78 (tq, $J_{H-H}$ = 18.3, $J_{P-H}$ = 18.3, $J_{H-H}$ 1.6 Hz, $J_{H-H}$ = 1.6, 1 H, OsC*H*=CHPh), 7.46 (d, $J_{H-H}$ = 7.3, 2 H, *o*-H of Ph), 7.23 (t, $J_{H-H}$ = 7.3, 2 H, *m*-H of Ph), 7.03 (dt, $J_{H-H}$ = 18.3, $J_{P-H}$ = 2.5, 1 H, OsCH=C*H*Ph), 6.96 (t, $J_{H-H}$ = 7.3, 1 H, *p*-H of Ph, 3.39 (d, $J_{P-H}$ = 10.1, 9 H, POMe), 2.47 (m, 6 H, PC*H*CH$_3$), 1.27 (dvt, *N* = 14.0, $J_{H-H}$ = 7.1 18 H, PCHC$H_3$), 1.20 (dvt, *N* = 11.9,

$J_{H-H}$ = 7.1 18 H, PCHC$H_3$) and −8.94 (dtd, $J_{P-H}$ = 134.4, $J_{P-H}$ = 24.5, $J_{H-H}$ = 1.6, 1 H, OsH); $^{13}$C-{$^1$H}, δ 190.8 (vq, $J_{P-C}$ = 8.3 CO), 145.3 (t, $J_{P-C}$ = 2.3 *ipso*-C of Ph), 144.4 (dt, $J_{P-C}$ = 10.1, 4.2, OsCH=*C*HPh), 143.3 (vq, $J_{P-C}$ = 13.4, Os*C*H=CHPh), 128.6 (s, *o*-CH of Ph), 124.4 (s, *m*-CH of Ph), 124.0 (s, *p*-CH of Ph), 51.6 (d, $J_{P-C}$ = 8.8 PO*Me*), 26.0 (vtd, *N* = 26.8, $J_{P-C}$ = 2.3, P*C*HCH$_3$), 20.8 (s, PCH*C*H$_3$) and 18.7 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 102.4 (t, $J_{P-P}$ = 18.6 POMe) and 17.5 (d, $J_{P-P}$ = 18.6 Hz, PPr$^i_3$).

**[OsH{(*E*)-CH=CHPh}(CO)$_2$(PPr$^i_3$)$_2$] 4.** A solution of complex **1** (100 mg, 0.15 mmol) in hexane (5 cm$^3$) was treated with LiBu$^n$ (0.01 cm$^3$, 1.6 mol dm$^{-3}$ solution in hexane) and stirred during *ca*. 5 min at room temperature. The resulting suspension was filtered through Kieselguhr and a slow stream of carbon monoxide was bubbled through it. After 30 min of reaction a white solid was formed, decanted, washed with hexane and dried *in vacuo*. Yield 74 mg (72%) (Found: C, 50.6; H, 8.4. Calc. for $C_{28}H_{50}O_2OsP_2$: C, 50.15; H, 7.55%). IR (Nujol, cm$^{-1}$): ν(OsH) 1990s, ν(CO) 1945s, 1865s, 1570m, ν(C=C). NMR ($C_6D_6$, 20 °C): $^1$H, δ 8.34 (br d, $J_{H-H}$ = 16.1, 1 H, OsC*H*=CHPh), 7.41 (d, $J_{H-H}$ = 7.3, 2 H, *o*-H of Ph), 7.23, (t, $J_{H-H}$ = 7.3, 2 H, *m*-H of Ph), 7.20 (d, $J_{H-H}$ = 16.1, 1 H, OsCH=C*H*Ph), 6.98 (t, $J_{H-H}$ = 7.3, 1 H, *p*-H of Ph), 2.24 (m, 6 H, PC*H*CH$_3$), 1.16 (dvt, *N* = 13.5, $J_{H-H}$ = 6.9, 32 H, PCHC*H*$_3$) and −7.13 (td, $J_{P-H}$ = 22.0, $J_{H-H}$ = 5.0, 1 H, OsH); $^{13}$C-{$^1$H}, δ 190.4 (t, $J_{P-C}$ = 5.5, CO), 185.5 (t, $J_{P-C}$ = 7.8, CO), 144.5 (t, $J_{P-C}$ = 1.9, *ipso*-C of Ph), 142.5 (t, $J_{P-C}$ = 3.7, OsCH=*C*HPh), 135.2 (t, $J_{P-C}$ = 12.9, Os*C*H=CHPh), 128.8 (s, *o*-C of Ph), 124.9 (s, *m*-C of Ph), 124.5 (s, *p*-C of Ph), 26.2 (vt, *N* = 27.6, $J_{P-C}$ = 2.3 Hz, P*C*HCH$_3$) and 19.0 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 19.0 (s).

**[OsH{C$_6$H$_4$(CD=CHH)}(CO)(PPr$^i_3$)$_2$] 2a.** The complex was prepared using the procedure described for **2** (100 mg, 0.15 mmol), starting for [Os{(*E*)-CH=CDPh}Cl(CO)(PPr$^i_3$)$_2$]. NMR: $^1$H ($C_6D_6$, 20 °C), δ 7.26 (d, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 7.03 (t, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 6.90 (t, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 6.56 (d, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 3.71 (t, $J_{P-H}$ = 5.7, 1 H, =CH$_2$), 2.74 (s, =CH$_2$), 2.15 (m, 6 H, PC*H*CH$_3$), 1.05 (dvt, *N* = 13.5, $J_{H-H}$ = 6.3, 36 H, PCHC*H*$_3$) and −8.01 (t, $J_{P-H}$ = 27.3 Hz, 1 H, OsH); $^2$H ($C_6H_6$, 20 °C), δ 5.03 (s, CD=); $^{31}$P-{$^1$H} ($C_6D_6$, 20 °C), δ 17.1 (s).

**[OsH{(*E*)-CH=CDPh}(CO){P(OMe)$_3$}(PPr$^i_3$)$_2$] 3a.** The complex was prepared using the procedure described for **3** (100 mg, 0.15 mmol), starting for [Os{(*E*)-CH=CDPh}Cl(CO)-(PPr$^i_3$)$_2$]. NMR: $^1$H ($C_6D_6$, 20 °C), δ 8.78 (d, $J_{P-H}$ = 18.3, 1 H, OsC*H*=CHPh), 7.46 (d, $J_{H-H}$ = 7.3, 2 H, *o*-H of Ph), 7.23 (t, $J_{H-H}$ = 7.3, 2 H, *m*-H of Ph), 6.96 (t, $J_{H-H}$ = 7.3, 1 H, *p*-H of Ph), 3.39 (d, $J_{P-H}$ = 10.1, 9 H, POMe), 2.47 (m, 6 H, PC*H*CH$_3$), 1.27 (dvt, *N* = 14.0, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$), 1.20 (dvt, *N* = 11.9, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$) and −8.94 (dt, $J_{P-H}$ = 134.4, 24.5, 1 H, OsH); $^2$H ($C_6H_6$, 20 °C), δ 7.01 (s, OsCH=CDPh); $^{31}$P-{$^1$H} ($C_6D_6$, 20 °C), δ 103.0 (t, $J_{P-P}$ = 18.6 POMe), 17.5 (d, $J_{P-P}$ = 18.6 Hz, PPr$^i_3$).

**[OsH{C$_6$H$_3$D(CH=CHH)}(CO)(PPr$^i_3$)$_2$] 2b, [OsH{C$_6$H$_4$(CH=CDH)}(CO)(PPr$^i_3$)$_2$] 2c, [OsH{C$_6$H$_4$(CH=CHD)}(CO)(PPr$^i_3$)$_2$] 2d and [OsD{C$_6$H$_4$(CH=CHH)}(CO)(PPr$^i_3$)$_2$] 2e.** The complexes were prepared using the procedure described for **2** (100 mg, 0.15 mmol), starting from [Os{(*E*)-CD=CHPh}Cl(CO)(PPr$^i_3$)$_2$]. NMR: $^1$H ($C_6D_6$, 20 °C), δ 7.26 (d, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 7.03 (t, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 6.90 (t, $J_{H-H}$ = 7.1, 1 H, H$_{Ph}$), 6.56 (d, $J_{H-H}$ = 7.1, H$_{Ph}$), 4.95 (br dd, $J_{H-H}$ = 9.0, *J* = 7.7, CH=), 3.71 (br dt, $J_{H-H}$ = 9.0, $J_{P-H}$ = 5.7, =CH$_2$), 2.74 (br d, $J_{H-H}$ = 7.7, 1 H, =CH$_2$), 2.15 (m, 6 H, PC*H*CH$_3$), 1.05 (dvt, *N* = 13.5, $J_{H-H}$ = 6.3, 36 H, PCHC*H*$_3$) and −8.01 (br t, $J_{P-H}$ = 27.3 Hz, 1 H, OsH); $^2$H ($C_6H_6$, 20 °C), δ 6.52 (s, D$_{Ph}$), 3.68 (s, =CHD), 2.65 (s, =CHD) and −8.02 (s, OsD); $^{31}$P-{$^1$H} ($C_6D_6$, 20 °C), δ 17.1 (s).

**[OsH{(*E*)-CD=CHPh}(CO){P(OMe)$_3$}(PPr$^i_3$)$_2$] 3b, [OsH-{(*E*)-CH=CHC$_6$H$_4$D}(CO){P(OMe)$_3$}(PPr$^i_3$)$_2$] 3c and [OsD-{(*E*)-CH=CHPh}(CO){P(OMe)$_3$}(PPr$^i_3$)$_2$ 3d.** The complexes were prepared using the procedure described for **3** (100 mg, 0.15 mmol), starting from [Os{(*E*)-CD=CHPh}Cl(CO)(PPr$^i_3$)$_2$]. NMR: $^1$H ($C_6D_6$, 20 °C), δ 8.78 (t, $J_{H-H}$ = 18.3, $J_{P-H}$ = 18.3, OsC*H*=CHPh), 7.46 (d, $J_{H-H}$ = 7.3, *o*-H of Ph), 7.23 (t, $J_{H-H}$ = 7.3, 2 H, *m*-H of Ph), 7.03 (br d, $J_{H-H}$ = 18.3, OsCH=C*H*Ph), 6.96 (t, $J_{H-H}$ = 7.3, 1 H, *p*-H of Ph), 3.39 (d, $J_{P-H}$ = 10.1, 9 H, POMe), 2.47 (m, 6 H, PC*H*CH$_3$), 1.27 (dvt, *N* = 14.0, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$), 1.20 (dvt, *N* = 11.9, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$) and −8.94 (dt, $J_{P-H}$ = 134.4, *J* 24.5, OsH); $^2$H ($C_6H_6$, 20 °C), δ 8.81 (s, OsCD=CHPh), 7.46 (s, *o*-D of Ph) and −8.88 (d, $J_{P-D}$ = 20.2, OsD); $^{31}$P-{$^1$H} ($C_6D_6$, 20 °C), δ 103.0 (dt, $J_{P-D}$ = 20.2, $J_{P-P}$ = 18.6, POMe) and 17.5 (d, $J_{P-P}$ = 18.6 Hz, PPr$^i_3$).

**[Os{(*E*)-CH=CHPh}(η$^2$-O$_2$CH)(CO)(PPr$^i_3$)$_2$] 8.** A solution of complex **1** (100 mg, 0.15 mmol) in hexane (5 cm$^3$) was treated with LiBu$^n$ (0.01 cm$^3$, 1.6 mol dm$^{-3}$ solution in hexane) and stirred during *ca*. 5 min at room temperature. The resulting pale yellow suspension was filtered through Kieselguhr and a slow stream of carbon dioxide was bubbled through it for *ca*. 30 min. The solution was cooled at −78 °C, resulting in crystallization of a yellow solid. This was decanted and dried *in vacuo*. Yield 77.3 mg (75%) (Found: C, 48.89; H, 7.2. Calc. for $C_{28}H_{50}O_3OsP_2$: C, 48.95; H, 7.35%). IR (Nujol, cm$^{-1}$): ν(CO) 1900s, ν$_{asym}$(OCO) 1560s, ν(C=C) 1540m, ν$_{sym}$(OCO) 1300s. NMR ($C_6D_6$, 20 °C): $^1$H, δ 9.09 (d, $J_{H-H}$ = 15.6, 1 H, OsC*H*=CHPh), 8.63 (t, $J_{P-H}$ = 1.9, 1 H, O$_2$C*H*), 7.38 (d, $J_{H-H}$ = 7.4 Hz, 2 H, *o*-H of Ph), 7.24 (t, $J_{H-H}$ = 7.4, 2 H, *m*-H of Ph), 6.93 (t, $J_{H-H}$ = 7.4, 1 H, *p*-H of Ph), 6.46 (dt, $J_{H-H}$ = 15.6, $J_{P-H}$ < 1, 1 H, OsCH=C*H*Ph), 2.44 (m, 6 H, PC*H*CH$_3$), 1.24 (dvt, *N* = 13.5, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$) and 1.17 (dvt, *N* = 13.2, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$). $^{13}$C-{$^1$H}, δ 185.9 (t, $J_{P-C}$ = 9.2, CO), 174.4 (t, $J_{P-C}$ = 1.4, O$_2$CH), 142.6 (t, $J_{P-C}$ = 1.2, *ipso*-C of Ph), 137.0 (t, $J_{P-C}$ = 9.7, Os*C*H=CHPh), 132.8 (t, $J_{P-C}$ = 2.7, OsCH=*C*HPh), 128.8 (s, *o*-CH of Ph), 124.1 (s, *m*-CH of Ph), 123.7 (s, *p*-CH of Ph), 24.8 (vt, *N* = 24.0 Hz, P*C*HC*H*$_3$), 19.7 (s, PCH*C*H$_3$) and 19.6 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 15.6 (s).

**[Os{(*E*)-CH=CHPh}{η$^1$-OC(O)H}(CO)$_2$(PPr$^i_3$)$_2$] 9.** A slow stream of carbon monoxide was bubbled through a hexane solution of complex **8** (100 mg, 0.15 mmol) during 5 min. The white solid obtained was decanted, washed with hexane and dried *in vacuo*. Yield 89.0 mg (83%) (Found: C, 48.75; H, 6.95. Calc. for $C_{29}H_{50}O_4OsP_2$: C, 48.75; H, 7.0%). IR (Nujol, cm$^{-1}$): ν(CO) 2020s, 1940s, ν$_{asym}$(OCO) 1625s, ν(C=C) 1590m, ν$_{sym}$-(OCO) 1295s. NMR ($C_6D_6$, 20 °C): δ $^1$H, 8.68 (dt, $J_{H-H}$ = 17.0, $J_{P-H}$ < 1, 1 H, OsC*H*=CHPh), 8.11 [s, 1 H, OC(O)H)], 7.44 (d, $J_{H-H}$ = 7.7, 2 H, *o*-H of Ph), 7.44 (t, $J_{H-H}$ = 7.7, 2 H, *m*-H of Ph) (the OsCH=C*H*Ph signal is masked by the $C_6D_6$ signal), 6.69 (t, $J_{H-H}$ = 7.7, 1 H, *p*-H of Ph), 2.38 (m, 6 H, PC*H*CH$_3$), 1.08 (dvt, *N* = 12.9, $J_{H-H}$ = 6.7, 18 H, PCHC*H*$_3$) and 1.04 (dvt, *N* = 12.1, $J_{H-H}$ = 6.9, 18 H, PCHC*H*$_3$); $^{13}$C-{$^1$H}, δ 186.8 (t, $J_{P-C}$ = 6.9, CO), 184.4 (t, $J_{P-C}$ = 7.8, CO), 168.4 [s, OC(O)H], 149.1 (t, $J_{P-C}$ = 12.9, *ipso*-*C* of Ph), 143.2 (t, $J_{P-C}$ = 2.3, OsCH=*C*HPh), 140.0 (t, $J_{P-C}$ = 4.6, Os*C*H=CHPh), 128.9 (s, CH$_o$ of Ph), 125.4 (s, CH$_m$ of Ph), 124.8 (s, *p*-CH of Ph), 25.3 (vt, *N* = 25.3 Hz, P*C*HCH$_3$), 19.6 (s, PCH*C*H$_3$) and 19.4 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 9.3 (s).

**[OsH(η$^2$-O$_2$CH)(CO)(PPr$^i_3$)$_2$] 10.** A slow stream of carbon dioxide was bubbled through a solution of [OsH$_2$(η$^2$-CH$_2$=CHEt)(CO)(PPr$^i_3$)$_2$] **11** (93 mg, 0.16 mmol) in hexane (5 cm$^3$) at room temperature. After *ca*. 20 min a yellow solid was formed. The solid was decanted, washed with hexane and dried

*in vacuo*. Yield 74.8 mg (82%) (Found: C, 41.6; H, 8.1. Calc. for $C_{20}H_{44}O_3OsP_2$: C, 41.1; H, 7.6%). IR (Nujol, $cm^{-1}$): ν(Os–H) 2180m, ν(CO) 1900s, $\nu_{asym}$(OCO) 1565s, $\nu_{sym}$(OCO) 1385m. NMR ($CDCl_3$, 20 °C): $^1$H, δ 8.81 (s, $O_2CH$), 2.42 (m, 6 H, PC*H*$CH_3$), 1.30 (dvt, $N$ = 13.6, $J_{H-H}$ = 7.4, 18 H, PCHC*H*$_3$), 1.26 (dvt, $N$ = 13.0, $J_{H-H}$ = 7.2, 18 H, PCHC*H*$_3$) and −21.58 (t, $J_{P-H}$ = 15.7, 1 H, OsH). $^{13}$C-{$^1$H}, δ 182.9 (t, $J_{P-C}$ = 9.1, CO), 173.3 (t, $J_{P-C}$ = 1.5, $O_2CH$), 25.6 (vt, $N$ = 24.8 Hz, PC*H*$CH_3$), 20.1 (s, PCH*C*$H_3$) and 19.4 (s, PCH*C*$H_3$); $^{31}$P-{$^1$H}, δ 39.6 (s).

**Reaction of complex 8 with $H_2$.** A solution of complex **8** (25 mg, 0.04 mmol) in $C_6D_6$ placed in a NMR tube was saturated with $H_2$ at room temperature and the tube sealed. The reaction was monitored by $^1$H and $^{31}$P-{$^1$H} NMR spectroscopy. After 72 h the spectra showed signals corresponding to **10** and styrene.

**[OsH{η$^1$-OC(O)H}(CO)$_2$(PPr$_3$)$_2$] 12.** A slow stream of carbon monoxide was bubbled through a suspension of complex **10** (90 mg, 0.156 mmol) in dichloromethane (5 $cm^3$) during 5 min. The solution was dried under vacuum, and the residue treated with hexane causing the precipitation of a white solid. The solid was washed with hexane and dried *in vacuo*. Yield 77.4 mg (82%) (Found: C, 41.15; H, 7.25. Calc. for $C_{21}H_{44}O_4OsP_2$: C, 40.6; H, 7.85%). IR (Nujol, $cm^{-1}$): ν(Os–H) 2050m, ν(CO) 1975s, 1915s, $\nu_{asym}$(OCO) 1643s, $\nu_{sym}$(OCO) 1370m. NMR ($C_6D_6$, 20 °C): $^1$H, δ 7.88 [s, 1 H, OC(O)H], 2.10 (m, 6 H, PC*H*$CH_3$), 1.14 (dvt, $N$ = 14.1, $J_{H-H}$ = 7.5, 18 H, PCHC*H*$_3$), 1.17 (dvt, $N$ = 14.1, $J_{H-H}$ = 7.5, 18 H, PCHC*H*$_3$) and −4.29 (t, $J_{P-H}$ = 21.0 Hz, 1 H, OsH); $^{31}$P-{$^1$H}, δ 29.1 (s).

**[OsH{η$^1$-OC(O)H}(CO){P(OMe)$_3$}(PPr$^i_3$)$_2$] 13.** A suspension of complex **10** (65 mg, 0.11 mmol) in hexane (7 $cm^3$) was treated with P(OMe)$_3$ (19 μl, 0.16 mmol). After *ca*. 15 min at room temperature a white solid was formed. The solid was decanted, washed with hexane and dried *in vacuo*. Yield 60.7 mg (80%) (Found: C, 38.95; H, 7.55. Calc. for $C_{23}H_{53}O_6OsP_3$: C, 39.55; H, 8.45%). IR (Nujol, $cm^{-1}$): ν(Os–H) 2030w, ν(CO) 1920s, $\nu_{asym}$(OCO) 1650s, $\nu_{sym}$(OCO) 1380m. NMR ($C_6D_6$, 20 °C): δ $^1$H, 8.37 [s, 1 H, OC(O)H], 3.43 (d, $J_{P-H}$ = 10.1, 9 H, POMe), 2.29 (m, 6 H, PC*H*$CH_3$), 1.30 (dvt, $N$ = 12.3, $J_{H-H}$ = 6.8, 18 H, PCHC*H*$_3$), 1.10 (dvt, $N$ = 12.3, $J_{H-H}$ = 6.8, 18 H, PCHC*H*$_3$) and −6.30 (dt, $J_{P-H}$ = 149.0, 23.8, 1 H, OsH); $^{31}$P-{$^1$H}, δ 102.9 (t, $J_{P-P}$ = 17.9, POMe) and 20.8 (d, $J_{P-P}$ = 17.9 Hz, PPr$^i_3$).

**[OsH{η$^1$-OC(O)H}(η$^2$-MeO$_2$CC≡CCO$_2$Me)(CO)(PPr$^i_3$)$_2$] 14.** A suspension of complex **10** (65 mg, 0.11 mmol) in hexane (6 $cm^3$) was treated with MeO$_2$CC≡CCO$_2$Me (14 μl, 0.11 mmol). After *ca*. 5 min at room temperature a white solid was formed. The solid was decanted, washed with hexane and dried *in vacuo*. Yield 60.7 mg (80%) (Found: C, 42.95; H, 6.95. Calc. for $C_{26}H_{50}O_7OsP_2$: C, 42.55; H, 7.2%). IR (Nujol, $cm^{-1}$): ν(Os–H) 2040w, ν(CO) 1955s, ν(C≡C) 1880m, ν(C=O) 1710s, $\nu_{asym}$(OCO) 1620s, $\nu_{sym}$(OCO) 1375m. The $^1$H and $^{31}$P-{$^1$H} NMR spectra of a solution of **14** (32 mg, 0.03 mmol) in $C_6D_6$ at room temperature showed signals corresponding to **14**, **10** and MeO$_2$CC≡CCO$_2$Me in *ca*. 1:1:1 molar ratio. Data for **14** ($CDCl_3$, 20 °C): δ $^1$H, 7.63 [s, 1 H, OC(O)H], 3.74 (s, 6 H, ≡CCO$_2$Me), 2.64 (m, 6 H, PC*H*$CH_3$), 1.27 (dvt, $N$ = 12.7, $J_{H-H}$ = 6.7, 18 H, PCHC*H*$_3$), 1.15 (dvt, $N$ = 14.9, $J_{H-H}$ = 6.6, 18 H, PCHC*H*$_3$) and −2.28 (dt, $J_{P-H}$ = 28.3, 1 H, OsH); $^{13}$C-{$^1$H}, δ 179.8 (t, $J_{P-C}$ = 9.1, CO), 167.4 (s, ≡C*C*O$_2$Me), 166.2 [t, $J_{P-C}$ = 5.3, OC(O)H], 107.3 (t, $J_{P-C}$ = 3.3, ≡*C*CO$_2$Me), 52.4 (s, ≡CCO$_2$*Me*), 25.5 (vt, $N$ = 28.0 Hz, P*C*HCH$_3$), 20.8 (s, PCH*C*H$_3$) and 18.8 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 30.8 (s).

**[OsH(η$^2$-O$_2$CNEt$_2$)(CO)(PPr$^i_3$)$_2$] 15.** A solution of complex **9** (28 mg, 0.05 mmol) in $C_6D_6$ placed in a NMR tube was treated with NEt$_2$H (5 μl, 0.05 mmol). The tube was sealed under Ar and heated at 60 °C for 1 h. Under these conditions complex **15** was the only detectable product. IR ($CH_2Cl_2$, $cm^{-1}$): ν(CO) 1870s, ν(OCO) 1525s. NMR ($C_6D_6$, 20 °C): $^1$H, δ 3.14, 3.02 (both q, $J_{H-H}$ = 7.2, 2 H, NC*H*$_2$), 2.37 (m, 6 H, PC*H*$CH_3$), 1.38 (dvt, $N$ = 13.5, $J_{H-H}$ = 6.9, 18 H, PCHC*H*$_3$), 1.25 (dvt, $N$ = 13.5, $J_{H-H}$ = 6.9, 18 H, PCHC*H*$_3$), 0.95, 0.91 (both t, $J_{H-H}$ = 7.0, 3 H, NCH$_2$C*H*$_2$) and −20.37 (t, $J_{P-H}$ = 16.2, 1 H, Os–H); $^{13}$C-{$^1$H}, δ 184.5 (t, $J_{P-C}$ = 9.2, CO), 165.4 (s, $O_2C$), 39.3, 39.0 (s, NCH$_2$), 25.7 (vt, $N$ = 24.8 Hz, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$), 19.5 (s, PCH*C*H$_3$), 14.2 (s, NCH$_2$*C*H$_3$); $^{31}$P-{$^1$H}, δ 38.4 (s).

**Reaction of complex 8 with NEt$_2$H: preparation of [Os{(*E*)-CH=CHPh}(η$^2$-O$_2$CNEt$_2$)(CO)(PPr$^i_3$)$_2$] 16.** A solution of complex **8** (25 mg, 0.04 mmol) in $C_6D_6$ placed in a NMR tube was treated with NEt$_2$H (4 μl, 0.04 mmol). After 3 h at room temperature the $^1$H and $^{31}$P-{$^1$H} NMR spectra of the solution showed a mixture of **8** (41), **10** (10), **15** (12) and **16** (37%). After 24 h at room temperature a mixture of complexes **15** (60) and **16** (40%) was obtained. NMR data for **16** ($C_6D_6$, 20 °C): $^1$H, δ 9.37 (d, $J_{H-H}$ = 15.6, 1 H, OsC*H*=CHPh), 7.43 (d, $J_{H-H}$ = 6.8 Hz, 2 H, *o*-H of Ph), 7.28 (t, $J_{H-H}$ = 6.8 Hz, 2 H, *m*-H of Ph, 7.09 (t, $J_{H-H}$ = 6.8 Hz, 1 H, *p*-H of Ph), 6.57 (dt, $J_{H-H}$ = 15.6 Hz, $J_{P-H}$ < 1 Hz, 1 H, OsCH=C*H*Ph), 3.14, 3.04 (q, $J_{H-H}$ = 7.0, 2 H, NCH$_2$), 2.40 (m, 6 H, PC*H*$CH_3$), 1.27 (dvt, $N$ = 12.0, $J_{H-H}$ = 6.9, 18 H, PCHC*H*$_3$), 1.17 (dvt, $N$ = 12.0, $J_{H-H}$ = 6.9, 18 H, PCHC*H*$_3$), 0.93, 0.91 (t, $J_{H-H}$ = 7.0, 3 H, NCH$_2$C*H*$_3$); $^{13}$C-{$^1$H}, δ 184.3 (t, $J_{P-C}$ = 9.1, CO), 165.0 (s, $O_2C$), 143.2 (s, *ipso*-C of Ph), 138.7 (t, $J_{P-C}$ = 7.7, Os*C*H=CHPh), 132.3 (br, OsCH=*C*HPh), 128.6 (s, *o*-CH of Ph), 124.0 (s, *m*-CH of Ph), 123.2 (s, *p*-CH of Ph), 39.1, 38.7 (s, NCH$_2$), 24.5 (vt, $N$ = 23.7 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$), 19.7 (s, PCH*C*H$_3$), 16.7, 16.6 (s, NCH$_2$*C*H$_3$); $^{31}$P-{$^1$H}, 16.1 (s).

**[Os{(*E*)-CH=CHPh}(CO)(MeCN)$_2$(PPr$^i_3$)$_2$]BF$_4$ 17.** A solution of complex **8** (100 mg, 0.15 mmol) was treated with HBF$_4$·OEt$_2$ (16 μl, 0.15 mmol) in diethyl ether. Addition of MeCN (8 μl, 0.15 mmol) caused the precipitatiion of a white solid, which was washed with ether and hexane and dried *in vacuo*. Yield 97.3 mg (80%) (Found: C, 45.4; H, 7.05; N, 3.15. Calc. for $C_{31}H_{55}BF_4N_2OOsP_2$: C, 45.95; H, 6.8; N, 3.45%). IR (Nujol, $cm^{-1}$): ν(C≡N) 2330w, 2300w, ν(CO) 1930s, ν(C=C) 1550m, ν([$BF_4$]$^-$) 1060 (br). NMR ($CDCl_3$, 20 °C); $^1$H, δ 8.28 (d, $J_{H-H}$ = 17.3, 1 H, OsC*H*=CHPh), 7.20 (t, $J_{H-H}$ = 7.7, 2 H, *m*-H of Ph), 7.07 (d, $J_{H-H}$ = 7.7, 2 H, *o*-H of Ph), 6.99 (t, $J_{H-H}$ = 7.7, 1 H, *p*-H of Ph), 6.42 (d, $J_{H-H}$ = 17.3, 1 H, OsCH=C*H*Ph), 2.68 (s, 3 H, NCCH$_3$), 2.58 (m, 6 H, PC*H*$CH_3$), 2.57 (s, 3 H, NCCH$_3$), 1.31 (dvt, $N$ = 13.5, $J_{H-H}$ = 7.2, 18 H, PCHC*H*$_3$) and 1.29 (dvt, $N$ = 13.5, $J_{H-H}$ = 7.2, 18 H, PCHC*H*$_3$); $^{13}$C-{$^1$H}, δ 185.0 (t, $J_{P-C}$ = 9.4, CO), 142.5 (br, *ipso*-C of Ph), 136.2 (t, $J_{P-C}$ = 3.0, OsCH=*C*HPh), 132.7 (t, $J_{P-C}$ = 8.9, Os*C*H=CHPh), 128.2 (br, *o*-CH of Ph), 126.0, 125.5 (both s, N*C*CH$_3$), 124.0 (br, $CH_{Ph}$, *m*-CH of Ph), 24.4 (vt, $N$ = 24.7 Hz, P*C*HCH$_3$), 19.4 (s, PCH*C*H$_3$), 19.0 (s, PCH*C*H$_3$), 4.4, 3.7 (both s, NC*C*H$_3$); $^{31}$P-{$^1$H}, δ 3.1 (s).

**[Os(η$^2$-O$_2$CH)(=CHCH$_2$Ph)(CO)(PPr$^i_3$)$_2$]BF$_4$ 18.** A solution of complex **8** (100 mg, 0.15 mmol) in chloroform was treated with HBF$_4$·OEt$_2$ (16 μl, 0.15 mmol). The solution was dried *in vacuo*, yielding a green oil. IR ($CH_2Cl_2$, $cm^{-1}$): ν(CO) 1980s, $\nu_{asym}$($O_2CH$) 1560s, $\nu_{sym}$($O_2CH$) 1355m. NMR ($CDCl_3$, 20 °C): $^1$H, δ 17.63 (t, $J_{H-H}$ = 6.1, 1 H, Os=CH), 9.19 (s, $O_2CH$), 7.35–7.22 (m, 5 H, Ph), 3.52 (d, $J_{H-H}$ = 6.1, 2 H, =CHC*H*$_2$Ph), 2.45 (m, 6 H, PC*H*$CH_3$), 1.34 (dvt, $N$ = 14.2, $J_{H-H}$ = 7.1, 18 H, PCHC*H*$_3$) and 1.19 (dvt, $N$ = 13.8, $J_{H-H}$ = 7.5, 18 H, PCHC*H*$_3$); $^{13}$C, δ 290.8 (br, Os=C), 179.6 (t, $J_{P-C}$ = 8.3, CO), 168.7 (s, $O_2CH$), 134.2 (s, *ipso*-C of Ph), 129.1 (s, *o*-CH of Ph), 127.8 (s, *p*-CH of Ph), 127.8 (s, *m*-CH of Ph), 65.3 (s, $CH_2Ph$), 25.8 (vt, $N$ = 25.9 Hz, P*C*HCH$_3$), 19.3 (s, PCH*C*H$_3$) and 19.1 (s, PCH*C*H$_3$); $^{31}$P-{$^1$H}, δ 38.3 (s).

**$[OsH(CO)(MeCN)_2(PPr^i_3)_2]BF_4$ 19.** A solution of complex **10** (65 mg, 0.11 mmol) in ether was treated with $HBF_4 \cdot OEt_2$ (11 μl, 0.11 mmol). The resulting suspension was treated with MeCN (6 μl, 0.11 mmol) causing the precipitation of a white solid. The solid was washed with ether and dried *in vacuo*. Yield 49.1 mg (75%) (Found: C, 39.3; H, 7.45; N, 3.8. Calc. for $C_{23}H_{49}BF_4N_2OOsP_2$: C, 39.0; H, 6.95; N, 3.95%). IR (Nujol, $cm^{-1}$): ν(C≡N) 2330w, 2290w, ν(Os–H) 2140w, ν(CO) 2140s. NMR ($CDCl_3$, 20 °C): $^1$H, δ 2.53 (s, 3 H, $NCCH_3$), 2.50 (s, 3 H, $NCCH_3$), 2.40 (m, 6 H, $PCHCH_3$), 1.30 (dvt, $N = 13.5$, $J_{H-H} = 7.0$, 36 H, $PCHCH_3$) and −14.87 (t, $J_{P-H} = 17.0$ Hz, 1 H, OsH); $^{31}$P-{$^1$H}, δ 24.94 (s).

**Reaction of complex 10 with $HBF_4$.** A $CDCl_3$ solution of complex **10** (8 mg, 0.01 mmol) placed in a NMR tube was treated with $HBF_4$ (1.9 μl, 0.01 mmol) and the tube sealed under argon. After 5 min four products were mainly formed (Fig. 1). Significant NMR signals ($CDCl_3$, 20 °C) are: A $^1$H, δ 7.98 (br, 1 H, $O_2CH$) and −6.80 (br, 2 H, $\eta^2$-$H_2$); $^{31}$P, δ 25.6 (s); $T_1$/ms [Os($\eta^2$-$H_2$), 300 MHz, $CDCl_3$] = 38 (293), 21 (253), 17 (233), 17 (218 K); B, $^1$H, δ 8.14 [br, 1 H, OC(O)H] and −6.94 (br, 2 H, $\eta^2$-$H_2$); $^{31}$P, δ 41.8 (s); $T_1$/ms [Os($\eta^2$-$H_2$), 300 MHz, $CDCl_3$] = 36 (293), 21 (253 K); C, $^1$H, δ 9.26 [br, 1 H, OC(O)H] and −9.04 (dd, $J_{P-H} = 28.6$, 15.7 Hz, OsH); $T_1$/ms (OsH, 300 MHz, $CDCl_3$) = 740 (293), 305 (253), 290 (233), 260 (218 K); D, $^1$H, δ 9.16 [br, 1 H, OC(O)H] and −9.70 (br, OsH); $^{31}$P, δ 35.6 (br).

### Computation

All calculations were performed with an *ab initio* molecular orbital method with introduction of correlation energy through the Møller–Plesset perturbational approach,[24] excluding excitations concerning the lowest-energy electrons (frozen-core approach). Effective core potentials were used to represent the 60 innermost electrons (up to the 4d shell) of the osmium atom,[25] as well as the 10-electron core of the phosphorus atoms.[26] The basis set used for the osmium atom is that associated with the pseudo-potential,[25] with a (541/41/111) contraction,[27] which is triple ζ for the 5d shell, double ζ for the 6s and single ζ for the 6p. For the phosphorus atoms a valence double ζ basis set[26] with a (21/21) contraction was used, while the standard 6-31G basis set was used for all the other atoms.[28]

Geometry optimizations were carried out at the second level of the Møller–Plesset theory (MP2). All geometrical parameters were optimized except the dihedral angle of one of the hydrogen atoms of each phosphine, which was fixed to be oriented towards the carbon of the carbonyl ligand, in order to avoid chemically meaningless rotations around the M–P axis. Single-point energy-only calculations were made at a higher computational level with the MP2 optimized geometries. This is the fourth level of the same perturbational theory (MP4), with consideration of single, double, triple and quadruple excitations.

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