Synthesis and Characterisation of Enynyl, Vinyl and Acetylide Complexes of Osmium(II)

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Treatment of $[OsH_2L_4]$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] first with CF_3SO_3Me and then with an excess of terminal alkynes RC≡CH (R = Bu^t, Ph or *p*-MeC_6H_4) produced enynyl derivatives $[Os\{\eta^3\text{-}RC_3C(H)R\}L_4]^+$ **1–3**. Sequential reactions of $[OsH_2L_4]$ with CF_3SO_3Me and activated alkynes $R'O_2CC{\equiv}CH$ (R' = Me or Et) or $MeO_2CC{\equiv}CCO_2Me$ yielded alkenyl $[Os\{CH{=}C(H)CO_2R'\}L_4]^+$ **4**, **5** and $[Os\{C(CO_2Me){=}C(H)CO_2Me\}L_4]^+$ **6** cations, respectively. Spectroscopic data (IR, ^1H, ^{31}P, ^{13}C NMR) suggest, in the case of L = $P(OEt)_3$, the presence of two isomers for the alkenyls **4** and **5**, with five- and four-membered chelate rings of the vinyl ligand. Hydride–alkynyl $[OsH(C{\equiv}CPh)L_4]$ complexes were also obtained by treating $[OsH_2L_4]$ with CF_3SO_3Me followed by treatment with lithium phenylacetylide.

In recent papers[1,2] we reported the reactivity of iron(II) and ruthenium(II) non-classical hydrides $[MH(\eta^2\text{-}H_2)L_4]^+$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] with alkynes, which allowed the syntheses of new η^3-enynyl, vinyl and acetylide complexes. As a logical extension of these studies, we treated the related[3] $[OsH(\eta^2\text{-}H_2)L_4]^+$ derivatives with terminal alkynes but always obtained the starting complexes as 'products', even using a large excess of alkyne and reflux conditions. These results may be interpreted on the basis of the requirement of a substitution-labile ligand[4] to be replaced by the incoming alkyne for reaction to take place. The known high hydridic character[3] of the η^2-H_2 ligand in $[OsH(\eta^2\text{-}H_2)L_4]^+$ derivatives, as compared to those of Fe[1] and Ru,[2] makes it a non-labile ligand, preventing reactions with acetylenes. We therefore attempted to create an open co-ordination site on the osmium species by treating dihydrides $[OsH_2L_4]$ with equimolecular amounts of methyl trifluoromethanesulfonate (methyl triflate), and to verify whether in this way reaction with acetylenes can take place and organoosmium[5] derivatives be prepared. The results of these studies, which did allow the synthesis of new enynyl, vinyl and acetylide osmium(II) derivatives, are reported here.

Experimental

General Considerations and Physical Measurements.—All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmospheres dry-box. Once isolated, the complexes appeared to be reasonably air-stable and were stored at −20 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. Triethyl phosphite was an Aldrich product, purified by distillation under nitrogen, whereas diethoxyphenylphosphine was prepared by the method of Rabinowitz and Pellon.[6] Acetylenes were Aldrich products, used without further purification. Lithium phenylacetylide was prepared by treating a slight excess of phenylacetylene (40 mmol, 4.4 cm^3) with lithium (35 mmol, 0.24 g) in tetrahydrofuran (thf) (10 cm^3). Other reagents were obtained from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer model 683 or a Digilab Bio-Rad FTS-40 spectrophotometer, NMR spectra (^1H, ^{31}P, ^{13}C) on a Bruker AC200 spectrometer at temperatures between −90 and +30 °C, unless otherwise noted. The ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}P\text{-}\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in $MeNO_2$ at 25 °C were measured on a Radiometer CDM 83 instrument.

Synthesis of Complexes.—The hydrides $[OsH_2L_4]$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] were prepared as previously described.[7]

$[Os\{\eta^3\text{-}RC_3C(H)R\}L_4][CF_3SO_3]$ [R = Bu^t **1**, Ph **2** *or p-tolyl* **3**; L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. To a solution of the appropriate hydride $[OsH_2L_4]$ (0.12 mmol) in diethyl ether (10 cm^3) cooled to −90 °C was added CF_3SO_3Me (13.2 μl, 0.12 mmol) and the reaction mixture was brought to room temperature. After 30 min of stirring the solution was cooled to −90 °C again and an excess (0.6 mmol) of the appropriate alkyne added. The resulting mixture was brought to 0 °C and stirred until a white or pale yellow solid separated (about 2 h), which was filtered off and crystallised from CH_2Cl_2 (0.5 cm^3) and diethyl ether (10 cm^3); yield between 60 and 80%.

$[Os\{\eta^3\text{-}(p\text{-}MeC_6H_4)C_3CH(C_6H_4Me\text{-}p)\}\{P(OEt)_3\}_4]BPh_4$ **3a**. This complex was prepared exactly like the related complexes **1–3**, by treating the hydride $[OsH_2\{P(OEt)_3\}_4]$ with CF_3SO_3Me in diethyl ether and then with an excess of *p*-$MeC_6H_4C{\equiv}CH$. However, only a little amount of complex precipitated as a triflate salt from the reaction mixture. Therefore, the suspension was evaporated at reduced pressure, giving an oil which was treated with ethanol (5 cm^3). The addition of an excess of $NaBPh_4$ (0.24 mmol, 0.082 g) in ethanol (2 cm^3) caused the precipitation of a yellow solid which was filtered off and crystallised from CH_2Cl_2 (2 cm^3) and ethanol (7 cm^3); yield ≥ 75%.

$[Os\{CH{=}C(H)CO_2R\}L_4][CF_3SO_3]$ [R = Me **4** *or* Et **5**; L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. Methyl triflate (0.12 mmol, 13.2 μl) was added to a solution of the appropriate $[OsH_2L_4]$ (0.12 mmol) in diethyl ether (10 cm^3) cooled to −90 °C. The reaction mixture was brought to room temperature, stirred for 30 min and then cooled again to −90 °C. An excess of methyl or ethyl propiolate $HC{\equiv}CCO_2R$ (0.48 mmol) was added and the solution stirred at room temperature for 2–3 h, until a solid began to separate. The precipitation of the complex was increased by cooling the reaction mixture to −25 °C overnight. The white or pale yellow solid obtained was crystallised from CH_2Cl_2 (1 cm^3) and diethyl ether (10 cm^3); yield ≥ 70%.

$[Os\{CH{=}C(H)CO_2Et\}\{P(OEt)_3\}_4]BPh_4$ **5a**. This compound was prepared exactly like the related **4** and **5**, but was isolated as a BPh_4 salt because the triflate precipitates slowly and often as an oil. Thus, the reaction mixture obtained after addition of an excess of ethyl propiolate was evaporated at reduced pressure, giving a yellow oil which was treated with ethanol (5 cm^3). The addition of an excess of $NaBPh_4$ (0.24 mmol, 0.082 g) to the resulting solution caused the precipitation of a pale yellow solid, which was filtered off and crystallised from CH_2Cl_2 (2 cm^3), ethanol (5 cm^3) and diethyl ether (5 cm^3); yield ≥ 80%.

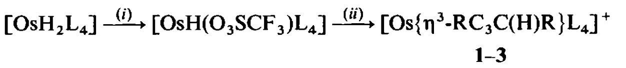
$[Os\{C(CO_2Me){=}C(H)CO_2Me\}L_4]BPh_4$ **6** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. A solution of the appropriate hydride $[OsH_2L_4]$ (0.12 mmol) in diethyl ether (10 cm^3) was treated at −90 °C with an equimolecular amount of methyl triflate (0.12 mmol, 13.2 μl). The reaction mixture was brought to room temperature, stirred for about 30 min and then an excess of dimethyl acetylenedicarboxylate $MeO_2CC{\equiv}CCO_2Me$ (0.48 mmol, 60 μl) was added at −90 °C. After 4 h of stirring at room temperature the solution was evaporated under reduced pressure, giving a yellow oil which was treated with ethanol (5 cm^3). The addition of $NaBPh_4$ (0.24 mmol, 0.082 g) in ethanol (2 cm^3) to the resulting solution caused the precipitation of a pale yellow solid, which was filtered off and crystallised from CH_2Cl_2 (2 cm^3) and ethanol (7 cm^3); yield ≥ 75%.

$[OsH(C{\equiv}CPh)L_4]$ **7** [L = $P(OEt)_3$ **a** *or* $PPh(OEt)_2$ **b**]. Methyl triflate (0.12 mmol, 13.2 μl) was added to a solution, cooled to −90 °C, of the appropriate hydride $[OsH_2L_4]$ (0.12 mmol) in diethyl ether (10 cm^3). The solution was brought to room temperature and, after 30 min of stirring, 0.20 cm^3 of a solution of 2.4 mol dm^{-3} $Li[C{\equiv}CPh]$ (0.48 mmol) in thf was added. After the addition of pure thf (5 cm^3), the reaction mixture was stirred for 3 h and the solvent was then removed under reduced pressure, giving an oil which was treated with ethanol (2 cm^3). The resulting solution was filtered and vigorously stirred at −5 °C, until a white solid began to separate. The precipitation of the complex can be increased by further cooling of the reaction mixture to −30 °C, and the solid obtained was filtered off and dried under vacuum; yield ≥ 60%.

Results and Discussion

The synthesis of enynyl derivatives $[Os\{\eta^3\text{-}RC_3C(H)R\}L_4]^+$ [R = Bu^t, Ph or p-MeC_6H_4; L = $P(OEt)_3$ *or* $PPh(OEt)_2$] was achieved by treating the hydrides $[OsH_2L_4]$ first with methyl triflate and then with an excess of the appropriate terminal alkyne, as shown in Scheme 1. The reaction with an equivalent amount of methyl triflate was used to create an open coordination site in the osmium complexes and to allow alkyne reaction to take place. Neither the $[OsH_2L_4]$ hydrides nor the η^2-H_2 complexes $[OsH(\eta^2\text{-}H_2)L_4]BF_4$ react with a large excess of terminal alkynes under refluxing conditions, whereas, on the contrary, butenynyl derivatives **1–3** can easily be obtained from $[OsH_2L_4]$ at room temperature after treatment with CF_3SO_3Me.

The reaction with methyl triflate has been studied by ^1H and ^{31}P NMR spectroscopy in order to get information on the nature of the resulting unsaturated hydride species and the results show that treatment of $[OsH_2\{P(OEt)_3\}_4]$ with equimolecular CF_3SO_3Me in [$^2H_8$]toluene gives gas evolution (CH_4, according to ^1H NMR spectroscopy). No solid is precipitated and the ^1H NMR spectra consist, besides the signals of the $P(OEt)_3$ ligands, of a hydride multiplet at δ −6.20 which replaces the multiplet at δ −12.3 of the starting $[OsH_2L_4]$. The ^{31}P-$\{^1H\}$ spectrum is an AB_2C multiplet, which can be simulated with the following parameters: δ_A 121.0, δ_B 114.4, δ_C 85.3, J_{AB} = 34.2, J_{AC} = 21.5, J_{BC} = 44.4 Hz. We were not able to isolate a pure complex from this solution, but the toluene solubility suggests[8] possible coordination of the triflate anion in a $[OsH(O_3SCF_3)L_4]$ complex, the *cis* geometry of which seems to be confirmed by ^1H and ^{31}P spectroscopy.



$$[OsH_2L_4] \xrightarrow{(i)} [OsH(O_3SCF_3)L_4] \xrightarrow{(ii)} \underset{\mathbf{1\text{–}3}}{[Os\{\eta^3\text{-}RC_3C(H)R\}L_4]^+}$$

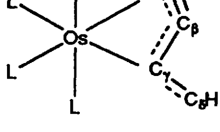
Scheme 1 R = Bu^t **1**, Ph **2** or p-MeC_6H_4 **3**; L = $P(OEt)_3$ **a** or $PPh(OEt)_2$ **b**. (*i*) CF_3SO_3Me, Et_2O; (*ii*) excess of $RC{\equiv}CH$, Et_2O

The elemental analyses and the ^1H, ^{31}P and ^{13}C NMR data for the butenynyl complexes **1–3** are reported in Tables 1–3. They are white or pale yellow solids, stable in the air and in polar organic solvents, where they behave as 1 : 1 electrolytes.[9] The ^{31}P-$\{^1H\}$ NMR spectra of all the complexes in the temperature range −90 to +30 °C are ABC_2 or AB_2C multiplets, which can easily be assigned with the parameters reported in Table 2. Furthermore, the ^1H NMR spectra show, besides the signals of phosphite ligands and phenyl protons, two singlets for the methyl protons of the R substituents (R = Bu^t or p-tolyl), indicating the existence of non-equivalent groups. In the vinyl proton region, a doublet of multiplets is also present at δ 4.66–5.37 for the $PPh(OEt)_2$ derivatives **1b**, **2b** and **3b** and at δ 5.88 for compound **1a**, attributable to the vinyl protons of the η^3-RC_3CHR ligand. Finally, the ^{13}C NMR spectra strongly support the formulation of these complexes as η^3-enynyl derivatives of the type **I**, with the butenynyl ligand almost coplanar with the two mutually *cis*-phosphite ligands. The proton-coupled ^{13}C and decoupled ^{13}C-$\{^1H\}$ NMR spectra of $[Os\{\eta^3\text{-}Bu^tC_3C(H)Bu^t\}\{P(OEt)_3\}_4][CF_3SO_3]$ **1a**, which does not contain phenyl carbon atoms masking the region of interest, clearly show the presence of a CH vinyl carbon atom at δ 138.3 with $^1J_{CH}$ = 160 Hz, attributed to the C_δ atom. Moreover, besides the signals of the $P(OEt)_3$ ligands and the CF_3SO_3 anion, three quaternary carbon atom signals are present in the spectra as multiplets, the first at δ 121.9 with the strong *trans*-$^2J_{CP}$ of 57 Hz, attributable to C_γ, and the other two at δ 109.0 and 108.3, assigned to C_α and/or C_β carbon atoms. Further support for the formulation of these complexes as butenynyl derivatives comes from a comparison with the related $[Ru(\eta^3\text{-}RC_3CHR)L_4]^+$ cations[2] the crystal structure of which is known. The NMR properties are strictly similar for the two series of osmium and ruthenium complexes and therefore it seems plausible to propose a type **I** geometry also for the osmium derivatives.

It may be noted that enynyl complexes have many precedents[1,2,10] for ruthenium and iron, whereas only two examples, $[Os\{P(CH_2CH_2PPh_2)_3\}\{\eta^3\text{-}(Me_3Si)C_3CH(SiMe_3)\}]BPh_4$ and $[Os(\eta^3\text{-}PhC_3CHPh)(PMe_3)_4]PF_6$, have been reported for osmium[5a,g] the synthesis of which involves, in the latter case, the reaction of $AgPF_6$ with $[Os(C{\equiv}CPh)_2(PMe_3)_4]$. Our results allow the completion of the iron triad butenynyl derivatives $[M\{\eta^3\text{-}RC_3C(H)R\}L_4]^+$ stabilised by phosphite ligands and the evidence indicates that the MHL_4 fragment bonded to a substitution-labile ligand, *i.e.* η^2-H_2 for Fe and Ru and CF_3SO_3 for Os, affords enynyl complexes by reaction with non-activated terminal alkynes $RC{\equiv}CH$ (R = Ph, p-tolyl or Bu^t).

Treatment of $[OsH_2L_4]$ with methyl triflate followed by an excess of activated alkynes such as $HC{\equiv}CCO_2R$ (R = Me or Et) and $MeO_2CC{\equiv}CCO_2Me$ did not afford enynyl complexes, but chelate vinyl derivatives $[Os\{CH{=}C(H)CO_2R\}L_4]^+$ **4** and **5** and $[Os\{C(CO_2Me){=}C(H)CO_2Me\}L_4]^+$ **6**, which can be isolated as $CF_3SO_3^-$ or BPh_4^- salts. Some spectroscopic properties of these complexes, which are stable solids, diamagnetic and 1 : 1 electrolytes,[9] are reported in Tables 1–4.

The $PPh(OEt)_2$ derivatives **4b** and **5b** show in their IR spectra

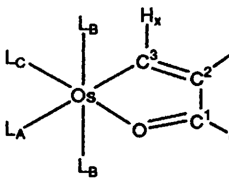


I

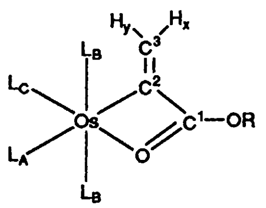
Table 1 Physical, analytical and selected IR data for the complexes

Compound		M.p./°C	Λ_M[a]/ S cm^2 mol^{-1}	Analysis[b] (%) C	H	IR[c]/cm^{-1}
1a	$[Os\{\eta^3\text{-}Bu^tC_3C(H)Bu^t\}\{P(OEt)_3\}_4][CF_3SO_3]$	155	90.6	37.80 (38.05)	6.85 (6.80)	
1b	$[Os\{\eta^3\text{-}Bu^tC_3C(H)Bu^t\}\{PPh(OEt)_2\}_4][CF_3SO_3]$	140	79.5	48.95 (49.15)	6.00 (6.15)	
2a	$[Os\{\eta^3\text{-}PhC_3C(H)Ph\}\{P(OEt)_3\}_4][CF_3SO_3]$	155	82.9	40.90 (40.80)	5.80 (5.95)	
2b	$[Os\{\eta^3\text{-}PhC_3C(H)Ph\}\{PPh(OEt)_2\}_4][CF_3SO_3]$	137	78.6	51.35 (51.25)	5.25 (5.35)	
3a	$[Os\{\eta^3\text{-}(p\text{-}MeC_6H_4)C_3CH(C_6H_4Me\text{-}p)\}\text{-}\{P(OEt)_3\}_4]BPh_4$	158	51.6	56.25 (56.40)	6.95 (6.80)	
3b	$[Os\{\eta^3\text{-}(p\text{-}MeC_6H_4)C_3CH(C_6H_4Me\text{-}p)\}\text{-}\{PPh(OEt)_2\}_4][CF_3SO_3]$	122	83.4	51.85 (51.95)	5.50 (5.55)	
4a	$[Os\{CH{=}C(H)CO_2Me\}\{P(OEt)_3\}_4][CF_3SO_3]$	—	80.4	31.80 (32.00)	6.10 (6.00)	1574s, 1563s ν(CO)
4b	$[Os\{CH{=}C(H)CO_2Me\}\{PPh(OEt)_2\}_4][CF_3SO_3]$	195	81.6	44.30 (44.40)	5.50 (5.40)	1575s ν(CO)
5a	$[Os\{CH{=}C(H)CO_2Et\}\{P(OEt)_3\}_4]BPh_4$	185	53.0	49.70 (50.00)	6.90 (6.90)	1567s, 1549s ν(CO)
5b	$[Os\{CH{=}C(H)CO_2Et\}\{PPh(OEt)_2\}_4][CF_3SO_3]$	—	82.1	44.70 (44.85)	5.65 (5.50)	1568s ν(CO)
6a	$[Os\{C(CO_2Me){=}C(H)CO_2Me\}\{P(OEt)_3\}_4]BPh_4$	88 (decomp.)	56.7	49.35 (49.25)	6.70 (6.65)	1729s, 1625s ν(CO)
6b	$[Os\{C(CO_2Me){=}C(H)CO_2Me\}\{PPh(OEt)_2\}_4]BPh_4$	—	51.8	58.30 (58.15)	6.15 (6.05)	1728s, 1620s ν(CO)
7a	$[OsH(C{\equiv}CPh)\{P(OEt)_3\}_4]$	—	—	40.30 (40.15)	6.85 (6.95)	2092s ν(C≡C)
7b	$[OsH(C{\equiv}CPh)\{PPh(OEt)_2\}_4]$	168	—	52.95 (53.15)	6.15 (6.15)	2075s ν(C≡C)

[a] In nitromethane solution (10^{-3} mol dm^{-3}) at 25 °C. [b] Calculated values in parentheses. [c] In KBr.



II



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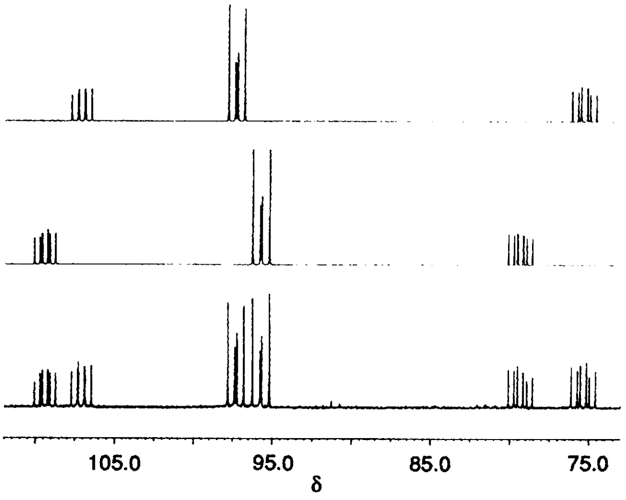


Fig. 1 Observed (bottom) and calculated (upper traces) $^{31}P\text{-}\{^1H\}$ NMR spectra of compound **4a** (two isomers) in CD_2Cl_2 at 25 °C. The simulated spectra were obtained with the parameters reported in Table 2. See text for discussion

only one strong band at 1575 and at 1568 cm^{-1}, respectively, attributed to ν(CO) of the co-ordinated carbonyl group of the vinyl ligand. In the temperature range −90 to +30 °C, the $^{31}P\text{-}\{^1H\}$ NMR spectra are AB_2C multiplets and their simulation is in very good agreement with the experimental spectra (Table 2). Furthermore, the ^1H NMR spectra of **4b** and **5b** display, apart from the signals of the $PPh(OEt)_2$ ligands and the Me or Et group of the $CH{=}C(H)CO_2R$ ligand, two multiplets at δ 9.24 and 6.56 for **4b** and at 9.24 and 6.55 for **5b**, reasonably attributable to the two vinyl protons of $CH{=}C(H)CO_2R$. These multiplets are due to the coupling of each proton with the other and with the phosphorus nuclei, as can be deduced by a computer simulation using an AB_2CXY model ($X = H_x$, $Y = H_y$) with the parameters reported in Table 4. The values of J_{HH} of 9.4 (**4b**) and 9.2 Hz (**5b**) are consistent with a mutually *cis* position[11] of the two vinyl protons. On the basis of these data, a type **II** geometry can reasonably be proposed for **4b** and **5b**, because for a type **III** structure a lower value of J_{HH} (1–3 Hz) is expected.

The ^{13}C NMR spectra confirm the proposed formulation, showing the two vinyl carbons, C^3 and C^2, as CH resonances at δ 210.0 (**4b**) and at δ 209.3 (**5b**), with $^1J_{CH}$ = 148 Hz and at δ 124.8 (**4b**) and at 125.0 (**5b**), with $^1J_{CH}$ = 167 Hz, respectively. Furthermore, apart from the signals of the $PPh(OEt)_2$ ligand and CF_3SO_3 anion, a multiplet is present at δ 186.7 and at 186.4 due to the carbonyl carbon atom C^1, whereas the CH_3 resonance of the OR substituents appears as a quartet at δ 53.1 (**4b**) and at 13.7 (**5b**).

Surprisingly, the related $P(OEt)_3$ vinyl derivatives **4a** and **5a** show two ν(CO) bands (at 1574 and 1563 and at 1567 and 1549 cm^{-1}) of the co-ordinated carbonyl group of the vinyl ligand. Furthermore, the $^{31}P\text{-}\{^1H\}$ NMR spectra of the complexes appear as two AB_2C multiplets, which can be simulated (Fig. 1) with the parameters reported in Table 2. Finally, also the ^1H NMR spectra are different with respect to those of the $PPh(OEt)_2$ derivatives **4b** and **5b**, showing four multiplets in the vinyl region, which are coupled two by two, as determined from proton-decoupled experiments. These signals can also be simulated as the XY part of two AB_2CXY ($X = H$, $Y = H$) spin systems (Table 4), as shown in Fig. 2. These infrared and NMR data for complexes **4a** and **5a** may be interpreted on the basis of the existence of two isomers of type **II** and **III** present in about equimolecular amounts, as indicated by the intensity ratio of the signals in the IR and NMR spectra. Two ν(CO) bands, two AB_2C multiplets and two ^1H vinyl signals (four multiplets) are expected for a mixture of complexes **II** and **III**, with a five- and a four-membered chelate ring, respectively. Furthermore, the H–H coupling constants of the two vinyl protons are different, near 9.5 Hz in one case, as expected for the vinyl proton in the *cis* position (**II**), whereas a value of about 2.4 Hz is observed in the other case, typical of two vinyl protons in a $CR{=}CH_2$ group,[5,12] as in a type **III** isomer. The proton-coupled (Table 3) and decoupled ^{13}C NMR spectra confirm the proposed existence of the two isomers **II** and **III** for **4a** and **5a**, showing (see Fig. 3) for each compound two carbonyl carbon (C^1) resonances between δ 187.5 and 188.7 and four vinyl carbon signals, two of which are CH resonances at δ 207.5 (J_{CH} = 150) and 122.6 (J_{CH} = 167 Hz) for **4a** and at δ 206.5 (J_{CH} = 146) and

Table 2 Proton and phosphorus-31 NMR data

	^{1}H NMR^{a,b}			
Compound	δ	Assignment	Spin system	^{31}P-{^{1}H} NMR, δ^{a,c}
1a^d	5.88 (dm)	C≡C–C=CH	ABC$_2$	δ_A 95.1, δ_B 84.0, δ_C 80.0
	4.20–4.06, 3.92–3.81 (m)	POCH_2CH$_3$		(J_{AB} = 16.1, J_{AC} = 41.3, J_{BC} = 46.7)
	1.47, 1.14 (s)	CMe$_3$		
	1.37, 1.32, 1.19 (t)	POCH$_2$CH_3		
1b	4.66 (dm)	C≡C–C=CH	AB$_2$C	δ_A 122.3, δ_B 109.1, δ_C 107.9
	4.20–3.35 (m)	POCH_2CH$_3$		(J_{AB} = 30.0, J_{AC} = 9.8, J_{BC} = 37.6)
	1.51, 1.43, 1.29, 1.20 (t)	POCH$_2$CH_3		
	1.06, 0.60 (s)	CMe$_3$		
2a	4.40–3.82 (m)	POCH_2CH$_3$	ABC$_2$	δ_A 94.1, δ_B 84.8, δ_C 84.0
	1.46, 1.35, 1.05 (t)	POCH$_2$CH_3		(J_{AB} = 24.1, J_{AC} = 41.6, J_{BC} = 32.7)
2b	5.37 (dm)	C≡C–C=CH	AB$_2$C	δ_A 119.6, δ_B 110.4, δ_C 108.2
	4.00–3.60 (m)	POCH_2CH$_3$		(J_{AB} = 30.9, J_{AC} = 17.7, J_{BC} = 34.0)
	1.44, 1.40, 1.28, 1.14 (t)	POCH$_2$CH_3		
3a^d	4.20–4.00, 3.80–3.60 (m)	POCH_2CH$_3$	ABC$_2$	δ_A 93.6, δ_B 83.6, δ_C 83.1
	2.39, 2.35 (s)	CH_3C$_6$H$_4$		(J_{AB} = 24.2, J_{AC} = 38.8, J_{BC} = 37.6)
	1.38, 1.28, 1.00 (t)	POCH$_2$CH_3		
3b	5.32 (dm)	C≡C–C=CH	AB$_2$C	δ_A 119.9, δ_B 110.5, δ_C 108.3
	4.10–3.40 (m)	POCH_2CH$_3$		(J_{AB} = 30.5, J_{AC} = 17.4, J_{BC} = 34.2)
	2.31, 2.27 (s)	CH_3C$_6$H$_4$		
	1.40, 1.37, 1.27, 1.15, 1.11 (t)	POCH$_2$CH_3		
4a^{d,e}	4.13–3.90 (m)	POCH_2CH$_3$	AB$_2$C	δ_A 107.1, δ_B 97.3, δ_C 75.4
	3.83, 3.77 (s)	CO$_2$CH$_3$		(J_{AB} = 35.4, J_{AC} = 31.2, J_{BC} = 46.2)
	1.30, 1.28, 1.27 (t)		AB$_2$C	δ_A 109.4, δ_B 95.7, δ_C 79.4
	1.24, 1.21 (t)	POCH$_2$CH_3		(J_{AB} = 39.9, J_{AC} = 28.7, J_{BC} = 47.0)
4b^{d,e}	4.20–3.62 (m)	POCH_2CH$_3$	AB$_2$C	δ_A 128.2, δ_B 119.4, δ_C 106.3
	1.40, 1.24 (t)	POCH$_2$CH_3		(J_{AB} = 30.9, J_{AC} = 24.1, J_{BC} = 35.0)
	2.74 (s)	CO$_2$CH$_3$		
5a^e	4.25–3.75 (m)	POCH_2CH$_3$^{d}	AB$_2$C	δ_A 110.7, δ_B 96.8, δ_C 80.7
	4.02, 3.98 (q)	CO$_2$CH_2CH$_3$		(J_{AB} = 39.9, J_{AC} = 28.6, J_{BC} = 47.2)
	1.33, 1.27 (t)			
	1.24, 1.21 (t)	POCH$_2$CH_3	AB$_2$C	δ_A 108.5, δ_B 98.3, δ_C 76.9
				(J_{AB} = 35.6, J_{AC} = 31.5, J_{BC} = 46.1)
5b^{d,e}	4.15–3.60 (m)	POCH_2CH$_3$	AB$_2$C	δ_A 128.3, δ_B 119.5, δ_C 106.4
	2.96 (q)	CO$_2$CH_2CH$_3$		(J_{AB} = 30.8, J_{AC} = 23.9, J_{BC} = 35.1)
	1.40, 1.24 (t)	POCH$_2$CH_3		
	0.84 (t)	CO$_2$CH$_2$CH_3		
6a	5.72 (s)	=C(H)CO$_2$Me	A$_2$BC	δ_A 92.9, δ_B 78.1, δ_C 74.5
	4.30–3.70 (m)	POCH_2CH$_3$		(J_{AB} = 40.2, J_{AC} = 42.8, J_{BC} = 55.7)
	3.71, 3.59 (s)	CO$_2$CH$_3$		
	1.36, 1.34, 1.32, 1.29, 1.25 (t)	POCH$_2$CH_3		
6b	5.44 (s)	=C(H)CO$_2$Me	A$_2$BC	δ_A 118.9, δ_B 108.5, δ_C 102.7
	4.14–3.40 (m)	POCH_2CH$_3$		(J_{AB} = 30.1, J_{AC} = 31.3, J_{BC} = 40.7)
	3.78, 3.62 (s)	CO$_2$CH$_3$		
	1.41, 1.33, 1.29, 1.26, 1.17 (t)	POCH$_2$CH_3		
7a^f	4.34–3.86 (m)	POCH_2CH$_3$		115–87 (m)
	1.27, 1.13, 1.09 (t)	POCH$_2$CH_3		
	−10.8 to −10.0 (m)	Hydride		
7b^{d,f}	3.97, 3.47 (m)	POCH_2CH$_3$		121.75 (s)
	1.07 (t)	POCH$_2$CH_3		
	−10.41 (qnt)	Hydride		
	(J_{PH} = 20)			

[a] At room temperature in (CD$_3$)$_2$CO. [b] Phenyl-proton resonances are omitted. [c] Coupling constants in Hz; positive shift downfield from 85% H$_3$PO$_4$. [d] In CD$_2$Cl$_2$. [e] Vinyl protons in Table 4. [f] In C$_6$D$_6$.

123.0 (J_{CH} = 167 Hz) for **5a**, respectively, attributable to C^3 and C^2 of isomer **II**. The other two vinyl signals appear as CH$_2$ resonances near δ 131 (J_{CH} = 157 Hz) and as a quaternary carbon resonance near δ 135, reasonably attributed to C^3 and C^2 of isomer **III**. Also two signals for the methyl carbon atom of the OR group are present in the ^{13}C NMR spectra of each

Table 3 Carbon-13 NMR data for selected osmium compounds[a]

Compound	δ	Assignment[b]	Coupling constant/Hz
1a	138.3 (dm)	C_δ	$^1J_{CH} = 160$
	121.9 (dm)	C_γ	$^2J_{CP\mathit{trans}} = 57$
	118.8 (q)	CF_3	$^1J_{CF} = 320$
	109.0, 108.3 (m)	C_α, C_β	
	62.2 (tm)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	36.2, 32.8 (d)	$\mathit{C}\mathrm{(CH_3)_3}$	
	32.0, 29.9 (q)	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	
	16.1 (qm)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
1b	136.6 (dm)	C_δ	$^1J_{CH} = 160$
	123.2 (dm)	C_γ	
	110.3 (m)	C_α or C_β	
	66.3, 64.9 (m)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	36.3, 32.8 (d)	$\mathit{C}\mathrm{(CH_3)_3}$	
	30.9, 29.9 (q)	$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	
	16.6 (m)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
4a	207.5 (dm)	C^3 (**II**)	$^1J_{CH} = 150$
	188.7, 187.8 (m)	C^1	
	134.9 (m)	C^2 (**III**)	
	131.7 (tm)	C^3 (**III**)	$^1J_{CH} = 158$
	122.6 (dm)	C^2 (**II**)	$^1J_{CH} = 167$
	62.2, 61.2 (m)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	53.6, 51.9 (q)	$\mathrm{CO_2}\mathit{C}\mathrm{H_3}$	
	16.2 (m)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
5a	206.5 (dm)	C^3 (**II**)	$^1J_{CH} = 146$
	188.5, 187.5 (m)	C^1	
	131.5 (tm)	C^3 (**III**)	$^1J_{CH} = 157$
	123.0 (dm)	C^2 (**II**)	$^1J_{CH} = 167$
	62.9, 61.6 (t)	$\mathrm{CO_2}\mathit{C}\mathrm{H_2CH_3}$	
	62.2, 61.2 (tm)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	16.3 (m)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
	14.5, 14.1 (q)	$\mathrm{CO_2CH_2}\mathit{C}\mathrm{H_3}$	
4b	210.0 (dm)	C^3	$^1J_{CH} = 148$
	186.7 (m)	C^1	
	124.8 (m)	C^2	$^1J_{CH} = 167$
	69.0–59.0 (m)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	53.1 (q)	$\mathrm{CO_2}\mathit{C}\mathrm{H_3}$	
	16.5 (qm)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
5b	209.3 (dm)	C^3	$^1J_{CH} = 148$
	186.4 (m)	C^1	
	125.0 (dm)	C^2	$^1J_{CH} = 167$
	69.0–59.0 (m)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	62.5 (t)	$\mathrm{CO_2}\mathit{C}\mathrm{H_2CH_3}$	
	16.5 (m)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
	13.7 (q)	$\mathrm{CO_2CH_2}\mathit{C}\mathrm{H_3}$	
6a	170.7 (m)	C^3	
	168.8 (s)	C^4	
	164.3 (m)	C^1	
	88.9 (d)	C^2	$^1J_{CH} = 167$
	62.4 (tm)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	53.9, 52.6 (q)	$\mathrm{CO_2}\mathit{C}\mathrm{H_3}$	
	16.3 (m)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	
7b	113.6 (m)	C_β	
	110.2 (qnt)	C_α	$^2J_{CP} = 13$
	61.6 (tm)	$\mathrm{PO}\mathit{C}\mathrm{H_2CH_3}$	
	16.2 (q)	$\mathrm{POCH_2}\mathit{C}\mathrm{H_3}$	

[a] At room temperature in CD_2Cl_2. All phenyl-carbon resonances are omitted. [b] For assignment see geometries **I**–**VI**.

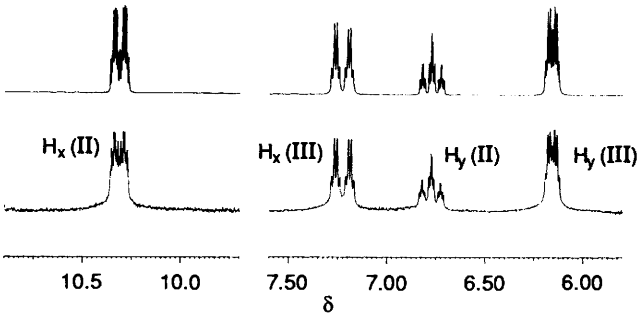


Fig. 2 Observed (bottom) and calculated (top) ^1H NMR spectra of the vinyl protons of compound **4a** (two isomers) in CD_2Cl_2 at 25 °C. The simulated spectra were obtained with the parameters reported in Table 4. See text for discussion

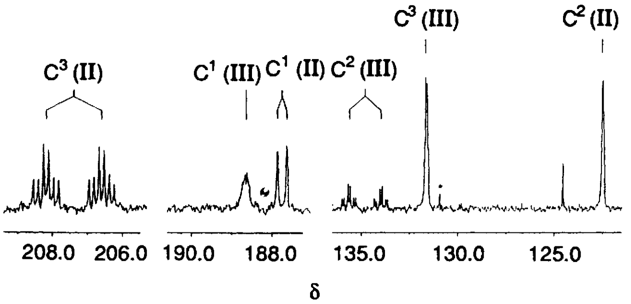


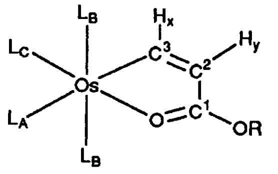
Fig. 3 The $^{13}C\text{-}\{^1H\}$ NMR spectrum of compound **4a** (two isomers) in CD_2Cl_2 at 25 °C, lower-field region. Peaks marked with asterisks (*) are due to the CF_3 carbon atom of the $CF_3SO_3^-$ anion

complex, together with the signal of the phosphite ligand, in agreement with the proposed formulation.

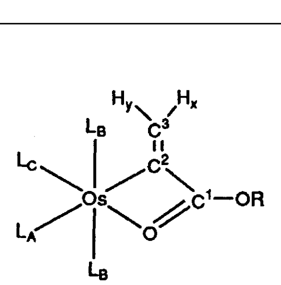
The formation of two isomers with one phosphite ligand [$P(OEt)_3$] and of only one with the other is rather unexpected, but seems to confirm that the nature of the product of the insertion of alkyne into the M–H bond is difficult to predict, depending on a delicate balance of factors.[13] The small change in steric and electronic properties on going from $PPh(OEt)_2$ to $P(OEt)_3$ determines the different isomers in the vinyl complexes. Furthermore, it is worth noting that the related iron derivatives[1] $[Fe\{CH{=}C(H)CO_2Me\}L_4]^+$ were obtained as only one isomer like **II** with both L = $P(OEt)_3$ and $PPh(OEt)_2$, while the related ruthenium[2] vinyl complexes were not obtained.

Dimethyl acetylenedicarboxylate also reacts with solutions containing $[OsH(O_3SCF_3)L_4]$ to afford $[Os\{C(CO_2Me){=}C(H)CO_2Me\}L_4]^+$ cations, which can be isolated as BPh_4 salts **6a** and **6b**. Elemental analyses, Λ_M values and spectroscopic data (IR and NMR, Tables 1–3) confirm the proposed formulation as chelate alkenyl complexes and suggest the presence of only one isomer of type **IV** or **V**. The infrared spectra show two ν(CO) bands at 1625 and 1729 cm^{-1} for **6a** and at 1620 and 1728 cm^{-1} for **6b**, attributed to one co-ordinated and one free carbonyl group, respectively, whereas the $^{31}P\text{-}\{^1H\}$ NMR spectra, between −90 and +30 °C, reveal a simple A_2BC multiplet. Moreover, the ^1H NMR spectra display two singlets at δ 3.71 and 3.59 for **6a** and at δ 3.78 and 3.62 for **6b**, attributed to two non-equivalent CO_2Me substituents and one singlet at δ 5.72 for **6a** and at δ 5.44 for **6b** due to the CH vinyl protons of the ligand. The ^{13}C NMR spectra confirm the presence of the vinyl chelate ligands, showing for **6a** two signals for the non-equivalent methyl groups of CO_2Me, two resonances at δ 168.8 and 164.3 for the free and co-ordinated carbonyl groups (C^4 and C^1) and two signals of two vinyl carbon atoms at δ 170.7 (carbenoid C atom) and at 88.9 (CH resonance with $J_{CH} = 167$ Hz). These data, however, do not allow us unambiguously to assign a geometry **IV** or **V** for the dimethyl dicarboxylate complexes **6a** and **6b**, although a comparison of the ^{13}C data for **6a** with those of compounds **4a** and **5a** may tentatively suggest a structure of type **IV**, on the basis of the chemical shift of the two vinyl carbon atoms. For a type **V** structure the C^2 and C^3 vinyl carbon atoms would show chemical shift values similar to those of isomer **III** of **4a** and **5a** (near δ 131 and 135, respectively),

Table 4 Proton NMR data for vinyl protons of alkenylosmium(II) complexes[a]



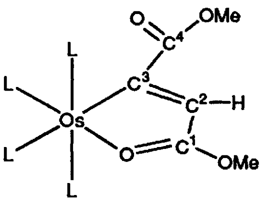
II



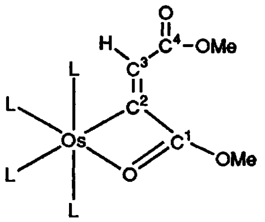
III

Compound[b]	Spectrum type	Chemical shift δ and J/Hz for XY part of spectrum (X, Y = vinyl H)	
		II	III
4a	AB_2CXY	δ_X 10.33, δ_Y 6.79 J_{AX} = 2.4, J_{AY} = 9.5, J_{BX} = 2.7, J_{BY} = 2.4, J_{CX} = 1.4, J_{CY} = 1.1, J_{XY} = 9.6	δ_x 7.24, δ_y 6.17 J_{AX} = 14.0, J_{AY} = 6.9, J_{BX} = 2.8, J_{BY} = 2.2, J_{CX} = 0.6, J_{CY} = 0.1, J_{XY} = 2.4
4b	AB_2CXY	δ_X 9.24, δ_Y 6.56 J_{AX} = 0.2, J_{AY} = 8.3, J_{BX} = 2.4, J_{BY} = 2.1, J_{CX} = 0.0, J_{CY} = 1.0, J_{XY} = 9.4	
5a[c]	AB_2CXY	δ_X 10.28, δ_Y 6.79 J_{AX} = 2.5, J_{AY} = 9.6, J_{BX} = 2.7, J_{BY} = 2.4, J_{CX} = 1.3, J_{CY} = 1.1, J_{XY} = 9.5	δ_x 7.24, δ_y 6.15 J_{AX} = 14.2, J_{AY} = 6.9, J_{BX} = 3.0, J_{BY} = 2.3, J_{CX} = 0.2, J_{CY} = 0.1, J_{XY} = 2.5
5b	ABC_2XY	δ_X 9.24, δ_Y 6.55 J_{AX} = 0.1, J_{AY} = 8.5, J_{BX} = 2.4, J_{BY} = 2.1, J_{CX} = 0.0, J_{CY} = 1.0, J_{XY} = 9.2	

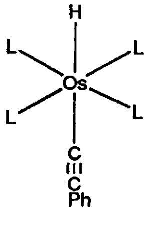
[a] At room temperature in CD_2Cl_2. [b] All compounds are $CF_3SO_3^-$ salts, except **5a**. [c] As BPh_4^- salt.



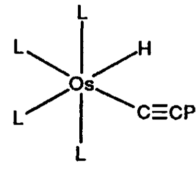
IV



V



VI



VII

$$[OsH_2L_4] \xrightarrow{(i)} [OsH(O_3SCF_3)L_4] \xrightarrow{(ii)} \underset{\textstyle 7}{[OsH(C{\equiv}CPh)L_4]}$$

Scheme 2 (*i*) CF_3SO_3Me, Et_2O; (*ii*) Li[C≡CPh], thf

whereas the values of δ 170.7 and 88.9 found for **6a** best agree with those of isomer **II**, suggesting a type **IV** geometry.

The reactivity shown by the unsaturated hydrides $[OsH(O_3SCF_3)L_4]$ toward alkynes prompted us to extend our study also to acetylides and the results show that the sequential reaction of the hydrides $[OsH_2L_4]$ with CF_3SO_3Me and with lithium phenylacetylides affords the hydride–alkynyl complexes $[OsH(C{\equiv}CPh)L_4]$, as in Scheme 2. The compounds are white solids, diamagnetic, stable in the solid state and in non-polar solvents, where they behave as non-electrolytes. The ν(C≡C) band is present at 2092 (**7a**) and 2075 cm^{-1} (**7b**). The ^1H and ^{31}P NMR spectra confirmed the formulation proposed for the acetylides and also suggest a different geometry for the two complexes. In the temperature range −90 to +30 °C a quintet at δ −10.41 (J_{PH} = 20 Hz) is present in the ^1H NMR spectrum of $[OsH(C{\equiv}CPh)\{PPh(OEt)_2\}_4]$ **7b**, due to the hydride resonance, while a sharp singlet is observed in its ^{31}P spectra, in agreement with four magnetically equivalent phosphorus atoms, as in a type **VI** *trans* geometry. In contrast, the ^1H spectrum of $[OsH(C{\equiv}CPh)\{P(OEt)_3\}_4]$ **7a** shows a complicated multiplet near δ −10.4 due to the hydride resonances, while a slightly broad multiplet is present in the ^{31}P-$\{^1H\}$ spectrum. This ^{31}P multiplet is practically unchanged as the temperature is lowered and also at −80 °C the linewidth does not allow any correct assignment of δ and J for an ABC_2 or AB_2C spin system. However, the presence of multiplets both in the ^{31}P NMR spectra and in the hydride region of the ^1H spectra strongly suggest a mutually *cis* position of H^- and $PhC{\equiv}C^-$ ligands, as in type **VII** geometry.

We have also studied the reactivity of these acetylide complexes toward $HBF_4{\cdot}Et_2O$, in order to verify whether protonation takes place at the hydride ligand giving an acetylide–dihydrogen derivative of the type $[Os(C{\equiv}CPh)(\eta^2\text{-}H_2)L_4]$,[14] or at the $PhC{\equiv}C^-$ ligand affording a vinylidene[15,16] or a π-alkyne complex.[17] The results obtained show that under H_2 (1 atm, *ca.* 10^5 Pa) protonation with $HBF_4{\cdot}Et_2O$ proceeds to give in both cases a white solid characterised as a $[OsH(\eta^2\text{-}H_2)L_4]BF_4$ derivative[3] [equation (1)]. Under an inert

$$[OsH(C{\equiv}CPh)L_4] \xrightarrow[H_2]{HBF_4{\cdot}Et_2O} [OsH(\eta^2\text{-}H_2)L_4]^+ \quad (1)$$

atmosphere (Ar), on the contrary, protonation of **7** always gives intractable oils, containing neither η^2-H_2 nor vinylidene complexes. These results may be tentatively explained on the basis of protonation of the acetylide $PhC\equiv C^-$ ligand, affording a vinylidene $[OsH\{C{=}C(H)Ph\}L_4]^+$ or a π-alkyne $[OsH(PhC\equiv CH)L_4]^+$ derivative. The $=C{=}C(H)Ph$ or $PhC\equiv CH$ ligands can be rather labile in these complexes and the $[OsH(\eta^2\text{-}H_2)L_4]^+$ compounds can be obtained only by substitution with H_2.

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