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MONONUCLEAR η^3-ALLYLOSMIUM HYDRIDE COMPLEXES AND THE X-RAY CRYSTAL STRUCTURE OF THE SOLVENTO COMPLEX $[OsH(H_2O)(CO)_2(PPh_3)_2]BF_4 \cdot EtOH$

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Summary

The osmium(II) hydride $[OsHCl(CO)(PPh_3)_3]$ reacts with 2-methylallylmagnesium chloride and allylmagnesium chloride to give the air-stable η^3-allylosmium hydride complexes $[OsH(CO)(\eta^3\text{-}CH_2CRCH_2)(PPh_3)_2]$ (R = Me or H). The orientation of the η^3-allyl ligand in these complexes has been established by NOE difference spectra. Treatment of $[OsH(CO)(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)_2]$ with fluoroboric acid in the presence of a ligand L (L = Ph_3P or CO) affords the cationic hydride complexes $[OsH(CO)(OH_2)(L)(PPh_3)_2][BF_4]$. The crystal structure of $[OsH(CO)_2(OH_2)(PPh_3)_2][BF_4] \cdot EtOH$ has been determined.

Introduction

Only a few η^3-allyl complexes of osmium have been reported and their chemistry has not been widely explored [1]. Herein we show that the hydride $[OsHCl(CO)(PPh_3)_3]$ readily reacts with allylmagnesium halides to afford good yields of air-stable η^3-allylosmium hydride complexes and report some of their reactions.

Results and discussion

Treatment of $[OsHCl(CO)(PPh_3)_3]$ with 2-methylallylmagnesium chloride results in displacement of a chloride and a triphenylphosphine ligand from this osmium(II) hydride complex to give a white crystalline air-stable complex (**1**) in good yield (69%). The ^1H NMR spectrum measured at room temperature established that the hydride ligand is *cis* to both phosphines and that the methallyl group is symmetrically coordinated. Moreover an NOE difference experiment clearly indicated that the orientation of the methylallyl ligand is such that the *anti*-allyl hydrogens are closer to the hydride ligand than the methyl group as in **1a**, there being no evidence

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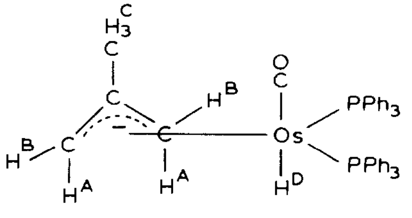
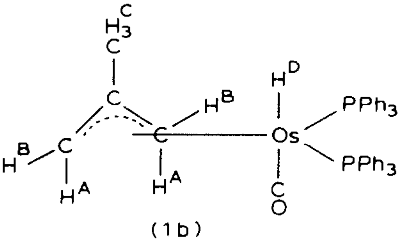
for the alternative conformation **1b**. Thus in the NOE difference spectrum, irradiation of the hydride H^D gave a clear enhancement at the resonance H^A assigned to the *anti*-hydrogens with no effect at the methyl protons H^C. It has also been possible to confirm the assignments of the *syn* and *anti* proton resonances by an NOE difference experiment. A simple molecular model indicates that the shortest H^B–H^C distance is approximately 3 Å whilst the corresponding H^A–H^C distance is about 4 Å. In the NOE difference spectrum irradiation at H^C gave a clear enhancement at the resonance assigned to the *syn* hydrogens H^B with no significant effect at H^A. It is noteworthy that the hydride resonance at $\delta - 8.47$ ppm appeared as a triplet of triplets due to coupling with two equivalent phosphines and the two equivalent *anti*-hydrogens of the methylallyl ligand, the H^A–H^D coupling being confirmed by a selective decoupling experiment. Interestingly in the corresponding ruthenium complex $[RuH(\eta^3\text{-}CH_2CHCHPh)(MeCN)(PPh_3)_2]$, coupling between the ruthenium hydride and the *syn*-hydrogen but not the *anti*-hydrogens is apparently observed [2].

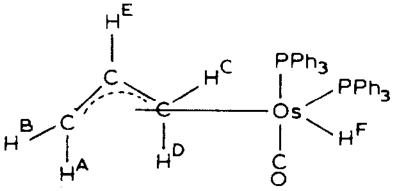


(1a)

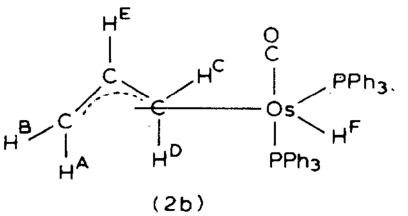


(1b)

Treatment of $[OsHCl(CO)(PPh_3)_3]$ with allylmagnesium chloride also affords an air-stable allylosmium hydride complex (**2**). However, the arrangement of ligands about the osmium is not the same as that in **1a**, the NMR data for **2** indicating the presence of two inequivalent phosphorus nuclei *cis* to the hydride ligand. The assignments for the *syn*- and *anti*-protons were again established by NOE difference spectra. Thus irradiation at H^E gave clear enhancements at the resonances assigned to the *syn*-hydrogens H^B and H^C with no significant effect at H^A or H^D. Furthermore the observation that there was also an enhancement of some of the phenyl-proton signals of the triphenylphosphine ligands suggests that the structure of **2** is **2a** rather than **2b**. In the η^3-allyl complex **1** no significant enhancement of the phenyl proton signals was detected in the NOE difference spectrum.



(2a)

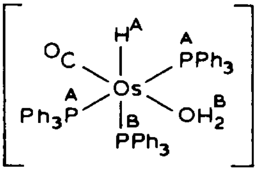


(2b)

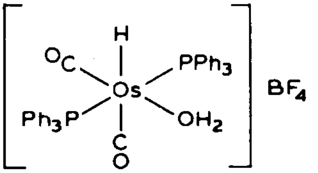
We have previously drawn attention to the observation that the magnitude of ^3J(*trans*-PH) is often greater for *anti*- than *syn*-hydrogens [3,4] and the complex **1** provides a further example of this effect. Further, since in the complex **2a**, the *anti*-hydrogen H^A exhibits appreciable coupling to phosphorus, H^A can be placed *trans* to the triphenylphosphine ligand. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2** ^{31}P–^{31}P coupling between the inequivalent phosphorus ligands was not observed.

In both complexes **1a** and **2a** the coordination geometry about osmium is considered to be pseudo octahedral with an η^3-allyl moiety occupying two coordination sites as has been established for the related d^6 species $[IrHCl(\eta^3\text{-}CH_2CHCHPh)(PPh_3)_2]$ [5]. We also note that in common with related ruthenium complexes $[RuH(\eta^3\text{-}C_3H_5)(MeCN)(PPh_3)_2]$ [6] and $[RuH(\eta^3\text{-}CH_2CHCHPh)(MeCN)(PPh_3)_2]$ [2], no exchange of hydride with allyl protons occurs with either **1a** or **2a** on the NMR time scale. The two allylruthenium hydride complexes have structures similar to **1** with the allyl group symmetrically coordinated and hydride *cis* to both phosphines. The reasons for the different geometry in **2** are not clear.

The current interest in solvento complexes of the transition metals obtained by acidolysis of metal hydrides [7] prompted us to investigate reactions of fluoroboric acid with the methylallyl complex **1a**. Treatment of an equimolar mixture of **1a** and triphenylphosphine in ethanol with fluoroboric acid afforded the cationic hydride complex $[OsH(CO)(OH_2)(PPh_3)_3][BF_4]\cdot EtOH$ (**3**), the geometry about the osmium being clearly established from the ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra. This complex has



(3)



(4)

previously been obtained by the action of fluoroboric acid upon $[OsH_2(CO)(PPh_3)_3]$ [8]. We also find that treatment of **1a** in dichloromethane with fluoroboric acid in the presence of carbon monoxide affords a new cationic hydride complex $[OsH(CO)_2(OH_2)(PPh_3)_2][BF_4]\cdot H_2O$ (**4**) which exhibits a hydride reference at δ -2.64 ppm. In ethanol as solvent fluoroboric acid reacts with **1a** to give a product **5** which appears to be a mixture of two hydride complexes since two hydride signals at δ -2.64 and -2.47 ppm can be detected in the NMR spectrum. The appearance of a resonance at -2.64 ppm is indicative of the aquo complex **4** and the resonance at -2.47 can be assigned to the ethanol solvate $[OsH(CO)_2(EtOH)(PPh_3)_2][BF_4]$. This solvate exhibits a hydride resonance at -2.47 ppm and can be obtained by heating a mixture of the hydrides **5** in 1/1 ethanol/dichloromethane under a pressure of carbon monoxide for one hour. Microanalytical data for the mixture **5** suggests that it crystallises as an approximate 1/1 mixture of the cationic species $[OsH(CO)_2(H_2O)(PPh_3)_2][BF_4]$ and $[OsH(CO)_2(EtOH)(PPh_3)_2][BF_4]$ together with a molecule of water and ethanol. The ratio of the integrated intensities of the two NMR signals at -2.64 and -2.47 ppm is approximately 1/1.

In view of the interest in the structures of solvento complexes containing hydride ligands [7] a single crystal X-ray structure determination of the aquo hydride complex **4** was carried out. Suitable crystals of **4** were grown from ethanol/light petroleum (b.p. 40–60°C). The results of the X-ray work are summarised in Table 1. The molecular structure of the cation is shown in Fig. 1.

The structure consists of $[BF_4]^-$ anions and $[OsH(OH_2)(CO)_2(PPh_3)_2]^+$ cations which crystallise with a molecule of solvent ethanol. Both the BF_4^- anion and the solvent molecule are disordered, in the latter case a complete molecule could not be

TABLE 1

SELECTED INTRAMOLECULAR BOND LENGTHS (Å) AND ANGLES (°) IN $[OsH(CO)_2(OH_2)(PPh_3)_2][BF_4]\cdot EtOH$ (**4**) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES [a]

Os–P	2.373(2)	C(2)–O(2)	1.131(18)
Os–C(1)	1.868(14)	P–C(11)	1.828(4)
Os–C(2)	1.944(15)	P–C(21)	1.833(4)
Os–O(3)	2.160(9)	P–C(31)	1.820(5)
C(1)–O(1)	1.133(16)		
P–Os–P′	165.2(1)	Os–C(2)–O(2)	178(1)
C(1)–Os–P	88.9(1)	Os–P–C(11)	111.9(2)
C(2)–Os–P	97.4	Os–P–C(21)	117.7(2)
C(2)–Os–C(1)	97.3(7)	Os–P–C(31)	113.5(2)
O(3)–Os–P	90.1(1)	C(11)–P–C(21)	103.3(3)
O(3)–Os–C(1)	171.9(5)	C(11)–P–C(31)	106.0(3)
O(3)–Os–C(2)	90.8(6)	C(21)–P–C(31)	103.2(3)
Os–C(1)–O(1)	177(1)		

[a] Primed atoms are generated by the symmetry operation x, $\frac{1}{2}-y$, z.

identified. A distance of 2.7 Å between O(3) and F(1) suggest that the coordinated water is hydrogen bonded to the $[BF_4]^-$ anion as has been observed in $[RuH(OH_2)(CO)_2(PPh_3)_2][BF_4]\cdot EtOH$ [9]. The molecule has crystallographic symmetry with atoms Os, C(1), O(1), C(2), O(2), and O(3) lying in the mirror plane. The geometry about the central Os atom is approximately octahedral. The two phosphine groups are *trans* to one another. One of the carbonyl groups is *trans* to the water ligand while the other is *trans* to the empty coordination position which must be occupied by the hydride ligand not detected in the X-ray analysis. There is some distortion from ideal octahedral geometry since the atoms P, C(1), P′, and O(3) are significantly displaced from a plane defined by the atoms Os, P, C(1), P′, and O(3) towards

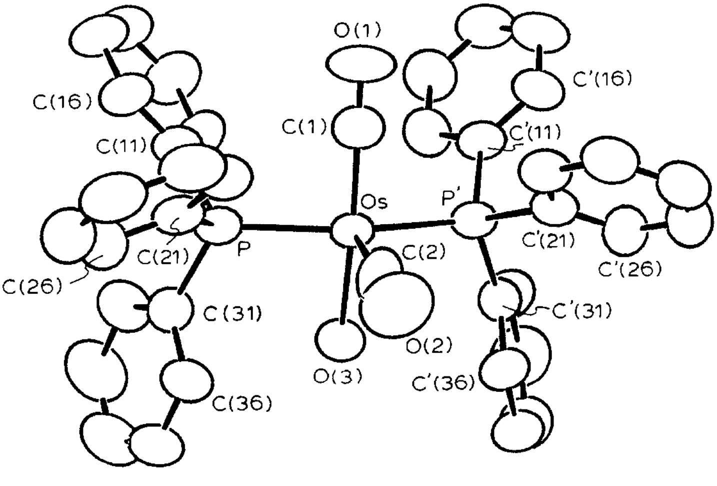


Fig. 1. Molecular structure of the cation in $[OsH(H_2O)(CO)_2(PPh_3)_2]BF_4\cdot EtOH$, showing the crystallographic numbering. Primed atoms are generated by the symmetry operation x, $\frac{1}{2}-y$, z.

TABLE 2

EQUATION OF A LEAST SQUARE PLANE IN THE FORM $Ax+By+Cz=D$, WHERE x, y, AND z ARE FRACTIONAL COORDINATES (distances (Å) of relevant atoms from these planes are given in square brackets)

Plane: Os, P, P′, C(1), O(3)

$-0.5593x+0.0000y-8.6603z=-5.5266$

(P 0.081, C(1)−0.088, O(3)−0.074, Os−0.223)

the hydride ligand (Table 2). However, the angles subtended at Os involving the P atoms and atoms C(1) and O(3) deviate little from their values of 90°.

The two Os–C bond distances (1.944(15), 1.868(14) Å) although differing from one another are in the range expected for osmium carbonyl complexes [10]. The different values reflect the *trans*-directing capabilities of the hydride and water ligands. The Os–P bond distances of 2.373(2) Å are within the range found in other osmium complexes (2.32–2.44 Å) [10]. However, the Os–O distance (2.160(9) Å) is long. The expected length of an Os–O single bond in an aquo complex is said to be 2.02 Å [11] and in the seven coordinate osmium(IV) aquo complex [Os(edta)(OH_2)] the Os–OH_2 distance is 2.049(7)Å[12].

Overall the geometry about the osmium is very similar to that found in the related species [RuH(OH_2)$(CO)_2$$(PPh_3)_2$][$BF_4$]·EtOH [9]. It is noteworthy that in both the ruthenium and osmium complexes hydride is *trans* to a carbonyl ligand. These complexes thus provide further examples of the tendency of a strongly π-bonding ligand to accomodate a strongly σ-bonding *trans*-ligand [13].

Experimental

Infrared spectra (2100–1800 cm^{-1}) were recorded as Nujol mulls on a Perkin–Elmer 580 spectrometer. Hydrogen-1 NMR spectra were recorded on a Varian EM-390 spectrometer at 90 MHz and on a Bruker Spectrospin WH400 spectrometer at 400.13 MHz with $SiMe_4$ (0.0 ppm) as internal reference, positive values being to high frequency (low field) in [D_1] chloroform unless otherwise stated. Carbon-13, hydrogen-1 decoupled NMR spectra were recorded on a Bruker Spectrospin WH 400 spectrometer at 100.62 MHz with $SiMe_4$ (0.0 ppm) as internal reference. Phosphorus-31, hydrogen-1 decoupled NMR spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.15 MHz with $[P(OH)_4]^+$ in D_2 water (0.0 ppm) as external references [14].

The compound [OsHCl(CO)$(PPh_3)_3$] [8] was prepared as described in the literature.

[OsH(CO)(η^3-CH_2CMeCH_2)$(PPh_3)_2$] (1)

[OsHCl(CO)$(PPh_3)_3$] (2.33 g, 2.24 mmol) was added to a suspension of 2-methylallylmagnesium chloride in diethyl ether (50 cm^3), (from magnesium (0.3 g) and 3-chloro-2-methylprop-1-ene (2 g)) under dry nitrogen. After stirring for 24 h, the mixture was poured into a saturated aqueous solution of ammonium chloride (100 cm^3) and the diethyl ether layer was separated. The aqueous layer was extracted with diethyl ether (2 × 30 cm^3) and the combined diethyl ether layers were evaporated to induce crystallisation of **1**. The product was filtered off to give 0.87 g of **1** and a further 0.35 g of **1** was obtained by addition of light petroleum (b.p. 40–60°C) to the filtrate. Yield 1.22 g, 69%, m.p. 149–151°C. (Found: C, 61.5; H, 4.9. $C_{41}H_{38}OOsP_2$ calcd.: C, 61.6; H, 4.8%). ν_{max} at 1941s and 1835w cm^{-1}. NMR spectra: ^{1}H (400 MHz), δ −8.47 [tt, 1H, OsH^D, ^2J(PH) 25.4, $^3J(H^DH^A)$ 7.0], 1.80 (s, 2H, H^B), 2.11 [t, 2H, H^A, $|{}^3J(PH)_{cis}+{}^3J(PH)_{trans}| = {}^3J(H^AH^D) = 7.0$ Hz], 2.51 (s, 3H, Me); ^{13}C-{^{1}H}, δ 190.2 (M, CO), 101.9 (s, *C*Me), 33.1 [d, CH_2, $|{}^2J(PC)_{cis}+{}^2J(PC)_{trans}|$ 18.7 Hz], 24.5 ppm (s, Me); ^{31}P-{^{1}H}, δ 18.3 ppm (s). The white crystalline compound **1** is stable in air showing only slight surface deterioration after several months. Decomposition in chloroform is apparent after 1 d.

$[OsH(CO)(\eta^3\text{-}C_3H_5)(PPh_3)_2]$

$[OsHCl(CO)(PPh_3)_3]$ (1 g, 0.96 mmol) was added to a solution of allylmagnesium chloride in diethyl ether (50 cm^3) (from magnesium (0.5 g) and 3-chloroprop-1-ene (3.7 g) under dry nitrogen. The mixture was stirred for 15 h and was poured into a saturated aqueous solution of ammonium chloride (100 cm^3). The resulting white solid was filtered off and dried in vacuo to give the white product **2**. Yield 0.55 g, 73%. (Found: C, 61.1; H, 4.7. $C_{40}H_{36}OOsP_2$ calcd.: C, 61.2; H, 4.6%). ν_{max} at 2005w and 1963s cm^{-1}. NMR spectra: ^{1}H (400 MHz), δ −9.22 [dd, 1H, OsH^F, ^2J(PH) 23.3 and 30.3], 0.05 (m, 1H, H^D), 0.84 (br, s, 1H, H^C), 1.02 [t, 1H, H^A, $^3J(PH^A)$ 10.2, $^3J(H^AH^E)$ 10.2], 2.78 (m, 1H, H^B), and 3.94 ppm (m, 1H, H^E). ^{31}P-{^{1}H} (dichloromethane), 21.2(s) and 22.2 ppm (s). The white crystalline compound is stable in air but solutions in trichloromethane exhibit extensive decomposition after about 1 h. The compound decomposes less rapidly in dichloromethane.

Reaction of $[OsH(CO)(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)_2]$ (1) with fluoroboric acid in the presence of triphenylphosphine

A solution (2 cm^3) of 0.25 *M* fluoroboric acid in aqueous ethanol was added to a mixture of **1** (0.24 g, 0.3 mmol) and triphenylphosphine in ethanol (30 cm^3). The mixture was stirred for 10 min and the clear solution was evaporated to give a white solid. Recrystallisation of the product from dichloromethane/light petroleum (b.p. 40–60°C) gave $[OsH(CO)(OH_2)(PPh_3)_3][BF_4]\cdot EtOH$ (0.17 g, 47%) identified by comparison of its IR and ^{1}H NMR spectra with that of an authentic sample [8].

Reactions of $[OsH(CO)(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)_2]$ (1) with fluoroboric acid in the presence of carbon monoxide

(a) In dichloromethane. A solution of **1** (0.34 g, 0.42 mmol) dichloromethane (40 cm^3) was purged with carbon monoxide and was treated with aqueous 0.01 *M* fluoroboric acid (1 cm^3, 0.88 mmol). The mixture was stirred at ca. 20°C for 1 h after which the product was isolated from the organic layer. The complex $[OsH(CO)_2(OH_2)(PPh_3)_2][BF_4]\cdot H_2O$ (**4**) was obtained as white crystals from dichloromethane/light petroleum (b.p. 40–60°C). Yield 0.17 g, 45%. (Found: C, 50.9; H, 3.9. $C_{38}H_{35}BF_4O_4OsP_2$ calcd.: C, 51.0; H, 3.9%). ν_{max} at 2060s, 1985s, and 1940s cm^{-1}. NMR spectrum: ^{1}H (90 MHz), δ −2.64 [t, 1H, Os*H*, ^2J(PH) 19.8 Hz], 4.57 (s, 2H, H_2O), and 7.4–7.7 ppm (m, 30H, Ph).

(b) In ethanol. A suspension of **1** (0.34 g, 0.42 mmol) in ethanol (40 cm^3) was purged with carbon monoxide and was treated with aqueous 0.01 *M* fluoroboric acid (1 cm^3, 0.88 mmol). After 1 h the reaction mixture was filtered and the filtrate was evaporated to an oil. Recrystallisation of the oil from ethanol/light petroleum

(b.p. 40–60°C) gave white crystals (0.31 g, 85%) which analysed as $OsH(CO)_2(PPh_3)_2(BF_4)(H_2O)(EtOH)$ and was formulated as a 1/1 mixture of salts $[OsH(CO)_2(OH_2)(PPh_3)_2][BF_4]$ and $[OsH(CO)_2(EtOH)(PPh_3)_2][BF_4]$ which contains one molecule water and one molecule of ethanol of crystallisation. (Found: C, 52.0; H, 4.2. $C_{40}H_{39}BF_4O_4OsP_2$ calcd.: C, 52.1; H, 4.3%). ν_{max} at 2070, 2060s, 1985s, 1982s, 1949s, and 1940s cm^{-1}. NMR spectrum: ^1H (400 MHz), δ −2.64 [t, 1H, Os*H*, $^2J(PH)$ 19.8], −2.47 [t, 1H, Os*H*, $^2J(PH)$ 18.8], −0.01 [t, 3H, $\mathit{CH}_3^ACH_2^BOH^C$ coordinated, $J(H^AH^B)$ 7.0], 2.22 [dq, 2H, $CH_3^A\mathit{C}H_2^BOH^C$ coordinated, $J(H^BH^A)$ 7.0], $J(H^BH^C)$ 4.22], 4.57(s, 2H, H_2O coordinated), and 4.71 ppm [t, 1H, $CH_3^ACH_2^BO\mathit{H}^C$ coordinated, $J(H^BH^C)$ 4.22]. Signals due to free ethanol and water were observed at 1.1 [t, 3H, Me, $J(HH)$ 6.99], 1.74 (free OH, H_2O + EtOH), and 3.49 [q, 2H, CH_2, $J(HH)$ 7.03]. A mixture of the hydrides (0.13 g) in 1/1 dichloromethane/ethanol (20 cm^3) was treated with carbon monoxide (75 psi) for 1 h. The solution was evaporated under reduced pressure to ca. 2 cm^3 and diethyl ether was added to give white crystals (0.1 g) of $[OsH(CO)_2(EtOH)(PPh_3)_2][BF_4]\cdot EtOH$. (Found: C, 53.9; H, 3.7. $C_{42}H_{33}BF_4O_4OsP_2$ calcd.: C, 53.6; H, 3.5%). ν_{max} at 2070s, 1982s, and 1949s cm^{-1}. NMR spectrum: ^1H (90 MHz), δ −2.47 [t, 1H, OsH, $^2J(PH)$18.8], −0.01 (t, 3H, CH_3CH_2OH coordinated, $J(HH)$7], 2.2 (m, 2H, $CH_3\mathit{CH}_2OH$ coordinated), and 4.7 ppm (m, $CH_3CH_2\mathit{OH}$, coordinated). Signals due to free ethanol were observed at 1.1 [t, CH_3, $J(HH)$ 7], 1.7 (br, OH), and 3.5 [q, 2H, CH_2, $J(HH)$ 7 Hz].

X-Ray data collection and structure determination

Crystal data for 4. Crystals of **4** were obtained as an ethanol solvate from ethanol/light petroleum (b.p. 40–60°C). $C_{37}H_{33}BF_4O_3OsP_2$. C_2H_5OH, $M = 922.7$, monoclinic, space group $P2_{1|m}$, *a* 9.845(5), *b* 22.68(5), *c* 9.37(1) Å, β 109.2(2)°, *U* 1976.4 $Å^3$, $Z = 2$, D_c 1.55 g cm^3, $F(000) = 871.9$; Mo-K_α radiation λ 0.71069 Å, μ(Mo-K_α) 32.01 cm^{-1}

Measurements. The crystal (0.48 × 0.19 × 0.11 mm) was mounted about the *c* axis in air. The cell dimensions were determined from an oscillation photograph about the *c* axis of the crystal and from its optimised counter angles for zero- and upper-layer reflections on a Weissenberg diffractometer. Intensity data were collected at room temperature on a Stoe Weissenberg diffractometer with an ω-scan technique in the range $7 \leqslant 2\theta < 60°$. The 3643 reflections collected from Weissenberg layers $hk(0-10)$ having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the computer program SHELX [15].

Structure solution and refinement. The molecular structure (Fig. 1) was solved by conventional Patterson and Fourier difference techniques. Scattering factors for the atoms were taken from ref. 16. In the final stages of blocked-matrix least-squares refinements all non-hydrogen atoms were given anisotropic thermal parameters. All the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The hydrogen atoms of the phenyl rings were refined at calculated positions [C–H 1.08(5) Å]. The BF_4^- anion was disordered and atoms F(2), F(22), F(3) and F(32) were given population parameters of 0.5. Only two atoms of the disordered ethanol were included in the refinement but additional peaks were seen in the difference Fourier map suggesting a high degree of disorder. Final cycles employed a weighting factor *w* calculated from $w = k/(\sigma^2F + gF^2)$, where $k = 3.560$, and $g = 0.000350$. Final values of *R* and R^1 are 0.0581 and 0.0599. Fractional

TABLE 3

ATOMIC POSITIONAL (fractional coordinates) FOR $[OsH(H_2O)(CO)_2(PPh_3)_2]BF_4 \cdot EtOH$.

	x	y	z
Os	0.02837(5)	0.25000	0.66206(5)
P	0.0183(2)	0.14624(10)	0.6276(2)
F(1)	0.2482(15)	−0.25000	0.0778(16)
F(2)	0.271(3)	−0.25000	−0.1498(16)
F(22)	0.4814(18)	−0.25000	0.095(4)
F(3)	0.431(3)	−0.2034(15)	0.039(3)
F(32)	0.325(2)	−0.2003(13)	−0.086(3)
O(1)	0.3137(11)	0.25000	0.6115(15)
O(2)	0.1412(15)	0.25000	1.0097(12)
O(3)	−0.1920(9)	0.25000	0.6591(12)
O(4)	0.3658(17)	−0.25000	0.607(2)
C(1)	0.2080(15)	0.25000	0.6349(16)
C(2)	0.0976(20)	0.25000	0.8817(17)
C(11)	0.0527(6)	0.1248(3)	0.4547(5)
C(12)	−0.0219(6)	0.1544(3)	0.3215(5)
C(13)	0.0033(6)	0.1405(3)	0.1874(5)
C(14)	0.1031(6)	0.0969(3)	0.1866(5)
C(15)	0.1777(6)	0.0673(3)	0.3198(5)
C(16)	0.1525(6)	0.0812(3)	0.4539(5)
C(21)	0.1461(5)	0.1011(2)	0.7732(6)
C(22)	0.2775(5)	0.1251(2)	0.8612(6)
C(23)	0.3751(5)	0.0908(2)	0.9720(6)
C(24)	0.3413(5)	0.0326(2)	0.9947(6)
C(25)	0.2098(5)	0.0087(2)	0.9067(6)
C(26)	0.1123(5)	0.0429(2)	0.7959(6)
C(31)	−0.1552(5)	0.1144(3)	0.6139(6)
C(32)	−0.2460(5)	0.0892(3)	0.4809(6)
C(33)	−0.3829(5)	0.0699(3)	0.4729(6)
C(34)	−0.4290(5)	0.0758(3)	0.5978(6)
C(35)	−0.3382(5)	0.1011(3)	0.7308(6)
C(36)	−0.2013(5)	0.1204(3)	0.7389(6)
C(4)	−0.551(3)	0.2207(11)	0.337(3)
B	0.3433(16)	−0.25000	0.0014(18)

atomic coordinates are given in Table 3. Lists of thermal parameters and observed and calculated structure factors can be obtained from the authors on request.

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References

1 R.D. Adams and J.P. Selegue, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Vol. 4, p. 967.

2 E.O. Sherman and M. Olson, J. Organomet. Chem., 172 (1979) C13.

3 R.D.W. Kemmitt, P. McKenna, D.R. Russell and L.J.S. Sherry, J. Organomet. Chem., 253 (1983) C59.

4 D.A. Clarke, R.D.W. Kemmitt, M.A. Mazid, P. McKenna, D.R. Russell, M.D. Schilling and L.J.S. Sherry, J. Chem. Soc., Dalton Trans., (1984) 1993.
5 T.H. Tulip and J.A. Ibers, J. Am. Chem. Soc., 101 (1979) 4201.
6 D.J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1979) 1283.
7 R.H. Crabtree, G.G. Hlatky, C.P. Parnell, B. Segmüller and R.J. Uriarte, Inorg. Chem., 23 (1984) 354.
8 T.J. Collins, I.R. Grundy and W.R. Roper, J. Organomet. Chem., 231 (1982) 161.
9 S.M. Boniface, G.R. Clark, T.J. Collins and W.R. Roper, J. Organomet. Chem., 206 (1981) 109.
10 J.M. Waters and J.A. Ibers, Inorg. Chem., 16 (1977) 3273.
11 E.M. Shustorovich, M.A. Porai-Koshits and Yu.A. Buslaev, Coord. Chem. Rev., 17 (1975) 1.
12 M. Saito, T. Uehiro, F. Ebina, T. Iwamoto, A. Ouchi and Y. Yoshino, Chem. Lett., (1979) 997.
13 R.H. Crabtree, M.W. Davis, M.F. Mellae, and J.M. Mihelcic, Inorg. Chim. Acta, 72 (1983) 223.
14 T. Glonek and J.R. van Wazer, J. Magn. Res., 13 (1974) 390.
15 G.M. Sheldrick, SHELX 76 Program for crystal structure determination, University of Cambridge, 1976.
16 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1975, Vol. 4.