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Vinylidene complexes of osmium(0) derived from 1-naphthyl- or 2-naphthyl-carbyne complexes by hydride addition to the naphthyl substituents. The crystal structure of $Os(=C=C_{10}H_8)(CO)_2(PPh_3)_2$[1]

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Abstract

When treated with lithium triethylborohydride, the cationic carbyne complexes $[Os(-CR)(CO)_2(PPh_3)_2]^+$ (R = 1-naphthyl, **1**; R = 2-naphthyl, **2**) form **3** and **4**, respectively, which both have the formula $Os(C_{11}H_8)(CO)_2(PPh_3)_2$. NMR studies of these two isomeric vinylidene complexes show that the product derived from the 1-naphthyl carbyne cation involves attack at the naphthyl ring in the position *para* to the carbyne carbon to give **3**, while that derived from the 2-naphthyl carbyne cation involves attack at the naphthyl ring in the position *ortho* to the carbyne carbon to give **4**. The structure of **4** has been confirmed by an X-ray crystal structure determination. Addition of HCl to the vinylidene complexes **3** or **4** results in the formation of the corresponding naphthylmethyl complexes, $Os(CH_2R)Cl(CO)_2(PPh_3)_2$ (R = 1-naphthyl, **5**; R = 2-naphthyl, **6**). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Naphthyl substituents; Hydride addition; Vinylidene complexes; Osmium(0)

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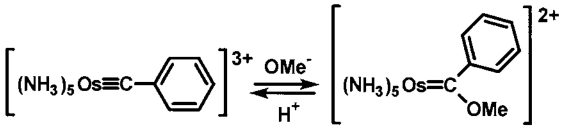
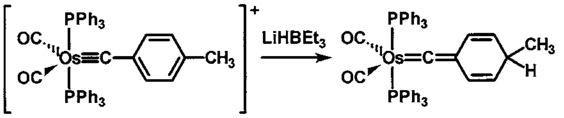
1. Introduction

The electrophilicity of the carbyne carbon in cationic carbyne complexes is well established [1] and a recent example is shown in Eq. 1 [2].



eqn. 1

However, in a quite unexpected reaction, we have shown that $[Os(-C\text{-}p\text{-tolyl})(CO)_2(PPh_3)_2]^+ClO_4^-$, when treated with $LiEt_3BH$, forms an unusual vinylidene complex of formula $Os(C_8H_8)(CO)_2(PPh_3)_2$ which results from hydride attack at the tolyl ring in the *para*-position (Eq. 2) [3].



eqn. 2

The explanation for the unexpected position of attack probably lies with the superior π-acceptor properties of the vinylidene ligand compared with the carbene ligand that would otherwise result from direct attack at C(carbyne) [4].

With the recent availability of $[Os(-CR)(CO)_2(PPh_3)_2]^+ClO_4^-$ (R = 1-naphthyl, **1**; R = 2-naphthyl, **2**) [5], we have investigated this reaction further because in these complexes there are a greater number of potential sites for hydride attack and, indeed, it is not possible for hydride to attack the *para*-position of a 2-naphthyl system as this is a bridgehead carbon. The possibility remained that here the hydride attack might occur at the carbyne carbon atom.

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[1] Dedicated to Professor Michael Bruce on the occasion of his 60th birthday.

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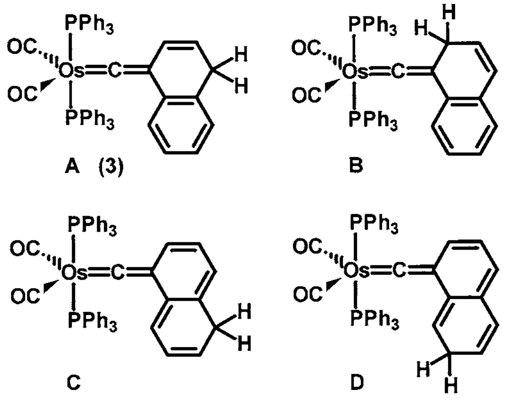
2. Results and discussion

The addition of $LiEt_3BH$ to THF solutions containing either of the dark red complexes $[Os(–CR)(CO)_2(PPh_3)_2]^+ClO_4^-$ (R = 1-naphthyl, **1**; R = 2-naphthyl, **2**) gives almost colourless solutions from which the corresponding pale yellow crystalline complexes, **3** or **4**, can be isolated. Elemental analyses and high-resolution mass spectra indicated that both **3** and **4** have the formula $Os(C_{11}H_8)(CO)_2(PPh_3)_2$, consistent with addition of a single hydride to each of the precursor complexes, **1** or **2**. In the ^{1}H-NMR spectrum of each compound, no high-field signals ($\delta < 0$ ppm) were observed which ruled out the possibility of osmium hydride formation and, in addition, no signals were observed in the δ 10–20 ppm region which showed that no hydrogen-substituted carbene ligands had been formed. Therefore, the most likely point of attack appeared to be at the naphthyl substituents to give vinylidene products, and indeed the ν(CO) values for **3** (1955, 1892 cm^{-1}) and **4** (1957, 1894 cm^{-1}) were very close to values found (1956, 1897 cm^{-1}) for the previously reported vinylidene complex derived from $[Os(\equiv C\text{-}p\text{-tolyl})(CO)_2(PPh_3)_2]^+$ (Eq. 2) [3].

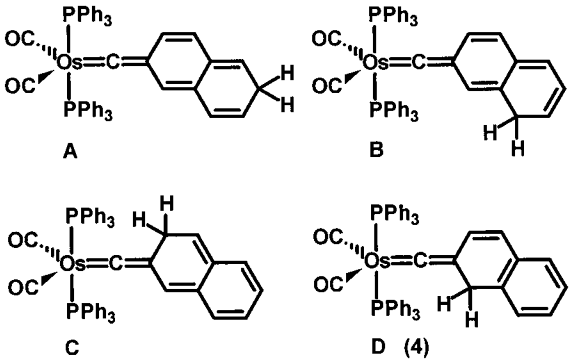
*2.1. Formation of the vinylidene complex **3** from reaction between LiEt$_3$BH and the 1-naphthyl carbyne complex **1***

There are four possible naphthyl ring positions in **1** at which hydride addition could occur to give vinylidene products (Scheme 1). However, in practice only one of the isomers (A–D) is formed.

The ^{1}H-NMR of **3** shows two methylene protons at δ 2.8 ppm, two vinyl protons at 4.8 and 5.7 ppm and four aromatic protons at 6.7–6.9 ppm. A COSY ^{1}H{^{1}H}-NMR spectrum shows that the aromatic protons couple only with each other, whereas the two vinyl protons couple with each other and the methylene protons. Two isomers that are consistent with these observations are A and B (Scheme 1). Both of these isomers have four aromatic protons (aromaticity is retained in at least one ring), two vinyl protons and two methylene protons, but they differ in the location of the methylene group. In order to distinguish between these two isomers, the ^{13}C-NMR spectrum of **3** was obtained. For isomer B it would be expected that the methylene carbon should couple to the two phosphorus nuclei with a coupling constant of about 7 Hz, as is seen in the product derived from the 2-naphthylcarbyne cation (see below). However, for isomer A the methylene carbon should display very much smaller, or non-observable, coupling to phosphorus in the ^{13}C-NMR spectrum. In practice, the ^{13}C{^{1}H}-NMR spectrum of **3** shows the methylene carbon as a singlet at 25.3 ppm. This implies that hydride attack occurs at the 4-position (see Scheme 3 for the numbering system used for the naphthyl rings in **3** and **4**) of the naphthyl ring in **1** and that isomer A is the correct formulation for compound **3**. Hydride attack occurred at an analogous position in the *p*-tolyl carbyne complex shown in Eq. 2. The data from an HMQC ^{13}C{^{1}H}-NMR spectrum were used to assign H and C chemical shifts. Complete ^{1}H- and ^{13}C-NMR spectral data are presented in the Section 3.



Scheme 1. The four possible vinylidene isomers (A–D) for complex (**3**).



Scheme 2. The four possible vinylidene isomers (A–D) for complex (**4**).

*2.2. Formation of the vinylidene complex **4** through reaction between LiEt$_3$BH and the 2-naphthyl carbyne-containing complex **2***

As with compound **1**, there are four possible naphthyl ring positions in **2** at which hydride addition could occur to give vinylidene products (Scheme 2). One important difference between compounds **2** and **1** is that attack at the position *para* to the carbyne carbon in **2** (C10, Scheme 3) is not possible as this is a bridgehead carbon atom.

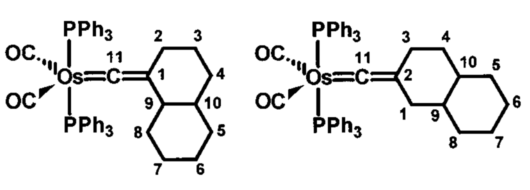
The ^{1}H-NMR spectrum of **4** revealed three distinctly different types of protons; two methylene protons at δ 2.9 ppm, two vinyl protons at 5.3–5.6 ppm and four aromatic protons at 6.5–7.0 ppm. A ^{1}H{^{1}H} COSY experiment showed that the two equivalent methylene protons did not couple with any other protons, the two vinyl protons only coupled with each other, and the aromatic protons coupled with each other, but no other protons. Isomer D (Scheme 2) is the only isomer consistent with all the ^{1}H-NMR data.

Although a $^{1}H\{^{1}H\}$ homonuclear decoupling NMR experiment confirmed that the methylene protons did not couple with any other protons, the signal at δ 2.9 ppm appeared as a triplet with a coupling constant of 7.7 Hz. This signal did collapse to a singlet, however, in the ^{31}P-decoupled ^{1}H-NMR spectrum of **4**, showing that coupling to two equivalent phosphorus nuclei was responsible for the multiplicity of the methylene signal. The other protons in the same ring as the methylene group show much smaller coupling (1.7 and 2.7 Hz) to the two phosphorus nuclei.

The results of an HMQC $^{13}C\{^{1}H\}$-NMR experiment enabled chemical shift assignments to be made for the atoms of the vinylidene group in this complex. The assignments listed in Section 3 should be read in conjunction with the numbering scheme given in Scheme 3. The ^{13}C-NMR spectrum showed that even for carbon atoms up to six bonds away from the phosphorus atoms, coupling to these nuclei was still discernible.

The vinylidene-carbon in **4** appears at the very lowfield position of δ 295.7 ppm in the ^{13}C-NMR spectrum. This is upfield from the carbyne carbon resonance of the precursor compound, $[Os(\equiv C\text{-}2\text{-}naphthyl)(CO)_2(PPh_3)_2]^+ClO_4^-$ (**1**), which appears at 331.8 ppm, but is very similar in position to the carbene carbon resonance in the complex $Os[{=}CH(2\text{-}naphthyl)]Cl_2(CO)(PPh_3)_2$ which appears at 291.3 ppm [5].

A single crystal X-ray structure determination of the complex $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**4**) confirmed the vinylidene (isomer D, Scheme 2) formulation. The ORTEP diagram is depicted in Fig. 1. Crystal data and structure refinement parameters, final atomic coordinates, and selected bond distances and angles are given in Tables 1–3, respectively. The coordination geometry about osmium is approximately trigonal bipyramidal with the two triphenylphosphine ligands in the axial positions. The vinylidene and the two carbonyl ligands are in the equatorial positions with the rings of the vinylidene substituent essentially in the equatorial plane. The hydrogen atoms were not located, but it can be clearly seen that hydride addition occurred at C(1). This carbon atom is displaced by 0.337(11) Å from the plane defined by the other ring carbon atoms (C(2)–C(10)), and the distances between C(1) and the neighbouring carbon atoms, C(2) (1.518(12) Å) and C(9) (1.562(12) Å), are consistent with there being only single bonds to these atoms. This confirms that the methylene group is at C(1). The short distance between C(3) and C(4) (1.339(12) Å) suggests that there is significant double bond character between these two atoms and a similar distance (1.356(11) Å) is found between C(2) and the vinylidene carbon atom, C(11). The Os–C(11) bond length of 1.900(8) Å is the same as the corresponding distance reported for the related vinylidene complex shown in Eq. 2 [3]. Two other osmium vinylidene complexes have been reported to have very similar Os–C(vinylidene) bond lengths to this, and both have carbonyl and cyclopentadienyl supporting ligands [6,7]. Shorter distances of ca. 1.81 Å have been reported for the Os–C(vinylidene) bond in complexes that contain no π-acid supporting ligands [8,9].



Scheme 3. Hydride attack of complex **2**.

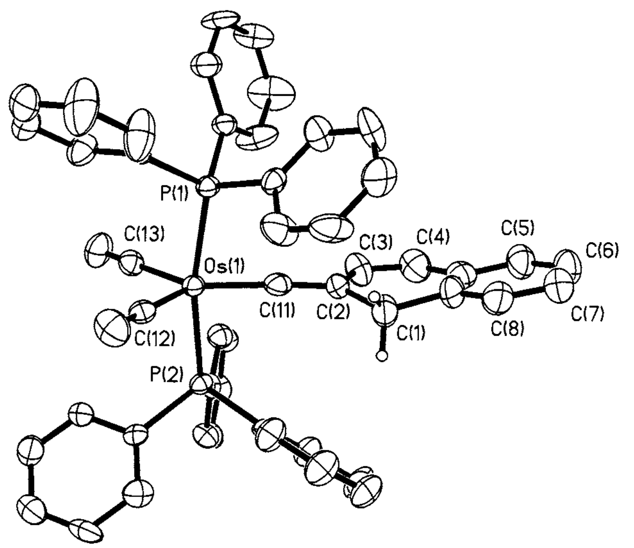


Fig. 1. Molecular structure of $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**4**) showing the atom numbering scheme. Thermal ellipsoids are at the 30% probability level.

It is noteworthy that hydride attacks **2** at the most sterically-protected ring carbon atom (C1) to give isomer D (Scheme 3). However, this isomer is the only one in which the aromaticity of both naphthyl rings is not disrupted and this probably provides an important driving force for hydride attack at this ring position. No evidence for any hydride attack at the carbyne carbon atom in **2** was obtained.

2.3. Formation of the 1- and 2-naphthylmethyl products ***5*** *and* ***6*** *through HCl addition to* ***3*** *and* ***4***

Addition of HCl to the vinylidene complexes, **3** or **4**, results in the formation of the corresponding naphthylmethyl complexes **5** or **6** (Scheme 4) in good yield. A similar reaction occurred on addition of HCl to the vinylidene complex shown in Eq. 2 [3] to give a 4-methylbenzyl complex. The mechanism by which these rearrangements proceed is not clear, but the initial steps may involve either direct addition of H^+ to the vinylidene carbon, or protonation of the osmium centre followed by hydride migration to the vinylidene carbon atom.

3. Experimental details

Standard Schlenk techniques were used for all manipulations involving oxygen- or moisture-sensitive compounds. Solvents used were freshly distilled over appropriate drying agents prior to use. When procedures involved materials that were not air-sensitive, solvent removal under reduced pressure was achieved using a rotary evaporator. Routine recrystallisations were achieved by the following method; the sample was dissolved in a low b.p. solvent and a higher b.p. sol-

Table 1
Crystal data and structure refinement parameters for $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (4)

Empirical formula	$C_{49}H_{38}O_2OsP_2$
Formula weight	910.93
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.4845(3)
b (Å)	18.6973(6)
c (Å)	22.3614(8)
β (°)	91.1550(10)
V (Å^3)	3964.6(2)
Z	4
$D_{calc.}$ (g cm^{-3})	1.526
Absorption coefficient (mm^{-1})	3.337
F(000)	1816
Crystal size	0.35 × 0.20 × 0.12 mm
Theta range for data collection (°)	1.42–25.00
Index ranges	$-9 \le h \le 11$, $-22 \le k \le 16$, $-26 \le l \le 26$
Reflections collected	21570
Reflections observed [$I > 2\sigma(I)$]	5667
Independent reflections	6975 [$R_{int} = 0.0587$]
Max/min transmission	0.6 902, 0.3880
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6975/0/487
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0463$, $^a wR_2 = 0.0929$
R indices (all data)	$R_1 = 0.0656$, $^a wR_2 = 0.1047$
Goodness-of-fit on F^2	0.957
Largest difference peak and hole	0. 642 and −0.957 e Å^{-3}

[a] Weighting scheme calc. $w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 36.8879P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**4**)

Atom	*x*	*y*	*z*	*U*(eq)
Os(1)	0.2716(1)	0.1952(1)	0.0891(1)	0.024(1)
P(1)	0.3068(2)	0.0880(1)	0.1436(1)	0.025(1)
P(2)	0.2835(2)	0.3094(1)	0.0437(1)	0.024(1)
O(1)	0.3327(7)	0.1152(3)	−0.0272(3)	0.054(2)
O(2)	−0.0518(6)	0.1951(3)	0.0905(3)	0.053(2)
C(1)	0.6398(10)	0.2714(6)	0.1771(4)	0.057(3)
C(2)	0.4819(9)	0.2710(4)	0.1868(4)	0.039(2)
C(3)	0.4288(10)	0.3112(5)	0.2377(4)	0.046(2)
C(4)	0.5154(11)	0.3379(5)	0.2801(4)	0.055(2)
C(5)	0.7512(11)	0.3458(5)	0.3301(4)	0.057(3)
C(6)	0.8915(12)	0.3303(5)	0.3305(5)	0.063(3)
C(7)	0.9516(11)	0.2959(6)	0.2844(4)	0.062(3)
C(8)	0.8681(11)	0.2741(5)	0.2347(4)	0.058(3)
C(9)	0.7327(9)	0.2890(5)	0.2336(4)	0.047(2)
C(10)	0.6643(10)	0.3260(4)	0.2799(4)	0.043(2)
C(11)	0.3937(8)	0.2376(4)	0.1474(3)	0.036(2)
C(12)	0.3039(8)	0.1455(4)	0.0156(3)	0.032(2)
C(13)	0.0701(8)	0.1923(4)	0.0884(3)	0.034(2)
C(21)	0.2461(8)	0.0060(4)	0.1047(3)	0.028(2)
C(22)	0.3321(11)	−0.0487(5)	0.0915(5)	0.068(3)
C(23)	0.2792(14)	−0.1105(6)	0.0625(6)	0.093(4)
C(24)	0.1431(12)	−0.1143(5)	0.0460(4)	0.061(3)
C(25)	0.0537(10)	−0.0586(5)	0.0585(4)	0.055(3)
C(26)	0.1065(9)	0.0020(4)	0.0872(4)	0.046(2)
C(31)	0.4926(7)	0.0689(4)	0.1605(3)	0.031(2)
C(32)	0.5893(9)	0.0766(5)	0.1145(4)	0.055(3)
C(33)	0.7300(10)	0.0613(5)	0.1241(5)	0.063(3)
C(34)	0.7769(9)	0.0391(5)	0.1796(5)	0.055(3)
C(35)	0.6837(10)	0.0316(6)	0.2252(4)	0.059(3)
C(36)	0.5423(8)	0.0463(5)	0.2150(4)	0.042(2)
C(41)	0.2230(7)	0.0796(4)	0.2169(3)	0.029(2)
C(42)	0.1803(9)	0.0148(4)	0.2385(4)	0.044(2)
C(43)	0.1227(10)	0.0075(5)	0.2948(4)	0.052(2)
C(44)	0.1520(13)	0.1320(6)	0.3098(4)	0.076(3)
C(45)	0.1104(10)	0.0665(5)	0.3304(4)	0.054(2)
C(46)	0.2073(11)	0.1392(5)	0.2526(4)	0.057(3)
C(51)	0.4644(7)	0.3436(4)	0.0403(3)	0.026(2)
C(52)	0.5659(8)	0.2996(5)	0.0157(4)	0.044(2)
C(53)	0.7044(9)	0.3210(5)	0.0136(4)	0.051(2)
C(54)	0.7464(9)	0.3856(5)	0.0372(4)	0.053(2)
C(55)	0.6483(10)	0.4291(5)	0.0627(4)	0.055(2)
C(56)	0.5072(8)	0.4086(4)	0.0634(4)	0.039(2)
C(61)	0.2192(7)	0.3163(3)	−0.0344(3)	0.025(2)
C(62)	0.0817(8)	0.2948(4)	−0.0467(4)	0.039(2)
C(63)	0.0247(9)	0.3003(5)	−0.1046(4)	0.047(2)
C(64)	0.1059(10)	0.3263(4)	−0.1504(4)	0.044(2)
C(65)	0.2405(10)	0.3480(5)	−0.1377(4)	0.048(2)
C(66)	0.2985(9)	0.3422(4)	−0.0812(4)	0.039(2)
C(71)	0.1816(7)	0.3810(4)	0.0785(3)	0.025(2)
C(72)	0.1171(8)	0.3698(4)	0.1337(3)	0.033(2)
C(73)	0.0343(9)	0.4224(4)	0.1586(3)	0.040(2)
C(74)	0.0162(8)	0.4873(4)	0.1301(3)	0.035(2)
C(75)	0.0788(9)	0.4990(4)	0.0767(4)	0.040(2)
C(76)	0.1615(8)	0.4462(4)	0.0506(3)	0.034(2)

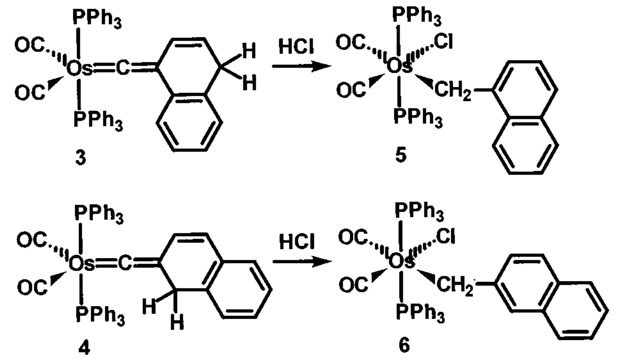
U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Selected bond lengths (Å) and bond angles (°) for $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**4**)

Bond lengths (Å)			
Os(1)–C(11)	1.900(8)	Os(1)–C(13)	1.912(8)
Os(1)–C(12)	1.916(8)	Os(1)–P(1)	2.3658(18)
Os(1)–P(2)	2.3680(18)	C(1)–C(2)	1.518(12)
C(1)–C(9)	1.562(12)	C(2)–C(11)	1.356(11)
C(2)–C(3)	1.461(12)	C(3)–C(4)	1.339(12)
C(4)–C(10)	1.429(13)	C(5)–C(6)	1.362(14)
C(5)–C(10)	1.428(12)	C(6)–C(7)	1.351(14)
C(7)–C(8)	1.411(13)	C(8)–C(9)	1.314(13)
C(9)–C(10)	1.413(12)		
Bond angles (°)			
C(11)–Os(1)–C(13)	127.8(3)	C(11)–Os(1)–C(12)	133.2(3)
C(13)–Os(1)–C(12)	99.0(3)	C(2)–C(1)–C(9)	115.2(7)
C(11)–C(2)–C(3)	121.7(8)	C(11)–C(2)–C(1)	120.4(8)
C(3)–C(2)–C(1)	117.8(7)	C(4)–C(3)–C(2)	121.8(9)
C(3)–C(4)–C(10)	122.1(9)	C(6)–C(5)–C(10)	119.9(10)
C(7)–C(6)–C(5)	121.6(9)	C(6)–C(7)–C(8)	119.9(10)
C(9)–C(8)–C(7)	119.1(10)	C(8)–C(9)–C(10)	123.6(9)
C(8)–C(9)–C(1)	120.4(9)	C(10)–C(9)–C(1)	115.9(8)
C(9)–C(10)–C(4)	123.2(8)	C(9)–C(10)–C(5)	115.8(9)
C(4)–C(10)–C(5)	120.7(9)		

vent, in which the compound was insoluble, was added. Evaporation at reduced pressure effected gradual crystallisation.

IR spectra (4000–400 cm^{-1}) were recorded on a Bio Rad FTS-7 FTIR spectrophotometer. All spectra were recorded as Nujol mulls between KBr plates. ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, COSY and HMQC spectra were recorded on Bruker DRX-400 or AC-200 instruments. All NMR experiments were performed at 25°C using $CDCl_3$ as solvent, referenced to TMS. All ^{13}C-NMR were recorded in the presence of chromium acetylacetonate as spin relaxant (d1 = 0.1 s). The numbering system used for proton and carbon assignments is given in Scheme 3. All ^{31}P-NMR were collected at 25°C in $CDCl_3$ and referenced to phosphoric acid ($\delta = 0.00$ ppm). FAB^{+} mass spectra were recorded on a VG 7070 spectrometer operating at 70 eV using argon as a source and *m*-nitrobenzyl alcohol was used as the matrix. Analytical data were obtained from the Microanalytical Laboratory, University of Otago. Melting points were determined on a Reichert microscope hot stage and are uncorrected.



Scheme 4. Addition of HCl to the vinylidene complexes, **3** or **4**, resulting in the corresponding naphthylmethyl complexes **5** or **6**.

[Os(≡C-1-naphthyl)$(CO)_2(PPh_3)_2$]ClO_4 and [Os(≡C-2-naphthyl)$(CO)_2(PPh_3)_2$]ClO_4 was synthesised by literature methods [5].

3.1. $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (3)

A sample of [Os(≡C-1-naphthyl)$(CO)_2(PPh_3)_2$]ClO_4 (200 mg, 0.200 mmol) was dissolved in THF (30 ml) in a small Schlenk tube and $LiEt_3BH$ (1 M solution in THF, 0.20 ml, 0.20 mmol) was added causing the red solution to discolour. Ethanol (30 ml) was added and the solvent volume decreased on a rotary evaporator. The product was collected and recrystallised from dichloromethane–ethanol (1:1) to give pure **3** as pale yellow crystals, 140 mg (78%), m.p. 175–176°C, $M =$ 910.99 g mol^{-1}, m/z 912.1942. $C_{49}H_{38}O_2OsP_2$ requires 912.1962. Anal. Found: C, 62.06; H, 4.08%. $C_{49}H_{38}O_2OsP_2 \cdot CH_2Cl_2$ requires C, 62.36; H, 4.12%. IR: 1955s, 1982s ν(CO); 1615, 1581m cm^{-1}. ^{1}H-NMR: 2.8 (m, 2H, *H4*); 4.8 (bd, 1H, *H3*, $^{3}J_{HH} = 9.1$); 5.7 (bd, 1H, *H2*, $^{3}J_{HH} = 9.6$); 6.7 (m, 4H, *H5, 6, 7, 8*); 7.17–7.54 (m, 30H, P*Ph*$_3$). ^{31}P-decoupled ^{1}H-NMR: δ 2.8 (m, 2H, *H4*); 4.8 (d, 1H, *H3*, $^{3}J_{HH} = 9.1$); 5.7 (d, 1H, *H2*, $^{3}J_{HH} = 9.6$); 6.7 (m, 4H, *H5, 6, 7, 8*); 7.17–7.54 (m, P*Ph*$_3$) ppm. ^{13}C-NMR: δ 300.7 (t, *C11*, $^{2}J_{CP} = 20.1$); 191.2 (t, *C*O, $^{2}J_{CP} = 7.0$); 190.8 (t, *C*O, $^{2}J_{CP} = 9.8$); 129.2 (t, *C1*, $^{3}J_{CP} = 9$); 127.0 (s, *C5/6/7/8*); 125.2 (s, *C5/6/7/8*); 124.4 (s, *C5/6/7/8*); 123.9 (s, *C5/6/7/8*); 121.0 (t, *C3*, $^{5}J_{CP} = 6$); 116.0 (t, *C2*, $^{4}J_{CP} = 5$); 30.8 (s, *C4*); 135.210 (t′ {see ref. [10] for explanations of symbols used and assignments made}, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} =$ 54.3); 134.37 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 10.9$); 130.23 (s, P*Ph*$_3$ *para*); 127.87 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 9.1$) ppm. ^{31}P-NMR: δ 12.56 (s, *P*Ph_3) ppm.

3.2. $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (4)

A sample of [Os(≡C-2-naphthyl)$(CO)_2(PPh_3)_2$]ClO_4 (200 mg, 0.200 mmol) was treated as in Section 3.1 to yield bright yellow crystals of **4**, 160 mg (89%), m.p. 232°C, $M = 910.99$ g mol^{-1}, m/z 912.1974. $C_{49}H_{38}O_2OsP_2$ requires 912.1962. Anal Found: C, 64.37; H, 4.33%. $C_{49}H_{38}O_2OsP_2$ requires C, 64.60; H, 4.20%. IR: 1957s, 1894s ν(CO); 1612m, 1587w, 1553w, 1220w cm^{-1}. ^{1}H-NMR: δ 2.9 (t, 2H, *H1*, $^{5}J_{HP} = 7.7$); 5.3 (dt, 1H, *H4*, $^{2}J_{HH} = 9.5$, $^{6}J_{HP} = 2.7$); 5.7 (dt, 1H, *H3*, $^{2}J_{HH} = 8.9$, $^{5}J_{HP} = 1.7$); 6.5 (dd, 1H, *H8*, $^{2}J_{HH} =$ 7.0); 6.6 (dd, 1H, *H5*, $^{2}J_{HH} = 6.9$); 6.8 (td, 1H, *H7*, $^{2}J_{HH} = 7.0$, $^{2}J_{HH} = 1.4$); 6.9 (td, 1H, *H6*, $^{2}J_{HH} = 7.0$, $^{2}J_{HH} = 1.4$); 7.25–7.54 (m, 30H, P*Ph*$_3$) ppm. ^{31}P-decoupled ^{1}H-NMR: δ 2.9 (s, 2H, *H1*); 5.3 (d, 1H, *H4*, $^2J_{HH} = 9.5$); 5.7 (d, 1H, *H3*, $^2J_{HH} = 8.9$); 6.5 (dd, 1H, *H8*, $^2J_{HH} = 7.0$); 6.6 (dd, 1H, *H5*, $^2J_{HH} = 6.9$); 6.8 (td, 1H, *H7*, $^2J_{HH} = 7.0$, $^3J_{HH} = 1.4$); 6.9 (td, 1H, *H6*, $^2J_{HH} = 7.0$, $^3J_{HH} = 1.4$); 7.25–7.54 (m, 30H, P*Ph*$_3$) ppm. ^{13}C-NMR: δ 295.7 (t, *C11*, $^2J_{CP} = 24.9$); 191.0 (m, *C*O); 127.2 (s, **8**); 126.5 (t, *C2*, $^3J_{CP} = 9$); 125.1 (s, *C6*); 124.8 (s, *C7*); 124.8 (s, *C5*); 123.7 (t, *C3*, $^4J_{CP} = 7$); 118.1 (t, *C4*, $^5J_{CP} = 4$); 25.6 (t, *C1*, $^4J_{CP} = 5$); 135.44 (t′, P*Ph*$_3$ *ipso*, $^{1,3}J_{CP} = 54.3$); 134.41 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 12.1$); 129.81 (s, P*Ph*$_3$ *para*); 127.85 (t′, P*Ph*$_3$ *ortho*, $^{2,4}J_{CP} = 10.1$) ppm. ^{31}P-NMR: δ 12.67 (s, *P*Ph$_3$) ppm.

3.3. *Os(CH$_2$-1-naphthyl)Cl(CO)$_2$(PPh$_3$)$_2$* (**5**)

A sample of $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**3**) (200 mg, 0.219 mmol) was dissolved in dichloromethane (25 ml) and ethanol (25 ml) in a 100 ml round bottom flask. Concentrated HCl (1 ml) was added and the solution was stirred at 30°C for 2 min. The resulting white product was collected by filtration and recrystallised from dichloromethane–ethanol to yield pure **7** as a cream powder, 150 mg (72%), m.p. 123–125°C, $M =$ 947.45 g mol^{-1}, *m*/*z* 948. Anal. Found: C, 60.54; H, 4.30%. $C_{49}H_{39}ClO_2P_2Os\cdot 1/2CH_2Cl_2$ requires C, 60.06; H, 4.07%. IR: δ 2017s, 1938s n(CO); 1582w, 1261w ppm. ^{1}H-NMR: δ 3.3 (t, 2H, C*H*$_2$, $^3J_{HP} = 8.0$); 7.0–8.5 (m, 7H, *naphthyl*, 30H, P*Ph*$_3$) ppm. ^{13}C-NMR: δ 181.0 (t, *C*O, $^2J_{CP} = 6.6$); 178.1 (t, *C*O, $^2J_{CP} = 8.0$); 31.8 (s, *C*H$_2$) ppm.

3.4. *Os(CH$_2$-2-naphthyl)Cl(CO)$_2$(PPh$_3$)$_2$* (**6**)

A sample of $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**4**) (200 mg, 0.219 mmol) was treated as in Section 3.3 above to yield pure **6** as white crystals, 165 mg (79%), m.p. 209–210°C, $M = 947.45$ g mol^{-1}, *m*/*z* 948. Anal. Found: C, 59.22; H, 3.56%. $C_{49}H_{39}ClO_2P_2Os\cdot 2/3CH_2Cl_2$ requires: C, 59.41; H, 4.05%. IR: 2025s, 1955s ν(CO); 1618w, 1597w, 592w cm^{-1}. ^{1}H-NMR: δ 3.2 (t, 2H, C*H*$_2$, $^3J_{HP} = 8.2$); 7.0–8.5, (m, 7H, *naphthyl*, 30H, P*Ph*$_3$) ppm. ^{13}C-NMR: δ 177.2 (t, *C*O, $^2J_{CP} = 8.0$); 176.2 (t, *C*O, $^2J_{CP} = 7.0$); 29.7 (s, *C*H$_2$); 134.02 (t′, P*Ph*$_3$ *meta*, $^{3,5}J_{CP} = 10.1$); 132.49 (t′, *PPh*$_3$ *ipso*, $^{1,3}J_{CP} = 51.3$); 130.26 (s, P*Ph*$_3$ *para*); 128.25 (t′, P*Ph*$_3$ *ortho* $^{2,4}J_{CP} =$ 10.1) ppm.

3.5. *X-ray crystal structure determination of Os(C$_{11}$H$_8$)(CO)$_2$(PPh$_3$)$_2$* (**4**)

Data were collected on a Siemens SMART area detector diffractometer using 0.3° frames and 3D profile fitting. Lorentz and polarisation corrections and an empirical absorption correction were applied to the 29113 measured reflections and equivalent reflections averaged, yielding 6973 unique reflections ($R_{int} =$ 0.0514). Unit cell parameters were obtained by least-squares fit to all reflections with $I > 10\sigma(I)$.

The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares on F^2. Hydrogen atoms were placed geometrically and refined with a riding model with U(iso) 20% > U(eq) of the carrier atom. All non-H atoms were allowed to assume anisotropic motion. Refinement converged to conventional $R = 0.0461$, $wR_2 = 0.0826$ for 5666 observed reflections with $I > 2\sigma(I)$. Programs: Siemens SMART and SAINT for data collection and reduction, SHELXTL [11] for structure solution and refinement. Crystal data and structure refinement parameters, final atomic coordinates, and selected bond distances and angles for $Os(C_{11}H_8)(CO)_2(PPh_3)_2$ (**4**) are given in Tables 1–3, respectively.

4. Supplementary material available

Supplementary data comprises H atom positions, anisotropic thermal parameters, and full listings of bond lengths and angles. Structure factor tables are available on request from the authors.

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