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Novel indenyl half-sandwich osmium(II) complexes. X-ray structure of $[Os\{=C=C(H)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]\cdot OEt_2$

José Gimeno [a,*], Mercedes Gonzalez-Cueva [a], Elena Lastra [a], Enrique Perez-Carreño [b], Santiago García-Granda [b]

[a] *Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica 'Enrique Moles' (Unidad Asociada al C.S.I.C.), Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain*
[b] *Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain*

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Dedicated to Profesor Rafael Usón with great admiration for his outstanding contribution to modern Inorganic Chemistry

Abstract

Reaction of LiC_9H_7 with $[OsBr_2(PPh_3)_3]$ gives the complex $[Os(\eta^5\text{-}C_9H_7)Br(PPh_3)_2]$ (**1**). The analogous complex $[Os(\eta^5\text{-}C_9H_7)I(PPh_3)_2]$ (**2**) is obtained from the metathesis reaction of $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ with NaI. The treatment of $[Os(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$ with NaOMe leads to the hydride derivative $[Os(\eta^5\text{-}C_9H_7)H(PPh_3)_2]$ (**3**) which can be protonated with HBF_4 to yield the cationic complex $[Os(\eta^5\text{-}C_9H_7)H_2(PPh_3)_2][BF_4]$ (**4**). Abstraction of the halide ligand in complexes $[Os(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$ with $NaPF_6$ or $AgBF_4$ followed by the treatment with NCMe or terminal alkynes yield complexes $[Os(\eta^5\text{-}C_9H_7)(NCMe)(PPh_3)_2][BF_4]$ (**6**) and $[Os\{=C\overline{OCH_2(CH_2)_3CH_2}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**7**), respectively. X-ray crystal structure of the vinylidene derivative $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ is reported along with variable temperature NMR studies.
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Keywords: Crystal structures; Osmium complexes; Indenyl complexes; Half-sandwich complexes

1. Introduction

During the last few years we have extensively studied the chemistry of indenyl half-sandwich ruthenium (II) complexes [1,2] including alkynyl, vinylidene and allenylidene derivatives. We have also reported the synthesis of the first indenyl half-sandwich osmium complexes containing the fragment '$Os(\eta^5\text{-}C_9H_7)(PPh_3)_2$' [3]. At present the chemistry of the indenyl osmium complexes is relatively much less known compared to that of the corresponding ruthenium derivatives [4]. Due to this fact we believed it of interest to extend the scope of the indenyl osmium derivatives. Here we report the synthesis and characterization of novel neutral $[Os(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$ (X = Br, I, H), $[Os(\eta^5\text{-}C_9H_7)Br(PPh_3)L]$ (L = PMe_3, PMe_2Ph) and cationic $[Os(\eta^5\text{-}C_9H_7)L(PPh_3)_2][X]$ complexes (L = H_2, NCMe, X = BF_4; L = $\overline{COCH_2(CH_2)_3CH_2}$, X = PF_6). Structural studies on the complex $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$, including dynamic processes in solution using NMR spectroscopy and its X-ray crystal structure, are also reported.

2. Experimental

2.1. Materials and measurements

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complexes $[OsX_2(PPh_3)_3]$ were synthesized as in reference [5] $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ and $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ were previously described [3]. LiC_9H_7 was prepared by modifications in a published method [6] and stored in a dry box. C_9H_8,

* Corresponding author. Tel.: +34-985-103-461; fax: +34-985-103-446.
E-mail address: jgh@sauron.quimica.uniovi.es (J. Gimeno).

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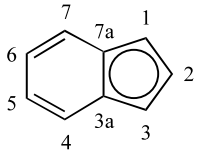
Li^nBu, $HBF_4 \cdot OEt_2$ and $AgBF_4$ were used as received from Aldrich Chemical Co. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The C and H analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 (^{1}H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) and on a Bruker AC200 instrument at 200 (^{1}H), 81.0 (^{31}P) or 50.3 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. The following atom labels are used for the ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic data.



The parameter $\Delta\delta$(C-3a,7a) is defined as the difference between δ(C-3a,7a) of the indenyl complex and δ(C-3a,7a) of sodium indenyl ($\delta = 130.7$ ppm). The term 'Ind' in the NMR data is used for the undefined signals of the benzoid ring.

2.2. Synthesis

2.2.1. [Os(η^5-C_9H_7)Br(PPh_3)$_2$] (1)

A solution of [$OsBr_2(PPh_3)_3$] (330 mg, 0.29 mmol) and LiInd (70 mg, 0.58 mmol) in tetrahydrofuran (30 ml) was stirred for 2 h at room temperature (r.t.). The solvent was then evaporated and the residue was extracted with diethyl ether, evaporated in vacuo and the obtained solid washed once with hexane and vacuum dried to yield complex **1** (209 mg, 79%) as an orange solid. *Anal.* Calc. for $C_{45}H_{37}BrOsP_2$: C, 59.4; H, 4.1. Found: C, 59.9; H, 4.3%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.23; ^{1}H NMR (C_6D_6): δ 4.53 (d, $J_{HH} = 1.9$ Hz, 2H, H-1,3), 5.11 (t, $J_{HH} = 1.9$ Hz, 1H, H-2), 6.90–7.93 (m, 34H, H-4,7, H-5,6 and Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 62.3 (C-1,3), 84.3 (C-2), 110.1 (C-3a,7a), 125.0 (Ind), 127.4–139.3 (Ind, Ph). $\Delta\delta$(C-3a,7a) = −20.6.

2.2.2. [Os(η^5-C_9H_7)I(PPh_3)$_2$] (2)

A suspension of complex [Os(η^5-C_9H_7)Cl(PPh_3)$_2$] (50 mg, 0.06 mmol) and NaI (17 mg, 0.12 mmol) in MeOH (1 ml) was refluxed for three hours. The solvent was then evaporated and the residue was extracted with diethyl ether and filtered with Kieselguhr. The solvent was removed in vacuo and the resulting solid washed with hexane (2x 10 ml) and vacuum dried to yield complex **2** (57 mg, 61%) as an orange solid. *Anal.* Calc. for $C_{45}H_{37}IOsP_2$: C, 56.5; H, 3.9. Found: C, 56.1; H, 4.0%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −4.26; ^{1}H NMR (C_6D_6): δ 4.51 (d, $J_{HH} = 2.2$ Hz, 2H, H-1,3), 4.93 (t, $J_{HH} = 2.2$ Hz, 1H, H-2), 6.22–7.41 (m, 34H, H-4,7, H-5,6 and Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 63.8 (C-1,3), 85.9 (C-2), 109.7 (C-3a,7a), 126.3 (Ind), 127.9–140.4 (Ind, Ph). $\Delta\delta$(C-3a,7a) = −21.0.

2.2.3. [Os(η^5-C_9H_7)H(PPh_3)$_2$] (3)

A solution of NaOMe prepared in situ stirring NaH (0.192 g, 8 mmol) in MeOH (12 ml), was added to a suspension of complex [OsCl(η^5-C_9H_7)(PPh_3)$_2$] (343 mg, 0.40 mmol) in MeOH (50 ml) and the mixture was refluxed for 1 hour. The solvent was evaporated and the residue was extracted with diethyl ether and filtered with Kieselguhr. The solvent was then removed in vacuo to yield complex **3** (283 mg, 86%) as a yellow solid mixture of two rotamers. *Anal.* Calc. for $C_{45}H_{38}OsP_2$: C, 65.0; H, 4.6. Found: C, 64.9; H, 4.5%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 17.21, 17.27; ^{1}H NMR (C_6D_6): δ −17.83 (t, $J_{HP} =$ 26.0 Hz, 1H, H), −17.82 (t, $J_{HP} = 26.0$ Hz, 1H, H), 4.57 (m, 4H, H-1,3), 5.77 (m, 2H, H-2), 6.01 (m, 4H, H-4,7 or H-5,6), 6.87–7.77 (m, 64H, H-4,7 or H-5,6 and Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 67.6 (C-1,3), 67.7 (C-1,3), 82.2 (C-2), 106.5 (C-3a,7a), 123.4 (Ind), 123.8 (Ind), 127.8–142.7 (Ind, Ph). $\Delta\delta$(C-3a,7a) = −24.2. IR (KBr, cm^{-1}): 2158 (OsH).

2.2.4. [Os(η^5-C_9H_7)Br(PPh_3)(PR_3)] ($PR_3 = PMe_3$ (4a), PMe_2Ph (4b)

A solution of complex [OsBr(η^5-C_9H_7)(PPh_3)$_2$] (100 mg, 0.11 mmol) and PR_3 (0.48 mmol) in toluene (10 ml) was heated at refluxing temperature for four hours. The solvent was then evaporated and the residue was extracted with diethyl ether and filtered through Kieselguhr. The solvent was then removed in vacuo and the solid washed once with hexane (5 ml) and vacuum dried to yield complexes **4a**, **b** as brown solids. $PR_3 = PMe_3$ (**4a**): 15% yield; $^{31}P\{^1H\}$ NMR (C_6D_6): δ –42.40 (d, $J_{PP} = 15.0$ Hz, PMe_3), 5.82 (d, $J_{PP} = 15.0$ Hz, PPh_3); ^{1}H NMR (C_6D_6): δ 1.34 (d, $J_{HP} = 9.4$ Hz, PMe_3), 3.87 (m,, 1H, H-2), 4.92 (m, 1H, H-1 or H-3), 4.97 (m, 1H, H-1 or H-3), 6.66–7.69 (m, 19H, H-4,7, H-5,6 and Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.2 (d, $J_{CP} = 37.2$ Hz, PMe_3), 58.9 (C-1 or C-3), 61.8 (C-1 or C-3), 81.9 (C-2), 110.2 (C-3a,7a), 110.3 (C-3a,7a), 125.5 (Ind), 127.2 (Ind), 132.3-140.4 (Ind, Ph). $\Delta\delta$(C-3a,7a) = −20.5; $PR_3 = PMe_2Ph$ (**4b**): 21% yield; $^{31}P\{^1H\}$ NMR (C_6D_6): δ −31.97 (d, $J_{PP} = 13.1$ Hz, PMe_2Ph), 3.90 (d, $J_{PP} =$ 13.1 Hz, PPh_3); ^{1}H NMR (C_6D_6): δ 1.26 (d, $J_{HP} = 9.9$ Hz, PMe_2Ph), 3.66 (m,, 1H, H-2), 4.51 (m, 1H, H-1 or H-3), 4.70 (m, 1H, H-1 or H-3), 6.50–7.74 (m, 24H, H-4,7, H-5,6 and Ph).

2.2.5. [Os(η^5-C_9H_7)H_2(PPh_3)$_2$][BF_4] (5)

To a solution of complex [OsH(η^5-C_9H_7)(PPh_3)$_2$] (**3**) (100 mg, 0.12 mmol) in diethyl ether (20 ml), $HBF_4 \cdot OEt_2$ (0.12 mmol) in diethyl ether (20 ml) was added dropwise at −80 °C and the mixture was stirred until r.t. was reached. Solvents were then decanted and the solid residue washed with diethyl ether (2 × 10 ml) and

vacuum dried to yield complex **5** (102 mg, 92%) as a grey solid. *Anal.* Calc. for $C_{45}H_{39}BF_4OsP_2$: C, 58.8; H, 4.3. Found: C, 58.2; H, 4.2%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 11.80; ^1H NMR (C_6D_6): δ −11.69 (t, $J_{PH} = 31.4$ Hz, 2H, H), 4.95 (t, $J_{HH} = 2.5$ Hz, 1H, H-2), 5.39 (d, $J_{HH} = 2.5$ Hz, 2H, H-1,3), 6.68 (m, 2H, H-4,7 or H-5,6), 6.77–7.49 (m, 32H, H-4,7 or H-5,6 and Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 76.9 (C-1,3), 83.0 (C-2), 107.2 (C-3a,7a), 124.4 (Ind), 128.7–134.7 (Ind, Ph). $\Delta\delta$(C-3a,7a) = −23.5. IR (KBr, cm^{-1}): 2116 (OsH), 2079 (OsH), 1085 (BF_4^-).

2.2.6. *[Os(η⁵-C₉H₇)(NCMe)(PPh₃)₂][BF₄] (6)*

Complex [Os(η⁵-C_9H_7)Cl(PPh_3)$_2$] (100 mg, 0.12 mmol) and $AgBF_4$ (25 mg, 0.13 mmol) in acetonitrile (20 ml) were stirred in absence of light at r.t. for 1 h. Solvent was then removed under reduced pressure and the solid residue was extracted with dichloromethane and filtered through Kieselguhr. Dichloromethane was removed in vacuo and the solid washed with diethyl ether (2 × 15 ml) and vacuum dried to yield complex **6** (61 mg, 55%) as a brown solid. *Anal.* Calc. for $C_{47}H_{40}BF_4NOsP_2$: C, 58.9; H, 4.2; N, 1.5. Found: C, 58.6; H, 4.1; N, 1.4%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.09; ^1H NMR ($CDCl_3$): δ 2.48 (s, 3H, Me), 4.78 (m, 2H, H-1,3), 4.84 (m, 1H, H-2), 6.85–7.37 (m, 34H, H-4,7, H-5,6 and Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 4.5 (Me), 64.0 (C-1,3), 89.1 (C-2), 108.1 (C-3a,7a), 124.4 (Ind), 128.2–135.5 (N*C*Me, Ind, Ph). $\Delta\delta$(C-3a,7a) = −22.6. IR (KBr, cm^{-1}): 2264 (C≡N), 1054 (BF_4^-).

2.2.7. *[Os{=C̄OCH₂(CH₂)₃CH₂}(η⁵-C₉H₇)(PPh₃)₂][PF₆] (7)*

A mixture of [Os(η⁵-C_9H_7)Cl(PPh_3)$_2$] ((120 mg, 0.14 mmol), $NaPF_6$ (94 mg, 0.56 mmol) and HC≡C$(CH_2)_3CH_2OH$ (69 mg, 0.70 mmol) in methanol (10 ml) was heated under reflux for 4 h. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane and filtered through Kieselguhr. The solvent was then removed in vacuo and the solid washed with diethyl ether (2 × 10 ml) and vacuum dried to give complex **7** as a brown solid (76 mg, 51% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.94; ^1H NMR ($CDCl_3$): δ 1.08 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 3.03 (m, 2H, OCH_2 or =CCH_2), 3.12 (m, 2H, OCH_2 or =CCH_2), 5.26 (m, 2H,, H-4,7 or H-5,6), 5.42 (m, 2H, H-1,3), 6.17 (m, 1H, H-2), 6.70–7.68 (m, 32H, H-4,7or H-5,6 and Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.3 (CH_2), 27.4 (CH_2), 28.8 (CH_2), 59.7 (CH_2), 75.2 (C-1,3), 77.4 (OCH_2), 95.2 (C-2), 114.2 (C-3a,7a), 123.6 (Ind), 124.4–136.2 (Ind, Ph), 257.4 (t, $J_{CP} = 7.6$ Hz, C_α). $\Delta\delta$(C-3a,7a) = −16.6. IR (KBr, cm^{-1}): 1239 (CO), 838 (PF_6^-).

2.2.8. *X-ray diffraction studies of [Os{=C=C(H)ᵗBu}(η⁵-C₉H₇)(PPh₃)₂][PF₆]*

Data collection, crystal, and refinement parameters are collected in Table 1. The unit-cell parameters were obtained from the least-squares fit of 25 reflections with θ between 10 and 13°. The intensity data were measured using the ω–2θ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.98 and 1.02. On all reflections, profile analysis [7,8] was performed. Lorentz and polarization corrections were applied, and the data were reduced to F_o^2 values.

The structure was solved by Patterson methods and phase expansion using the program DIRDIF [9], and refined by least-squares using SHELXL-93 [10]. The hydrogen atoms were geometrically placed.

During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined except to the high disordered molecule of ether which was refined as a rigid model with a common isotropic thermal parameter to carbon atoms. The hydrogen atoms were isotropically refined with a common thermal parameter to each

Table 1
Crystal data and structure refinement for [Os{=C=C(H)ᵗBu}(η⁵-C_9H_7)(PPh_3)$_2$][PF_6]

Empirical formula	$C_{55}H_{57}F_6OOsP_3$
Formula weight	1131.12
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.043(4)
b (Å)	19.75(2)
c (Å)	19.223(6)
α (°)	90
β (°)	90.35(3)
γ (°)	90
V (Å^3)	4951(6)
Z	4
D_{calc} (Mg m^{-3})	1.518
Absorption coefficient (v)	2.734
F(000)	2280
Crystal size (mm^3)	0.26 × 0.23 × 0.19
Theta Range for data collection (°)	1.48–25.98
Index ranges	$-16 \le h \le 16$, $0 \le k \le 24$, $0 \le l \le 23$
Reflections collected	9697
Independent reflections	9697 [$R_{int} = 0.0871$]
Completeness to theta = 25.98° (%)	99.9
Absorption correction	empirical
Max. and min. transmission	0.6246 and 0.5367
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	9697/0/558
Goodness-of-fit on F^2	0.992
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0537$, $wR_2 = 0.1147$
R indices (all data)	$R_1 = 0.1998$, $wR_2 = 0.1631$
Largest difference peak and hole (e Å^{-3})	1.796 and −2.036

group of hydrogen atoms riding to the same carbon atom. The function minimized was $[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(0.0605P)^2+(0.00P)]$ where $P=(\max(F_o^2,O)+2F_c^2)/3$ with $\sigma(F_o^2)^2$ from counting statistics. The maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was 0.02. The final difference Fourier map showed no peaks higher than 1.80 e $Å^{-3}$ or deeper than -2.04 e $Å^{-3}$; most of the highest peaks were found near to the disordered ether molecule.

Atomic scattering factors were taken from reference [11]. Geometrical calculations were made with PARST [12]. The figure showing the coordination and the atomic numbering scheme was drawn by EUCLID [13]. All calculations were performed at University of Oviedo on the Scientific Computer Center and X-ray group DEC-ALPHA computers.

3. Results and discussion

3.1. Synthesis of $[Os(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$ X = Br (1), I (2), H (3)

Following the reported synthetic approach to $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ [3], the bromide derivative (**1**) is prepared from the reaction of $[OsBr_2(PPh_3)_3]$, with LiC_9H_7 in tetrahydrofurane (79%). (Eq. (1))

$$[OsBr_2(PPh_3)_3] \xrightarrow[THF]{LiC_9H_7} \underset{\mathbf{1}}{[Os(\eta^5\text{-}C_9H_7)Br(PPh_3)_2]} \quad (1)$$

Treatment of $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ with an excess of NaI in refluxing methanol affords complex **2** (61%) (Eq. (2)). Complexes **1** and **2** are isolated as orange air-stable crystalline solids and fully characterized by elemental analyses and spectroscopic methods (see Section 2). The spectroscopic data can be compared to those reported for the parent chloride complex [3] and therefore, they will not be further discussed.

$$[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2] \xrightarrow[MeOH]{NaI} \underset{\mathbf{2}}{[Os(\eta^5\text{-}C_9H_7)I(PPh_3)_2]} \quad (2)$$

One of the most efficient synthetic methods for transition metal hydrides is that using sodiumalkoxides bearing β-hydrogen atoms as a hydrogen transfer agent. Thus, the reaction of complex $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ with NaOMe in methanol yields the hydride derivative $[Os(\eta^5\text{-}C_9H_7)H(PPh_3)_2]$ (**3**) which is isolated as a yellow solid in 86% yield after work-up (Eq. (3)).

$$[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2] \xrightarrow[-NaCl,\ -H_2CO]{NaOMe/MeOH} \underset{\mathbf{3}}{[Os(\eta^5\text{-}C_9H_7)H(PPh_3)_2]} \quad (3)$$

Elemental analyses, IR and NMR spectroscopy data of **3** are in accordance with the proposed formulation. (see Section 2 for details). Significantly, NMR spectra at room temperature indicate the existence of two rotamers in solution. Thus, ^1H NMR spectrum shows two triplet hydride resonances at high field (δ −17.82 and −17.83 ppm, $J_{PH} = 26.0$ Hz). ^{31}P NMR spectrum which displays two resonances at δ 17.21 and 17.27 ppm, is also in agreement with the presence of two rotamers. They arise from the formally *cis* and *trans* orientations of the benzo ring of the indenyl group with respect to the hydride ligand (Fig. 1). Similar rotamers have been described for the complexes $[Ru(\eta^5\text{-}C_9H_7)I(CO)(PR_3)]$ R = ^{i}Pr, Cy [14]. Variable temperature $^{31}P\{^1H\}$ and ^1H NMR spectra up to ca. 80 °C remain practically unchanged indicating that the rotation is not allowed within this temperature range. This is probably due to the steric hinderance of the PPh_3 ligands which block the complete rotation of the indenyl ring.

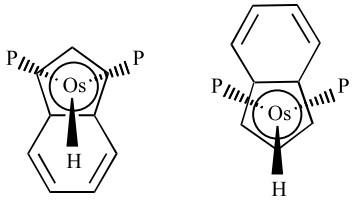


Fig. 1. Representation of the two rotamers of $[Os(\eta^5\text{-}C_9H_7)H(PPh_3)_2]$.

Attempts to use this complex in typical insertion reactions have failed. Thus, complex **3** does not react with $MeO_2CC{\equiv}CCO_2Me$ in refluxing toluene recovering the starting material unchanged after 4 h. The inertness of complex **3** is in accord with the observed unreactivity of the analogous ruthenium complex $[Ru(\eta^5\text{-}C_9H_7)H(PPh_3)_2]$ towards terminal and internal alkynes. We have reported that the presence of small bite ligands favours the insertion as observed for the complex $[Ru(\eta^5\text{-}C_9H_7)H(dppm)]$ [15].

3.2. Synthesis of $[Os(\eta^5\text{-}C_9H_7)Br(PPh_3)L]$ (L = PMe_3 (4a); PMe_2Ph (4b))

We have previously reported that $[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ is able to undergo phosphine exchange reactions which proceed through a dissociative pathway with rate constants one order higher in magnitude than those of the corresponding cyclopentadienyl derivatives. This has been attributed to a type of dissociative indenyl effect [16]. In order to check this kinetic effect in osmium complexes, ligand exchange processes have been studied using the parent complexes $[Os(\eta^5\text{-}C_9H_7)X(PPh_3)_2]$.

Thus, the treatment of $[Os(\eta^5\text{-}C_9H_7)Br(PPh_3)_2]$ (**1**) with PMe_3 and PMe_2Ph in refluxing toluene for 4 hours gives complexes **4a** (15%) and **4b** (21%). In contrast, heating under reflux a toluene solution of $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ leads to decomposition products or remains unchanged in the presence of an excess of PR_3

at room temperature. The characterization of complexes **4a** and **4b** is supported by elemental analyses and the standard spectroscopic techniques (see Section 2 for details). Although no kinetic studies have been performed we note that analogous phosphine exchange reactions starting from $[Os(\eta^5\text{-}C_5H_5)Br(PPh_3)_2]$ require 12 h in refluxing toluene [17] indicating that the indenyl kinetic effect is operative [18].

3.3. Synthesis of cationic complexes $[Os(\eta^5\text{-}C_9H_7)L(PPh_3)_2][X]$

3.3.1. Synthesis of $[Os(\eta^5\text{-}C_9H_7)H_2(PPh_3)_2][BF_4]$ (5)

As expected for the typical electron richness of analogous hydride derivatives [19], the addition of tetrafluoroboric acid to a solution of **3** in diethyl ether at −80 °C leads, to the precipitation of the desired cationic complex $[Os(\eta^5\text{-}C_9H_7)H_2(PPh_3)_2][BF_4]$ (**5**) (Eq. (4)).

$$[Os(\eta^5\text{-}C_9H_7)H(PPh_3)_2] \xrightarrow[Et_2O]{HBF_4\cdot OEt_2} \underset{\mathbf{5}}{[Os(\eta^5\text{-}C_9H_7)H_2(PPh_3)_2][BF_4]} \quad (4)$$

Complex **5** can be easily identified as the dihydride derivative on the basis of the spectroscopic data. Thus, the IR spectrum displays ν(Os–H) absorptions at 2116 and 2079 cm^{-1}. ^1H NMR shows a triplet resonance at δ −11.69 ($J_{PH} = 31.4$ Hz) which is consistent with a trans arrangement of the two hydride ligands. A similar geometry has been described for the analogous complexes $[Os(\eta^5\text{-}C_5H_5)H_2(PPh_3)_2]^+$ (δ −11.3 $J_{PH} = 29$ Hz) [17,20] and $[Os(\eta^5\text{-}C_5H_5)H_2(CO)(P^iPr_3)]^+$ (δ −11.4 $J_{PH} = 28.8$ Hz) [21].

Analogous dihydride cyclopentadienyl complexes $[Os(\eta^5\text{-}C_5H_5)H_2(PR_3)_2]^+$ [17,20–22] have been reported to be formed through a transient dihydrogen derivative. To find out whether an intermediate dihydrogen species is formed the addition of acid was monitored by ^1H NMR at low temperature (−78 °C). However, no further signals besides those assigned to complex **5**, are observed. This fact probably arises from the electronic-rich nature of the metallic fragment which determines the favourable stabilization of the dihydride complex. [22]

3.3.2. Synthesis of $[Os(\eta^5\text{-}C_9H_7)(NCMe)(PPh_3)_2][BF_4]$ (6) and $[Os\{=\overline{COCH_2(CH_2)_3CH_2}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (7)

We have extensively used the ability of the indenyl complexes in the activation of terminal alkynes *via* in situ generation of the sixteen electron species $[M(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (M = Ru, Os) [4]. These unsaturated species are easily prepared from the parent chloride complexes by reaction with an appropriate chloride abstractor. Although the formation of this species follows unequivocally from its reactivity, we have now been able to isolate it in the presence of acetonitrile giving rise quantitatively to the adduct $[Os(\eta^5\text{-}C_9H_7)(NCMe)(PPh_3)_2][BF_4]$ (**6**) (Eq. (5)).

$$[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2] \xrightarrow[NCMe]{AgBF_4} \underset{\mathbf{6}}{[Os(\eta^5\text{-}C_9H_7)(NCMe)(PPh_3)_2][BF_4]} \quad (5)$$

All attempts to displace the co-ordinated acetonitrile by typical two electron ligands such as CO and monodentate phosphines have been unsuccessful.

In a previous paper [3] we have described the synthesis of the oxacycliccarbenes $[Os\{=\overline{COCH_2(CH_2)_n}CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ ($n = 1, 2$) which are obtained from the reaction of $[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$ with ω-hydroxyalk-1-ynes, $HC{\equiv}C(CH_2)_nCH_2OH$ ($n = 1$, 2) and $NaPF_6$. However, the reaction with 5-hexin-1-ol ($n = 3$) does not proceed in the same way giving instead the intermediate hydroxivinylidene complex $[Os\{=C=C(H)(CH_2)_3CH_2OH\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$. We have now succeeded in converting this specie in the final oxacyclic carbene $[Os\{=\overline{COCH_2(CH_2)_3CH_2}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (**7**) which is formed via intramolecular cyclization of the hydroxivinylidene complex (Eq. (6)).

$$[Os(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2] \xrightarrow[HC{\equiv}C(CH_2)_3CH_2OH]{NaPF_6/MeOH} [Os\{=\overline{COCH_2(CH_2)_3CH_2}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6] \quad (6)$$

Complexes **6** and **7** have been characterized by IR and NMR spectroscopy and analytical methods (see Section 2 for details). Relevant features are: (a) the weak $\nu(C{\equiv}N)$ absorption at 2264 cm^{-1} in the IR spectrum of **6**; (b) a singlet signal at in the $^{31}P\{^1H\}$ NMR spectrum of **7** indicating the chemical equivalence of the phosphines. This is consistent with the free rotation of the carbene group around the ruthenium carbene bond; (c) the characteristic low-field carbenic C_α resonance (δ 311.5 ppm) which appears as a triplet due to the coupling to the two equivalent phosphorous nuclei.

3.4. Structural studies of $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ in solution and in the solid state

The preferred conformation of the indenyl ring in half-sandwich metal complexes have been the subject of longstanding studies both in solution and solid state [4]. We have reported that the orientation of the indenyl ligand with respect to the vinylidene, alkynyl, alkenyl and allenylidene groups (formally *cis* or *trans*) in ruthenium(II) complexes is clearly dependent on the nature of the unsaturated hydrocarbon groups. In order to have comparative information between ruthenium and osmium vinylidene derivatives, we have performed structural studies on the conformational features of the

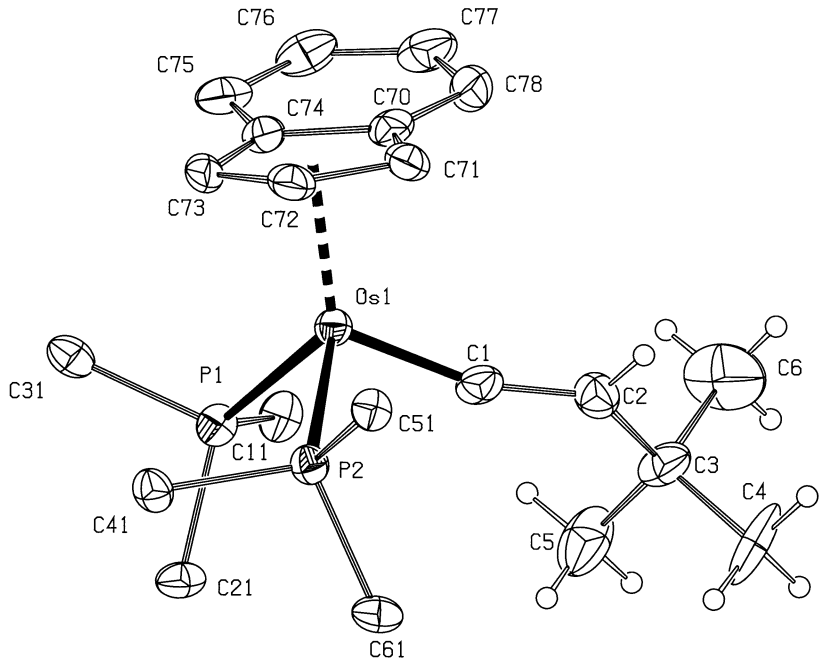


Fig. 2. Perspective view of the structure of the cationic complex $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$. Ph groups have been omited for clarity.

indenyl ligand in the vinylidene complex $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ [3].

3.4.1. NMR studies

The room-temperature $^{31}P\{^1H\}$ NMR spectrum shows one singlet resonance at δ −6.8 ppm indicating the chemical equivalence of the two phosphorus atoms. This is consistent with the existence of two simultaneous dynamic processes in solution, both of them rapid on the NMR time scale: (a) the rotation of the vinylidene group around the Ru=C bond; and (b) the rotation of the indenyl ring.

Variable temperature $^{31}P\{^1H\}$ NMR experiments show that the singlet resonance observable in the spectra at room temperature (δ −6.8 ppm) gives rise to two broad singlets at δ 0.68 and −9.80 ppm below 208 K. The coalescence temperature is in the range 228–208 K with an estimated energy barrier $\Delta G^{\#}$ in the range 8.8–9.7 kcal mol^{-1} [23].[1] Since only a single coalescence temperature was observed, it is not possible to distinguish whether one or both of the two possible fluxional processes have been frozen [24].[2]

3.4.2. X-ray crystal structure of $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$

A view of the molecular geometry is shown in Fig. 2. Selected bond distances and angles are listed in Table 2.

Table 2
Selected bond lengths and slip parameter Δ (Å) and bond angles and dihedral angles FA, HA, DA and CA (°) for $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$

Bond lengths			
Os–C*	1.981(7)	C(1)–C(2)	1.343(16)
Os–P(1)	2.365(3)	C(2)–C(3)	1.536(16)
Os–P(2)	2.313(3)	Δ [a]	0.12(1)
Os–C(1)	1.841(13)		
Bond angles			
Os–C(1)–C(2)	162.1(11)	C(1)–Os–C*	120.2(4)
C(1)–C(2)–C(3)	129.7(13)	P(1)–Os–C*	120.75(8)
C(1)–C(2)–H(2)	115.1	P(2)–Os–C*	120.95(8)
C(3)–C(2)–H(2)	115.1	DA [b]	53.4(7)
P(2)–Os–P(1)	97.08(11)	CA [c]	63.8(3)
C(1)–Os–P(1)	97.7(4)	FA [d]	10.0(1)
C(1)–Os–P(2)	94.2(4)	HA [e]	5.0(1)

[a] $\Delta = d(Os–C(74),C70)) – d(Os–C(71),C(73))$.

[b] DA (dihedral angle) = angle between normals to least-squares planes defined by C*, Os, C(1) and Os, C(1), C(2), C(3).

[c] CA (conformational angle) = angle between normals to least-squares planes defined by C**, C*, Os and C*, Os, C(1). C* = centroid of C(70), C(71), C(72), C(73) and C(74).C** = C(70), C(74), C(75), C(76), C(77), C(78).

[d] FA (fold angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(70), C(74), C(75), C(76), C(77), C(78).

[e] HA (hinge angle) = angle between normals to least-squares planes defined by C(71), C(72), C(73) and C(71),C(74), C(70), C(73).

[1] Estimated from the coalescence temperature using the Eyring equation.

[2] Rotation of the vinylidene ligand at room temperature is well stablished, having similar energy barriers (7–9 kcal mol^{-1}) and extend Hückel calculations for the model $[Os(\eta^5\text{-}C_9H_7)(PH_3)_2(=C=CH_2)]^+$ show a rotation barrier for the rotation of the indenyl ring of 6.46 kcal mol^{-1}.

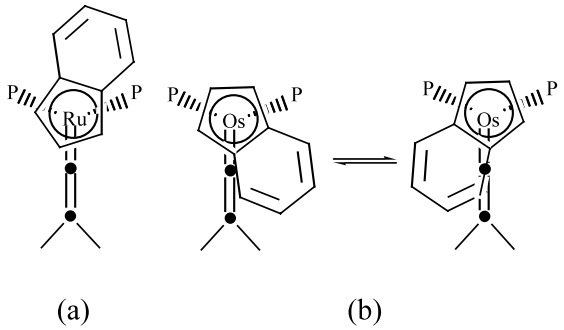


Fig. 3. Representation of cis and trans rotamers for the cation $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$.

The unit cell consists of $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ cations, hexafluorophosphate anions and one diethyl ether molecule. The indenyl ligand exhibits the usual allylene η^5 coordination type in the pseudooctahedral three-legged piano-stool geometry around the ruthenium atom. The interligand angles (94.2(4), 97.08(11) and 97.7(4)°) and those between the centroid C* and the legs (120.2(4), 120.75(8) and 120.95(8)°) show values typical of a pseudooctahedron.

The most relevant feature concerning the indenyl ring is the conformational angle CA (CA = 63.8(3)°), defined between the planes C**–C*,Os and C*,Os,C(1) for benzo ring cis to the vinylidene). This value shows a trans orientation of benzo ring with respect to the triphenylphosphine ligand. However, analogous indenyl ruthenium derivatives $[Ru(=C=CMe_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (CA = 157.8(4)°) [25] and $[Ru\{=C=CH(Ph)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ (CA = 164.6(3)°) [4], show the benzo ring and the vinylidene ligand in a *trans* disposition (Fig. 3(a)).

As shown by the space filling representation of $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (Fig. 4), the indenyl ligand and the vinylidene chain do not show steric interactions. However, the model shows that the indenyl ring and the phenyl groups of the phosphines are sterically hindered. On the basis of this fact, we propose a limited rotation of the indenyl ring above the vinilydene chain between the two phosphines (Fig. 3(b)). This disposition for the indenyl ligand can also explain the inertness of the osmium vinilydenes towards alcohols [3] since the C_α is protected by the indenyl ligand.

The dihedral angle DA between the planes C* and Os,Cl(1),Os,C(1),C(2),C(3) of 53.4(7)° shows that the orientation of the vinylidene chain is largely deviated from the horizontal position (DA = 90°) which is the most favourable according theoretical calculations [26]. This deviation probably arises from the steric interactions between the substituents of the vinylidene group and the phenyl groups of the phosphine ligands.

The angle Os–C(1)–C(2) in the vinylidene moiety (162.1(11)°) is slightly smaller than for the cyclopentadienyl derivative $[Os(\eta^5\text{-}C_5Me_5)(CO)(PPh_3)_2\{=C=C(H)^tBu\}]^+$ (175.0°) [27], but the distances Os–C(1) and C(1)–C(2) are comparable in both derivatives.

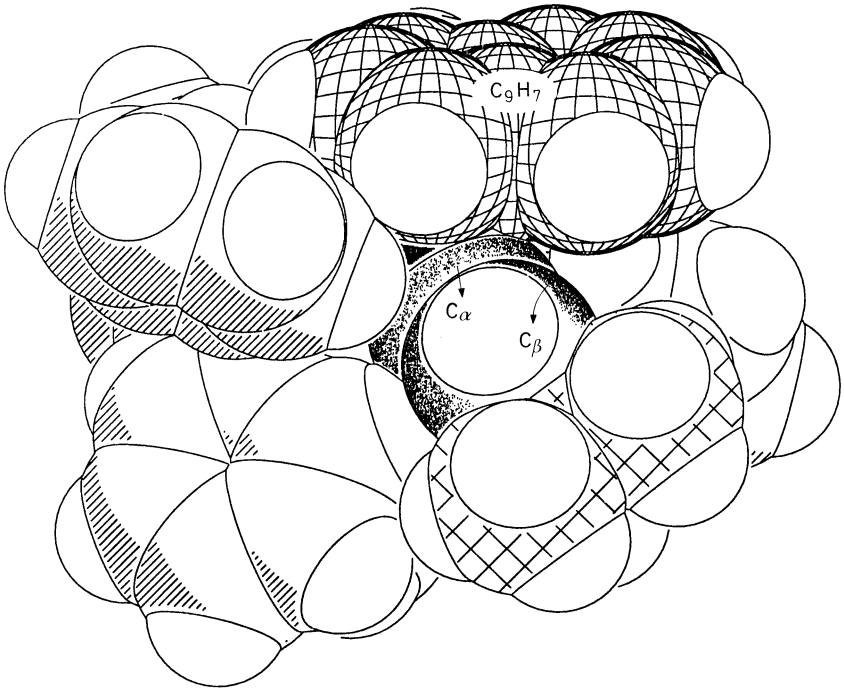


Fig. 4. Van der Waals representation for the cation $[Os\{=C=C(H)^tBu\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 198991 . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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