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Synthesis of alkynyl, cyclic carbene and vinylidene osmium(II) complexes: first indenyl half-sandwich osmium(II) complexes

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The reaction of $[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **1** with 3,3-dimethylbut-1-yne and $NaPF_6$ in refluxing methanol gave the vinylidene complex $[Os\{=C=C(H)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **2a** and with $HC\equiv CSiMe_3$ and NH_4PF_6 in refluxing methanol gave the unsubstituted vinylidene complex $[Os(=C=CH_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **2b**. 2-Oxacyclo-pentylidene and -hexylidene complexes $[Os\{=COCH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (n = 1 **3a** or 2 **3b**) have been prepared by reaction of **1** with $HC\equiv C(CH_2)_nCH_2OH$. Reaction of **1** and hex-5-yn-1-ol afforded the hydroxyvinylidene complex $[Os\{=C=C(H)(CH_2)_3CH_2OH\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ **4** and with 1-ethynyl-1-cycloalkanols in the presence of $NaPF_6$ in refluxing methanol it gave regioselectively the alkenylvinylidene complexes $[Os\{=C=C(H)CCHCH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (n = 1 **5a**, 2 **5b** or 3 **5c**). Deprotonation of the vinylidene complexes **2a**, **2b** and **5a**–**5c** with potassium *tert*-butoxide yielded the neutral alkynyl complexes $[Os(C\equiv CR)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R = Bu^t **6a** or H **6b**) and $[Os\{C\equiv CCCHCH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **7a**–**7c** respectively. Methylation of complex **6a** with $MeOSO_2CF_3$ yielded the vinylidene complex $[Os\{=C=C(Me)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]$ **8**.

It is well known that half-sandwich complexes of most transition metals display a rich chemistry.[1] In particular, indenyl derivatives have been extensively studied in the last decade as a consequence of the greater role played by these organometallic species in ligand substitution[2a–e] and migratory insertion[3] reactions as well as in catalytic processes[4] as compared with the chemistry of their cyclopentadienyl analogues. During the last few years we have been involved in the synthesis and reactivity of σ-alkynyl and unsaturated carbene complexes containing indenylruthenium(II) moieties as a metal auxiliary.[5] However, to the best of our knowledge, half-sandwich indenylosmium(II) complexes have not been described as yet, probably due to the fact of the lack of an appropriate precursor.[†] We report herein the synthesis of the first indenylosmium(II) complex, namely $[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **1**, which has proven to be a good precursor for the preparation of novel vinylidene and carbene complexes.

Results and Discussion

Synthesis of $[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ 1

The reaction of $[OsCl_2(PPh_3)_3]$ with indenyllithium in tetrahydrofuran permits the isolation of the first indenylosmium complex $[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **1**, which can be used as a precursor of interesting half-sandwich indenylosmium complexes. Complex **1** is perfectly stable in the solid state and has been characterized by conventional spectroscopic and analytical techniques (see Experimental section).

Activation of alkynes

The reactions are summarized in Scheme 1. Complex **1** reacts with alk-1-ynes in the presence of sodium or ammonium hexafluorophosphate in refluxing methanol to afford vinylidene (**2a**, **2b**, **4**, **5a**–**5c**) and carbene (**3a**, **3b**) complexes. Deprotonation of the former complexes with $KOBu^t$ in tetrahydrofuran (thf) leads to the formation of the corresponding alkynyl derivatives (**6a**, **6b**, **7a**–**7c**). Similar cyclopentadienyl derivatives $[Os\{C=C(H)Ph\}(\eta^5\text{-}C_5H_5)(PPh_3)_2][PF_6]$ and $[Os(C\equiv CPh)(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ are also known.[7]

***(a)* Non-functionalized alkynes.** The reaction of complex **1** with 3,3-dimethylbut-1-yne and $NaPF_6$ in refluxing methanol for 4 h gives the monosubstituted vinylidene complex **2a**. The reaction is slower than that of the analogous ruthenium complex $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ which requires refluxing in methanol for 15 min.[5c] Complex **2b** can be obtained by the treatment of **1** with trimethylsilylacetylene in the presence of ammonium hexafluorophosphate; in this case the ammonium salt generates an acidic solution and allows cleavage of the C–Si bond giving rise to the unsubstituted vinylidene complex **2b**. It is worth mentioning that, in contrast, under similar reaction conditions the alkoxycarbene complex $[Ru\{=C(OMe)Me\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ is formed in the reaction with the analogous indenylruthenium(II) precursor.[5c] These vinylideneosmium(II) complexes **2a**, **2b** are unreactive towards alcohols (the ethenylidene complex **2b** is recovered unchanged after refluxing in methanol for 12 h).

***(b)* Functionalized alkynes.** As described above, the vinylidene complexes **2a** and **2b** are unreactive towards nucleophilic addition of alcohols. We became interested in comparing these intermolecular reactions with the possible intramolecular cyclization reactions involving vinylidene complexes derived from ω-hydroxyalk-1-ynes. When **1** and but-3-yn-1-ol are heated in methanol in the presence of $NaPF_6$ under the conditions used for the synthesis of the vinylidene complexes **2a**, **2b** (see above) the 2-oxacyclopentylidene complex **3a** is formed selectively. Similarly, the reaction of **1** with pent-4-yn-1-ol leads to the analogous carbene complex **3b**. However, the reaction with $HC\equiv C(CH_2)_3CH_2OH$ does not result in formation of the expected carbene complex giving instead the hydroxyvinylidene complex **4**. The expected intramolecular attack is not observed probably due to the less favoured cyclization which would result in the formation of a seven-

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[†] We have just been able to prepare the first allenylideneosmium complexes.[6]

membered ring. Nevertheless we have recently been able to isolate the first seven-membered cyclic Fischer carbene complex $[Ru\{=\overline{COCH_2(CH_2)_3CH_2}\}(\eta^5\text{-}C_9H_7)L_2][PF_6]$ $[L_2 = (PPh_3)_2$ or $Ph_2PCH_2PPh_2]$.[8]

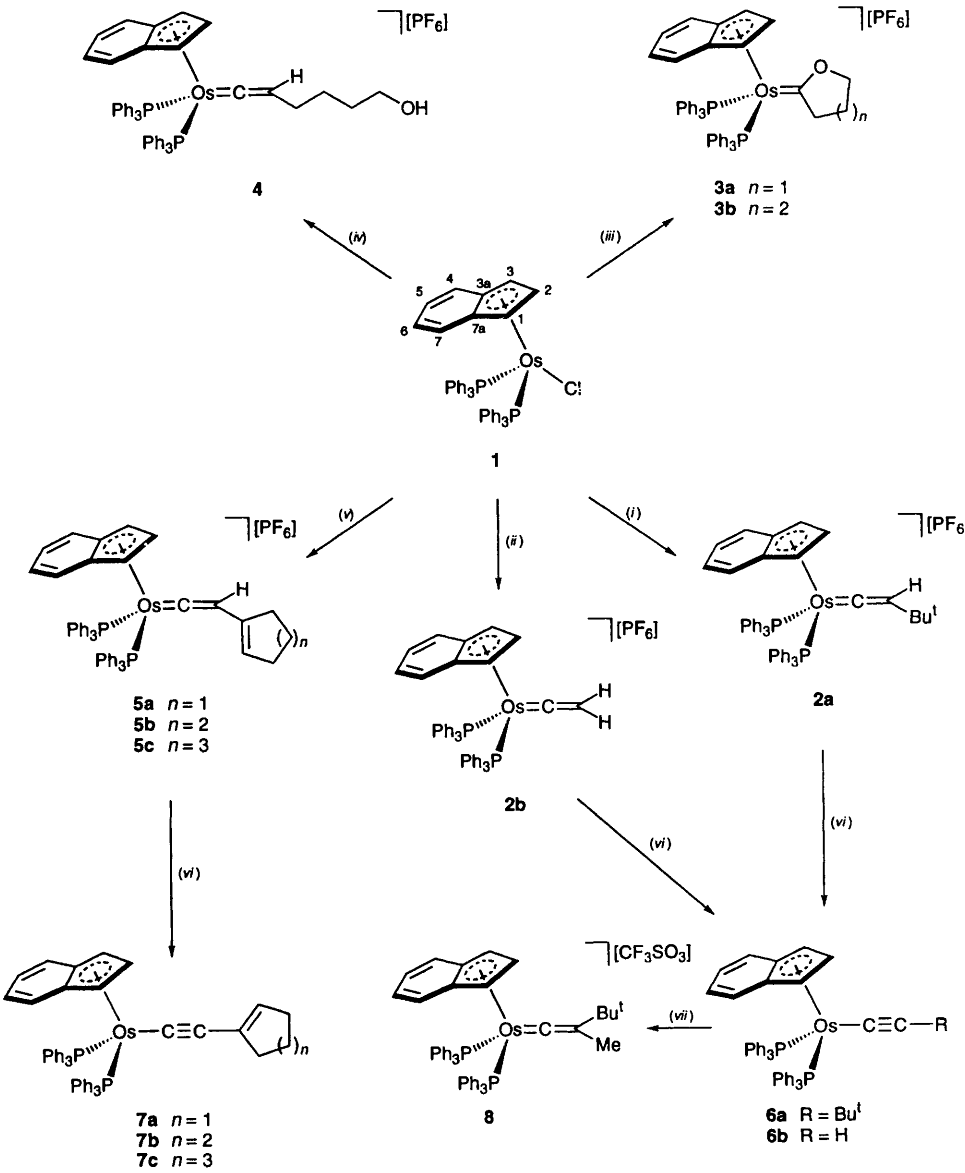
(*c*) **Propargyl alcohols.** The reaction of complex **1** with 1-ethynyl-1-cycloalkanols and $NaPF_6$ in refluxing methanol for 4 h results in the formation of the α,β-unsaturated vinylidene complexes **5a**–**5c** in *ca.* 75% yield (see Scheme 1). The reactions proceed through the formation in a first step of the hydroxyvinylidene complex $[Os\{=C=C(H)\overline{C(OH)CH_2(CH_2)_nCH_2}\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ which undergoes spontaneous dehydration to give rise regioselectively to the alkenylvinylidene complexes (allenylidene isomers are not detected).[5a,9]

The vinylidene complexes **2a**, **2b**, **5a**–**5c** can readily be deprotonated using $KOBu^t$ in thf to yield the alkynyl derivatives $[Os(C{\equiv}CR)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ ($R = Bu^t$ **6a** or H **6b**) and the α,β-unsaturated alkynyl derivatives **7a**–**7c**. These complexes can be used as suitable precursors of methyl-substituted vinylidene complexes. Thus, the reaction of **6a** with an excess of $MeOSO_2CF_3$ in diethyl ether leads to the formation of the complex $[Os\{=C=C(Me)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]$ **8** which was isolated as an insoluble solid in the reaction mixture.

All the novel complexes have been characterized by infrared spectroscopy, elemental analyses and NMR (^1H, $^{31}P\text{-}\{^1H\}$, $^{13}C\text{-}\{^1H\}$) spectroscopy (details are given in the Experimental section and in Table 1). The IR spectra (KBr) of the vinylidene derivatives exhibit the expected absorptions for the anions PF_6^- and $CF_3SO_3^-$. Absorption bands which appear in the range 1600–1700 cm^{-1} can be tentatively assigned to ν(C=C) of the vinylidene group; however, they are in general overlapped by those of the phosphines, the assignment being thus uncertain. The infrared spectra of the alkynyl complexes exhibit ν(C≡C) absorption bands in the range 2064–2091 (**6a** and **7a**–**7c**) and at 1954 cm^{-1} (**6b**), as expected for ethynyl derivatives.[5c,10]

NMR spectra

The room-temperature $^{31}P\text{-}\{^1H\}$ NMR spectra of all the complexes exhibit a single resonance. The spectra of the vinylidene complexes show this signal at a higher field (δ −7.27 to −3.43) than those of the corresponding alkynyl complexes



Scheme 1 (*i*) $+HC{\equiv}CBu^t$ + $NaPF_6$ (refluxing MeOH, 4 h); (*ii*) $+HC{\equiv}CSiMe_3$ + NH_4PF_6 (refluxing MeOH, 4 h); (*iii*) $+HC{\equiv}C(CH_2)_nCH_2OH$ + $NaPF_6$ (refluxing MeOH, 4 h); (*iv*) + $HC{\equiv}C(CH_2)_3CH_2OH$ + $NaPF_6$ (refluxing MeOH, 4 h); (*v*) $+HC{\equiv}C\overline{C(OH)CH_2(CH_2)_nCH_2CH_2}$ + $NaPF_6$ (refluxing MeOH, 4 h); (*vi*) $+KOBu^t$ [thf, room temperature (r.t.), 45–60 min]; (*vii*) $+MeOSO_2CF_3$ (Et_2O, r.t., 30 min)

Table 1 $^{31}P\text{-}\{^1H\}$ and ^1H NMR data for complexes **2**–**8**[a]

			^1H				
			$\eta^5\text{-}C_9H_7$				
	Complex	$^{31}P\text{-}\{^1H\}$	$H^{1,3}$	H^2	J_{HH}	$H^{4,7}$, $H^{5,6}$	Others
2a	$[Os\{{=}C{=}C(H)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−6.82 (s)	5.67 (d)	5.78 (t)	2.4	5.96 (m) [c]	1.01 (s, Bu^t), 6.77–7.50 (m, PPh_3)
2b	$[Os({=}C{=}CH_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−3.43 (s)	5.57 (d)	5.67 (t)	2.5	6.15 (m) [c]	6.87–7.60 (m, PPh_3)
3a	$[Os\{{=}\overline{CO(CH_2)_2C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−0.55 (s)	5.40 (m)	5.27 (m)	—	6.27 (m) [c]	1.61 (m, CH_2), 3.08 (t, J_{HH} = 6.7, OCH_2 or $=CCH_2$), 3.35 (t, J_{HH} = 5.6, OCH_2 or $=CCH_2$), 6.66–7.80 (m, PPh_3)
3b	$[Os\{{=}\overline{CO(CH_2)_3C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−0.70 (s)	5.39 (m)	5.20 (m)	—	6.21 (m) [c]	1.10, 1.64, (m, CH_2), 3.00 (t, J_{HH} = 6.5, OCH_2 or $=CCH_2$), 3.19 (t, J_{HH} = 5.9, OCH_2 or $=CCH_2$), 6.65–7.74 (m, PPh_3)
4	$[Os\{{=}C{=}C(H)(CH_2)_3CH_2OH\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−4.59 (s)	5.56 (m)	5.87 (m)	—	5.97 (m) [c]	1.30, 1.86 (m, CH_2), 2.31 (m, $=CCH_2$), 3.45 (m, CH_2OH), 6.80–7.79 (m, PPh_3)
5a	$[Os\{{=}C{=}C(H)\overline{CCH(CH_2)_2C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−6.83 (s)	5.74 (d)	5.87 (t)	2.2	5.96 (m) [c]	1.74, 1.92, 2.76 (m, CH_2), 2.51 (s, br, $Os{=}C{=}CH$), 5.07 (m, $C{=}CH$), 6.21–7.70 (m, PPh_3)
5b	$[Os\{{=}C{=}C(H)\overline{CCH(CH_2)_3C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−7.27 (s)	5.72 (m)	5.92 (m)	—	5.88 (m) [c]	1.45, 1.56, 1.90, 2.47 (m, CH_2), 2.49 (s, br, $Os{=}C{=}CH$), 5.13 (m, $C{=}CH$), 6.78–7.46 (m, PPh_3)
5c	$[Os\{{=}C{=}C(H)\overline{CCH(CH_2)_4C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$[b]	−6.93 (s)	5.71 (d)	5.85 (t)	2.4	6.02 (m)	1.41, 1.59, 1.92, 2.33 (m, CH_2), 2.26 (s, br, $Os{=}C{=}CH$), 5.23 (t, J_{HH} = 6.5, $C{=}CH$), 6.80–7.72 (m, PPh_3)
6a	$[Os(C{\equiv}CBu^t)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[d]	2.28 (s)	4.63 (d)	5.05 (t)	2.2	6.67 (m) 6.83 (m)	1.59 (s, Bu^t), 6.97–7.81 (m, PPh_3)
6b	$[Os(C{\equiv}CH)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[d]	1.36 (s)	4.69 (d)	5.27 (t)	2.1	6.62 (m) 6.75 (m)	2.35 (s, $\equiv CH$), 6.93–7.80 (m, PPh_3)
7a	$[Os\{C{\equiv}C\overline{CCH(CH)_2)_2C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[d]	1.69 (s)	4.69 (d)	5.25 (t)	2.4	6.53 (m) 6.74 (m)	1.96 (m, CH_2), 2.61 (m, 4 H, CH_2), 5.79 (m, $=CH$), 6.93–7.80 (m, PPh_3)
7b	$[Os\{C{\equiv}C\overline{CCH(CH_2)_3C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[d]	2.15 (s)	4.67 (d)	5.19(t)	2.5	6.61 (m) 6.74 (m)	1.63, 1.74, 2.35, 2.40 (m, CH_2), 5.97 (m, $=CH$), 6.92–7.98 (m, PPh_3)
7c	$[Os\{C{\equiv}C\overline{CCH(CH_2)_4C}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$[d]	1.98 (s)	4.90 (d)	5.44 (t)	2.4	6.81 (m) 6.99 (m)	1.43–2.35, 2.60, 2.83 (m, CH_2), 6.41 (t, J_{HH} = 6.8, $=CH$), 7.17–8.04 (m, PPh_3)
8	$[Os\{{=}C{=}C(Me)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]$[b]	−4.66 (s)	5.55 (d)	6.01 (t)	2.1	5.65 (m) [c]	0.97 (s, Bu^t), 1.64 (s, CH_3), 6.54–7.90 (m, PPh_3)

[a] δ in ppm and J in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [b] Spectra recorded in $CDCl_3$. [c] Overlapped by aromatic signals. [d] Spectra recorded in C_6D_6.

(δ 1.36 to −2.28). The chemical equivalence of the phosphorus atoms in the unsymmetrically substituted vinylidene as well as in the 2-oxacycloalkylidene complexes is consistent with rapid rotation of the vinylidene or carbene group around the Os=C bond on the NMR time-scale and is in agreement with data reported for analogous ruthenium complexes.[5c]

Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra exhibit aromatic, indenyl as well as organic ligand signals in accordance with the proposed structures (see Table 1 and Experimental section). The ^1H NMR spectra of the vinylidene and carbene complexes show the $H^{1,3}$ and H^2 resonances of the indenyl ligand in the ranges δ 5.39–5.74 ($H^{1,3}$) and 5.05–6.01 (H^2) as a doublet [J(HH) = 2.1–2.5] and a triplet [J(HH) = 2.1–2.5 Hz], respectively (occasionally as two unresolved multiplets) while the $H^{1,3}$ of the alkynyl complexes appear at higher field (δ 4.63–4.90). The resonance of the vinylidene hydrogen in the monosubstituted vinylidene complexes **5a**–**5c** appears as a broad signal in the range δ 2.26–2.51 (resonances for **2a**, **2b** and **4** are not observed) in agreement with previously reported data.[11] The olefinic proton of the alkenyl-vinylidene and -alkynyl ligands appears as a triplet signal at δ 5.23 [J(HH) = 6.5 Hz] for **5c**, 6.41 [J(HH) = 6.8 Hz] for **7c** and as a multiplet in the range 5.07–5.97 for **5a**, **5b** and **7a**, **7b**.

The $^{13}C\text{-}\{^1H\}$ NMR spectra display the characteristic low-field resonances for the C_α atom of the vinylidene (δ 301.5–311.5) and carbene (256.1–261.6) groups as well as showing the signals for the $C_{\alpha,\beta}$ atoms of alkynyl complexes (see Experimental section). Indenyl carbon resonances have been also assigned and the chemical shifts can be compared with those of the ruthenium derivatives.[5c] It is interesting that the parameter $\Delta\delta(C^{3a,7a}) = \delta[C^{3a,7a}$ (indenyl complex)] $-$ $\delta[C^{3a,7a}$ (indenyl sodium)] generally used [12] as an indication of the indenyl distortion shows similar values to those of the ruthenium complexes [5c] with larger distortions found for the vinylidene and carbene complexes [-17.30 (**2a**), -17.70 (**2b**), -15.80 (**5b**), -16.60 (**5c**), -18.00 (**4**), -17.80 (**3a**) and -17.00 ppm (**3b**)].

Conclusion

The present study reports a synthetic route for preparing the first reported half-sandwich indenylosmium(II) derivative $[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ **1** which has been isolated as an air-stable solid. It has been prepared in good yield from the reaction of $[OsCl_2(PPh_3)_3]$ with indenyllithium. Complex **1** behaves like the analogous ruthenium(II) complex as a good precursor for the preparation of vinylidene and carbene derivatives by the reaction with appropriate terminal alkynes. Thus, unsubstituted $[Os]^+{=}C{=}CH_2$ and monosubstituted $[Os]^+{=}C{=}C(H)Bu^t$ vinylidene complexes have been prepared. On the other hand it reacts with cyclic alkyn-1-ols to give alkenylvinylidene complexes $[Os]^+{=}C{=}C(H)\text{-}\overline{CCHCH_2(CH_2)_nC}H_2$ **5a**–**5c**. Novel alkynyl derivatives **6a**, **6b** and **7a**–**7c** have also been prepared from the vinylidene complexes by deprotonation reactions. Complex **1** also reacts with ω-hydroxyalk-1-ynes leading to the formation of the hydroxyvinylidene complex **4** or cyclic Fischer-type carbene complexes **3a**,**3b** depending on the nature of the alkynol. Thus, cyclic carbenes **3a**,**3b** are formed through intramolecular attack of the alcohol group on the carbenic atom of the initially formed vinylidene complexes obtained from the reaction of **1** with $HC{\equiv}C(CH_2)_nCH_2OH$ (n = 1 or 2). The reaction with hex-5-yn-1-ol affords the vinylidene complex **4**. In contrast to the behaviour shown by their analogous indenylruthenium(II) derivatives, the vinylidene complexes are stable in alcohols exhibiting the typical inertness of the osmium derivatives. This behaviour is also shown by the precursor complex which undergoes substitution of PPh_3 by other phosphines in refluxing toluene [13] after longer reaction times (*ca.* 4 h) as compared with the reactivity of the analogous ruthenium complex.[2d]

Experimental

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 complex $[OsCl_2(PPh_3)_3]$ was prepared by literature methods.[14] Indene, $NaPF_6$, NH_4PF_6, $HBF_4{\cdot}OEt_2$, $MeOSO_2CF_3$, $KOBu^t$, $AgBF_4$ and all the alkynes were used as received from Aldrich Chemical Co. and Lancaster 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 microanalyser (incomplete combustion was observed for complexes **3a**, **5a** and **7a**). The NMR spectra were recorded on a Bruker AC300 instrument at 300 (^1H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) and on an AC200 instrument at 200 (^1H), 81.0 (^{31}P) or 50.3 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards.

Preparations

$[OsCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ 1. Butyllithium in hexane (0.36 cm³, 1.6 mol dm⁻³ solution) was added to a solution of indene (0.067 cm³, 0.57 mmol) in tetrahydrofuran (20 cm³) at -20 °C and the mixture stirred for 24 h. To the resulting solution was added a solution of $[OsCl_2(PPh_3)_3]$ (0.3 g, 0.29 mmol) in tetrahydrofuran (10 cm³). After stirring for 3 h the solvent was evaporated and the residue extracted with diethyl ether. The solvent was then removed *in vacuo* and the solid washed once with hexane and vacuum dried to yield complex **1** (0.152 g, 62%) as a brown solid (Found: C, 63.1; H, 4.7. $C_{45}H_{37}ClOsP_2$ requires C, 62.5; H, 4.3%). $\delta_P(C_6D_6)$ -0.61; $\delta_H(C_6D_6)$ 4.35 (2 H, m, $H^{1,3}$), 5.01 (1 H, m, H^2), 6.89 (18 H, m, Ph), 6.98 and 7.05 (2 H each, m, $H^{4,7}$ and $H^{5,6}$) and 7.45 (12 H, m, Ph); $\delta_C(C_6D_6)$ 62.1 ($C^{1,3}$), 84.8 (C^2), 110.9 ($C^{3a,7a}$), 124.8 (C_9H_7) and 126.4–139.2 (C_9H_7, Ph).

$[Os\{=C=C(H)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ 2a. A mixture of complex **1** (0.120 g, 0.19 mmol), $NaPF_6$ (0.047 g, 0.28 mmol) and $HC{\equiv}CBu^t$ (0.086 cm³, 0.69 mmol) in methanol (20 cm³) was heated under reflux for 4 h. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane. The solvent was then removed *in vacuo* and the solid washed twice with diethyl ether and vacuum dried to give complex **2a** (0.054 g, 37%) as a brown solid (Found: C, 57.9; H, 4.5. $C_{51}H_{47}F_6OsP_3$ requires C, 58.0; H, 4.5%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 839s (PF_6^-); $\delta_C(CD_2Cl_2)$ 29.0 [$C(CH_3)_3$], 33.2 (CH_3), 78.7 ($C^{1,3}$), 94.8 (C^2), 113.4 ($C^{3a,7a}$), 123.5–135.0 (C_β, C^{4-7}, Ph) and 303.6 (C_α); $\Delta\delta(C^{3a,7a}) = -17.30$.

$[Os(=C=CH_2)(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ 2b. A mixture of complex **1** (0.050 g, 0.06 mmol), NH_4PF_6 (0.018 g, 0.17 mmol) and $HC{\equiv}CSiMe_3$ (0.033 cm³, 0.23 mmol) in methanol (10 cm³) was heated under reflux for 4 h. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane. The solvent was then removed *in vacuo* and the solid washed twice with diethyl ether and vacuum dried to yield complex **2b** (0.028 g, 56%) as a brown solid (Found: C, 56.2; H, 4.0. $C_{47}H_{39}F_6OsP_3$ requires C, 56.4; H, 3.9%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 838s (PF_6^-); $\delta_C(CD_2Cl_2)$ 80.1 ($C^{1,3}$), 94.7 (C^2), 95.3 (C_β), 113.0 ($C^{3a,7a}$), 123.0–134.5 (C^{4-7}, Ph) and 301.5 [t, J(CP) = 10.4 Hz, C_α]; $\Delta\delta(C^{3a,7a}) = -17.70$.

$[Os\{=\overline{COCH_2(CH_2)_nC}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (n = 1 3a or 2 3b). A mixture of complex **1** (0.110 g, 0.18 mmol), $NaPF_6$ (0.085 g, 0.51 mmol) and $HC{\equiv}C(CH_2)_nCH_2OH$ (0.635 mmol) in methanol (10 cm³) was heated under reflux for 4 h. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane. The solvent was then removed *in vacuo* and the solid washed twice with diethyl ether and vacuum dried to give complexes **3a** and **3b** as brown solids.

Complex **3a**: yield 57% (Found: C, 55.6; H, 4.6. $C_{49}H_{43}F_6OOsP_3$ requires C, 56.3; H, 4.2%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 839s (PF_6^-); $\delta_C(CD_2Cl_2)$ 23.9 and 59.1 (CH_2), 74.1 ($C^{1,3}$), 80.1 (OCH_2), 96.5 (C^2), 112.9 ($C^{3a,7a}$), 123.6–136.0 (C^{4-7}, Ph), 256.1 [t, J(CP) 8.9 Hz, C_α]; $\Delta\delta(C^{3a,7a}) = -17.80$. Complex **3b**: yield 94% (Found: C, 56.9; H, 4.4. $C_{50}H_{45}F_6OOsP_3$ requires C, 56.7; H, 4.3%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 840s (PF_6^-); $\delta_C(CDCl_3)$ 15.9, 19.7 and 58.0 (CH_2), 72.1 (OCH_2), 74.3 ($C^{1,3}$), 96.2 (C^2), 113.7 ($C^{3a,7a}$), 123.5–136.2 (C^{4-7}, Ph) and 261.6 [t, J(CP) 9.5 Hz, C_α]; $\Delta\delta(C^{3a,7a}) = -17.00$.

$[Os\{=C=C(H)(CH_2)_3CH_2OH\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ 4. A mixture of complex **1** (0.040 g, 0.05 mmol), $NaPF_6$ (0.031 g, 0.18 mmol) and hex-5-yn-1-ol (0.23 mmol) in methanol (5 cm³) was heated under reflux for 4 h. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane. The solvent was then removed *in vacuo* and the solid washed twice with diethyl ether and vacuum dried to give complex **4** (0.019 g, 39%) as a brown solid (Found: C, 57.6; H, 5.0. $C_{51}H_{47}F_6OOsP_3$ requires C, 57.1; H, 4.4%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 839s (PF_6^-); $\delta_C(CDCl_3)$ 17.7, 29.0 and 32.1 (CH_2), 62.4 (CH_2OH), 79.2 ($C^{1,3}$), 94.9 (C^2), 110.5 (C_β), 112.7 ($C^{3a,7a}$), 122.9–134.7 (C^{4-7}, Ph) and 302.7 [t, J(CP) 10.9 Hz, C_α]; $\Delta\delta(C^{3a,7a}) = -18.00$.

$[Os\{=C=C(H)\overline{CCHCH_2(CH_2)_nC}H_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][PF_6]$ (n = 1 5a, 2 5b or 3 5c). A mixture of complex **1** (0.150 g, 0.17 mmol), $NaPF_6$ (0.058 g, 0.35 mmol) and $HC{\equiv}C\text{-}C(OH)CH_2(CH_2)_nCH_2CH_2$ (0.150 mmol) in methanol (35 cm^3) was heated under reflux for 4 h. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane. The solvent was then removed *in vacuo* and the solid washed twice with diethyl ether and vacuum dried to give complexes **5a**–**5c** as brown solids.

Complex **5a**: yield 74% (Found: C, 57.6; H, 4.4. $C_{52}H_{45}F_6OsP_3$ requires C, 58.5; H, 4.3%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 840s (PF_6^-); $\delta_C(CD_2Cl_2)$ 24.2, 31.8 and 35.7 (CH_2), 79.2 [t, *J*(CP) 3.1, $C^{1,3}$], 94.9 (C^2), 113.4–135.0 (C_β, =CH, $C^{3a,7a}$, C^{4-7}, Ph) and 310.3 [t, *J*(CP) 10.4 Hz, C_α]. Complex **5b**: yield 75% (Found: C, 59.1; H, 4.8. $C_{53}H_{47}F_6OsP_3$ requires C, 58.9; H, 4.4%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 838s (PF_6^-); $\delta_C(CDCl_3)$ 22.8, 23.3, 25.1 and 25.9 (CH_2), 79.0 ($C^{1,3}$), 95.5 (C^2), 114.9 ($C^{3a,7a}$), 123.9–135.2 (=CH, Ph, C^{4-7}) and 299.0 [t, *J*(CP) 9.3 Hz, C_α]; $\Delta\delta(C^{3a,7a}) = -15.80$. Complex **5c**: yield 75% (Found: C, 59.2; H, 4.6. $C_{54}H_{49}F_6OsP_3$ requires C, 59.2; H, 4.5%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 839s (PF_6^-); $\delta_C(CD_2Cl_2)$ 26.5, 28.2, 28.3, 32.4 and 34.6 (CH_2), 79.2 ($C^{1,3}$), 94.9 (C^2), 114.1 ($C^{3a,7a}$), 121.5 (C_β), 123.5 (C_9H_7), 127.5–135.1 (C_9H_7, Ph, =CH) and 311.5 [t, *J*(CP) 10.7 Hz, C_α]; $\Delta\delta(C^{3a,7a}) = -16.60$.

Alkynyl complexes $[Os(C{\equiv}CR)(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (R = Bu^t 6a or H 6b). A solution of complex **2a** or **2b** (0.07 mmol) and KOBu^t (0.07 mmol) was stirred in tetrahydrofuran (15 cm^3) for 1 h. The solvent was then evaporated and the solid residue extracted with diethyl ether. Evaporation of the solvent gave quantitatively the complexes **6a** and **6b**.

Complex **6a**: $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2091 (C≡C). Complex **6b** (Found: C, 65.8; H, 4.7. $C_{47}H_{38}OsP_2$ requires C, 66.0; H, 4.5%): $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1954 (C≡C); $\delta_C(C_6D_6)$ 74.1 ($C^{1,3}$), 95.0 (C^2), 99.1 (C_β), 112.3 ($C^{3a,7a}$) and 128.0–144.1 (C_α, C^{4-7}, Ph); $\Delta\delta(C^{3a,7a}) = -18.4$.

$[Os\{C{\equiv}CCCHCH_2(CH_2)_nCH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ (*n* = 1 7a, 2 7b or 3 7c). A solution of complexes **5a**–**5c** (0.08 mmol) and KOBu^t (0.08 mmol) in tetrahydrofuran (5 cm^3) was stirred for 45 min. The solvent was then evaporated at reduced pressure and the residue extracted with diethyl ether. The evaporation of the solvent gave complexes **7a**–**7c** as brown solids.

Complex **7a**: yield 65% (Found: C, 65.8; H, 5.1. $C_{52}H_{44}OsP_2$ requires C, 67.8; H, 4.8%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2067 (C≡C); $\delta_C(CD_2Cl_2)$ 23.8, 32.6 and 38.5 (CH_2), 69.4 ($C^{1,3}$), 90.0 (C^2), 106.6 ($C^{3a,7a}$) and 123.3–139.4 (C_α, C_β, =C, =CH, C^{4-7}, Ph); $\Delta\delta(C^{3a,7a}) = -24.12$. Complex **7b**: yield 57%; $\tilde{\nu}_{max}$/cm^{-1}(KBr) 2066 (C≡C). Complex **7c**: yield 39%; $\tilde{\nu}_{max}$/cm^{-1}(KBr) 2064 (C≡C); $\delta_C(CD_2Cl_2)$ 27.3, 28.5, 29.0, 33.4 and 37.0 (CH_2), 69.3 ($C^{1,3}$), 89.6 (C^2), 106.6 ($C^{3a,7a}$), 113.5–139.2 (C_α, C_β, =C, =CH, C^{4-7}, Ph); $\Delta\delta(C^{3a,7a}) = -24.10$.

$[Os\{{=}C{=}C(Me)Bu^t\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][CF_3SO_3]$ 8. The compound $MeOSO_2CF_3$ in diethyl ether was added to a solution of **6a** (63 mg, 0.07 mmol) in diethyl ether (5 cm^3) until no further precipitation was observed. The resulting suspension was stirred for 30 min and evaporated to dryness. The solid residue was extracted with dichloromethane, the extract was concentrated *in vacuo* and the solid washed once with diethyl ether and vacuum dried to give 38 mg (51% yield) of complex **8** as a brown solid (Found: C, 59.1; H, 4.7. $C_{53}H_{49}F_3O_3OsP_2S$ requires C, 59.2; H, 4.6%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1265s (br), 1223s and 1149s ($CF_3SO_3^-$); $\delta_C(CD_2Cl_2)$ 4.2 (CH_3), 27.9 [*C*(CH_3)$_3$], 30.7 [(CH_3)$_3$], 75.6 ($C^{1,3}$), 95.2 (C^2), 114.8 ($C^{3a,7a}$) and 123.5–134.3 (C_β, C^{4-7}, Ph); $\Delta\delta(C^{3a,7a}) = -15.90$.

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