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Synthesis, molecular structure, and reactivity of allenylideneosmium complexes of the half-sandwich-type

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The reaction of the areneosmium(II) compunds $[Os(\eta^6\text{-arene})(L)X_2]$ **2a**–**2e**, **3**, **4** with propargylic alcohols $HC{\equiv}CCR_2(OH)$ (where R = phenyl or *p*-tolyl) in the presence of $AgPF_6$ leads to the formation of the cationic osmium allenylidenes $[Os(\eta^6\text{-arene})(=C=C=CR_2)(L)X]PF_6$ **5a**–**5h** in good to excellent yields. Salt metathesis of **5a** (L = PMe_3) and **5b** (L = PCy_3) with $NaB(Ar_F)_4$ gives $[Os(\eta^6\text{-mes})(=C=C=CPh_2)(PR_3)Cl]B(Ar_F)_4$ **6a**, **6b** while treatment of **5b** with KBr, NaI and CF_3CO_2Ag affords the corresponding bromo, iodo and trifluoracetato complexes $[Os(\eta^6\text{-mes})(=C=C=CPh_2)(PCy_3)X]PF_6$ **7a**–**7c**. Compound **5a** reacts with MeOH and EtOH to give the Fischer-type osmium carbenes $[Os(\eta^6\text{-mes})\{=C(OR)CH=CPh_2\}(PMe_3)Cl]PF_6$ **8a** and **8b**, of which **8a** has been converted by treatment with NaH to the neutral allenyl complex $[Os(\eta^6\text{-mes})\{C(OMe)=C=CPh_2\}(PMe_3)Cl]$ **9**. The reaction of **5a** and **5b** with tertiary phosphines PR′$_3$ yields a mixture of $[Os(\eta^6\text{-mes})\{C(PR'_3)=C=CPh_2\}(PR_3)Cl]PF_6$ **10a**–**10c** and $[Os(\eta^6\text{-mes})(PR_3)(PR'_3)Cl]PF_6$ **11a**–**11c**, which could not be separated by analytical tools. The cationic bis(phosphine) compounds **11a**–**11c** were prepared independently from **2a**–**2c** and PMe_3 in the presence of NH_4PF_6. The molecular structures of **5a** and **8b** were determined crystallographically.

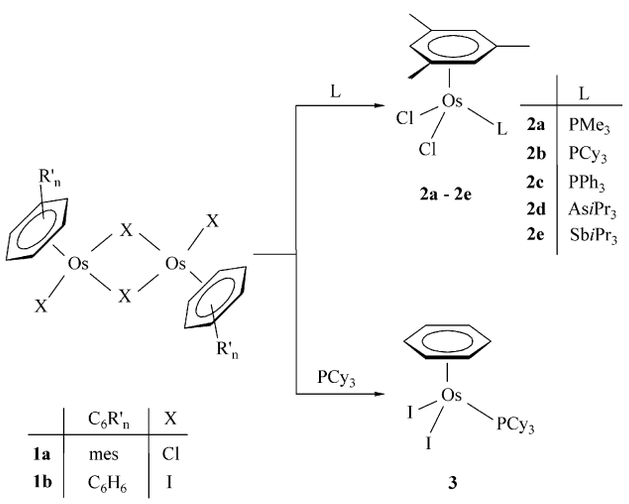
Recently, we reported that the carbeneosmium(II) complexes $[Os(\eta^6\text{-mes})(=CR_2)(\kappa^1\text{-}O_2CCF_3)_2]$ can be prepared from $[Os(\eta^6\text{-mes})(\kappa^1\text{-}O_2CCF_3)(\kappa^2\text{-}O_2CCF_3)]$ (mes = mesitylene; 1,3,5-trimethylbenzene) and diaryldiazomethanes.[1] These half-sandwich-type compounds react with Me_3SiCl to give the corresponding dichloro derivatives $[Os(\eta^6\text{-mes})(=CR_2)Cl_2]$ which upon treatment with PPh_3 in the presence of $AgPF_6$ afford the cationic osmium carbenes $[Os(\eta^6\text{-mes})(=CR_2)(PPh_3)Cl]PF_6$ in nearly quantitative yields.[1] In the context of these studies, we were interested to find out whether unsaturated carbenes such as allenylidenes could also be coordinated to an $[Os(\eta^6\text{-arene})(PR'_3)X]^+$ fragment thus completing the series of compounds of the general composition $[Os(\eta^6\text{-arene})\{=(C=)_nCR_2\}(PR'_3)X]^+$ with n = 0,[1] 1,[2] and 2. We note that the ruthenium analogues of the hitherto unknown allenylideneosmium(II) cations were recently prepared by the groups of Dixneuf and Fürstner and proved to be excellent catalysts for ring closing olefin metathesis.[3]

In the present article we describe the synthesis of a series of allenylideneosmium(II) compounds $[Os(\eta^6\text{-arene})(=C=C=CR_2)(L)X]PF_6$, including As*i*Pr$_3$ and Sb*i*Pr$_3$ as spectator ligand L, and show that the Os=C=C=CR$_2$ moiety of these cations behaves as a centre of electrophilicity.

Results and discussion

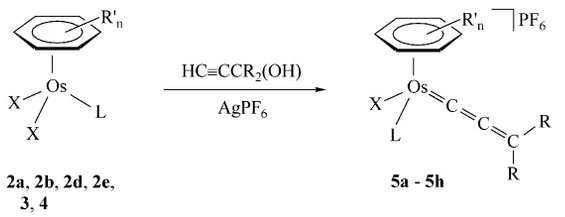
Preparation and molecular structure of allenylideneosmium(II) cations

The chloro bridges of the starting material **1a**[4,5] can be split not only by tertiary phosphines such as PMe_3, PPh_3 and PCy_3[6] but also by As*i*Pr$_3$ and Sb*i*Pr$_3$ to give the mononuclear products **2d** and **2e** in more than 90% isolated yield (Scheme 1). The benzene analogue **1b**[7] behaves similarly to **1a** and affords compound **3** upon treatment with PCy_3 in CH_2Cl_2. Both **2d** and **2e** as well as **3** are yellow to orange solids that are moderately air-stable and readily soluble in polar organic solvents such as chloroform or dichloromethane.



Scheme 1 (For the preparation of **2a**–**2c** see ref. 6.)

For the preparation of the cationic allenylidene complexes **5a**–**5h**, we followed the methodology developed by Selegue[8,9] using propargylic alcohols to generate the cumulated C_3 ligands in the coordination sphere of areneosmium(II). In order to avoid side-reactions, such as the formation of vinylvinylidene ligands from $HC{\equiv}CCMe_2(OH)$ or $HC{\equiv}CC(Me)Ph(OH)$,[10] we restricted our efforts to propargylic alcohols $HC{\equiv}CCR_2(OH)$ with R = aryl. As shown in Scheme 2, the reactions of the neutral mononuclear compounds **2a**–**e**, **3** and **4** with $HC{\equiv}CCPh_2(OH)$ or $HC{\equiv}CC(p\text{-tol})_2(OH)$ (*p*-tol = C_6H_4Me-*p*) in the molar ratio of 1 : 1 in THF, in the presence of one equiv. of $AgPF_6$, gave the target molecules **5a**–**5h** in good to excellent yields. These cationic osmium(II) allenylidenes are violet solids which (with the exception of **5e**) are thermally quite stable and for short periods of time can be handled in air. The conductivity of **5a**–**5h** in nitromethane corresponds to that of 1 : 1 electrolytes. Typical spectroscopic features of **5a**–**5h** are the strong C=C=C stretching mode at around 1940 to 1960 cm^{-1} in the IR



2a, **2b**, **2d**, **2e**, **3**, **4** — **5a - 5h**

4: [(*p*-cym)$OsCl_2(PCy_3)$]

	$C_6R'_n$	X	L	R
5a	mes	Cl	PMe_3	Ph
5b	mes	Cl	PCy_3	Ph
5c	mes	Cl	PPh_3	Ph
5d	mes	Cl	PCy_3	*p*-tol
5e	mes	Cl	As*i*Pr_3	Ph
5f	mes	Cl	Sb*i*Pr_3	Ph
5g	C_6H_6	I	PCy_3	Ph
5h	*p*-cym	Cl	PCy_3	Ph

Scheme 2

and the three low-field resonances for the allenylidene carbon atoms in the ^{13}C NMR spectra. Since both in the ^{1}H and ^{13}C NMR spectra of the complexes containing C=C=CPh_2 as the ligand only one set of signals for the hydrogen and carbon atoms of the phenyl substituents is observed, we assume that the barrier for rotation around the Os–C bond is relatively small on the NMR time scale. We note that our attempts to prepare stable salts of the cations $[Os(\eta^6\text{-mes})(=C=C=CPh_2)(L)Cl]^+$ with L = CO and CNMe failed which we explain with the labilising effect of the π-acidic allenylidene ligand upon the Os–CO and Os–CNMe bond in these cationic species.[11]

The result of the X-ray crystal structure analysis of **5a** is shown in Fig. 1. The ORTEP plot illustrates the somewhat distorted piano-stool configuration of the cation with two bond angles [Cl–Os–P(1) and C(1)–Os–P(1)] that are smaller and one bond angle [C(1)–Os–Cl] that is larger than the ideal value of 90° (see Table 1). The Os–C(1)–C(2)–C(3) axis is nearly linear with a small bending at the α-carbon atom C(1). The Os–C(1) bond length of 1.90(1) Å is almost identical to that in $[Os(\eta^5\text{-}C_9H_7)(=C=C=CPh_2)(PPh_3)_2]^+$ [1.895(4) Å][12] and $[Ru(\eta^6\text{-}p\text{-cymene})(=C=C=CPh_2)(P{i}Pr_3)Cl]^+$ [1.894(3) Å],[3] and it is only slightly longer than in the neutral compound $[Os(\eta^5\text{-}C_5H_5)(=C=C=CPh_2)(P{i}Pr_3)Cl]$ [1.875(6) Å].[13] The two carbon–carbon

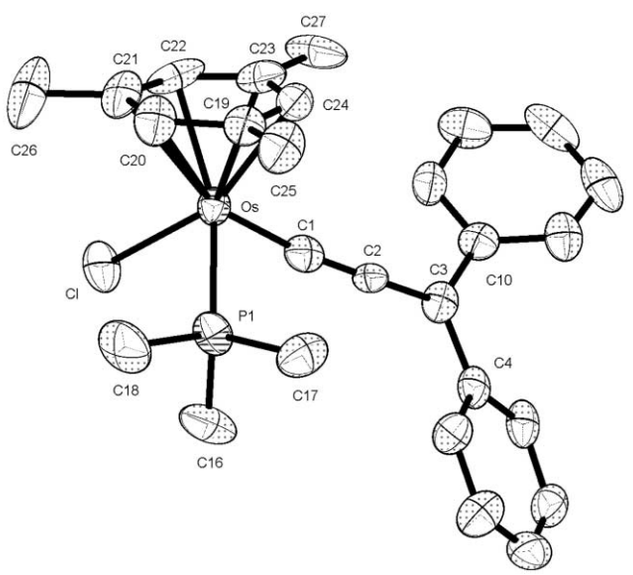


Fig. 1 An ORTEP plot of compound **5a**.[25]

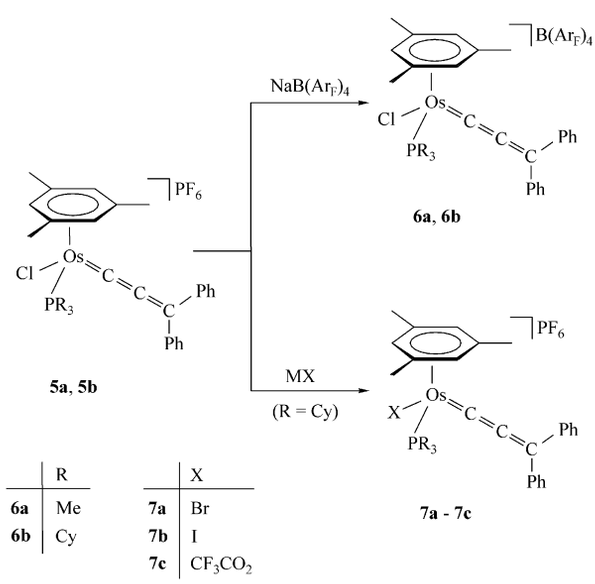
Table 1 Selected bond lengths (Å) and angles (°) for compound **5a**

Os–C(1)	1.90(1)	Os–C(22)	2.28(1)
Os–P(1)	2.318(3)	Os–C(23)	2.27(1)
Os–Cl	2.382(3)	Os–C(24)	2.22(1)
Os–C(19)	2.26(1)	C(1)–C(2)	1.27(1)
Os–C(20)	2.32(1)	C(2)–C(3)	1.37(1)
Os–C(21)	2.35(1)		
C(1)–Os–P(1)	84.4(3)	Os–C(1)–C(2)	172.5(9)
C(1)–Os–Cl	98.3(3)	C(1)–C(2)–C(3)	177(1)
Cl–Os–P(1)	83.4(1)	C(4)–C(3)–C(10)	121.2(9)

distances in the Os=C=C=C chain of 1.27(1) Å [C(1)–C(2)] and 1.37(1) Å [C(2)–C(3)] are quite similar to those in the above-mentioned η^5-cyclopentadienyl [1.222(9) and 1.344(9) Å][13] and η^5-indenyl osmium(II) complexes [1.265(6) and 1.349(7) Å][12] which indicates that besides the usual bonding description Os=C=C=C a second zwitterionic resonance structure has to be taken into consideration.[9] A view along the Os–C(3) axis reveals that the bonds Os–P(1) and C(3)–C(4) are eclipsed which is in contrast to the structure of the cationic ruthenium allenylidenes $[Ru(\eta^6\text{-}p\text{-cymene})(=C=C=CPh_2)(P{i}Pr_3)Cl]^+$ and $[Ru(\eta^6\text{-}C_6H_5(CH_2)_3PCy_2\text{-}\kappa\text{-}P)(=C=C=CPh_2)Cl]^+$ where the bonds Ru–Cl (not Ru–P) and C(3)–C(4) form a nearly eclipsed configuration.[3]

Reactions of the allenylideneosmium(II) cations with nucleophiles

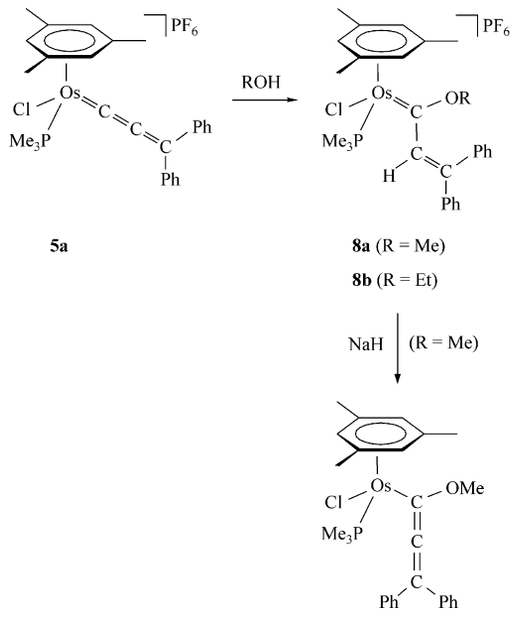
The diphenylallenylidene complex **5b** does not only react with $NaB(Ar_F)_4$ by exchange of the anion to afford **6b** (for the analogous preparation of **6a** see Scheme 3) but also with KBr,



Scheme 3

NaI and CF_3CO_2Ag in acetone or dichloromethane at room temperature to give the corresponding bromo, iodo and trifluoracetato derivatives **7a**–**7c** in about 80–90% yield. For the preparation of **7a** and **7b** it is necessary to use an eight- to ten-fold excess of KBr and NaI because otherwise the substitution takes an extremely long period of time. The products **7a**–**7c** are red or violet solids which are moderately air-sensitive and readily soluble in common polar organic solvents. The IR and NMR spectra of **7a** and **7b** differ only slightly from those of the precursors **6a** and **6b** indicating that the halide ligand of the cations $[Os(\eta^6\text{-mes})(=C=C=CPh_2)(PCy_3)X]^+$ has a marginal influence on the bonding between the metal centre and the allenylidene unit. The IR spectrum of **7c** displays two bands at 1448 and 1712 cm^{-1} for the symmetrical and the unsymmetrical OCO stretching vibrations which is in agreement with the monodentate coordination of the CF_3CO_2 unit.[14]

Similarly to the vinylideneosmium compounds $[Os(\eta^6\text{-}C_6H_6)(=C=CHR')(PMe^tBu_2)I]PF_6$,[2] the related cationic allenylidene complex **5a** also reacts with ROH (R = Me, Et) at room temperature *via* addition of the alcohol at the $C_\alpha=C_\beta$ bond of the C_3 unit (Scheme 4). After chromatographic work-up, the Fischer-



5a **8a** (R = Me) **8b** (R = Et) **9**

Scheme 4

type carbenes $[Os(\eta^6\text{-mes})\{=C(OR)CH=CPh_2\}(PMe_3)Cl]PF_6$ **8a** and **8b** are isolated as orange-red solids in about 70% yield. Noteworthy spectroscopic data of the carbene complexes are the signal for the vinylic CH proton at δ 6.71 (**8a**) and 6.86 (**8b**) in the ^{1}H NMR and the low-field resonance for the carbene carbon atom at δ 276.6 (**8a**) and 276.4 (**8b**) in the ^{13}C NMR spectra. The chemical shift of the latter is nearly identical to that of the signal for the Os=C carbons in the compounds $[Os(\eta^6\text{-}C_6H_6)\{=C(OR)CH_2R'\}(PMe^tBu_2)I]PF_6$, which were generated from the above-mentioned vinylidene derivatives and ROH.[2]

To confirm the molecular structure of the osmium carbenes, an X-ray crystal structure analysis of **8b** has been carried out. As shown in Fig. 2, the cation possesses, in analogy to **5a**, a

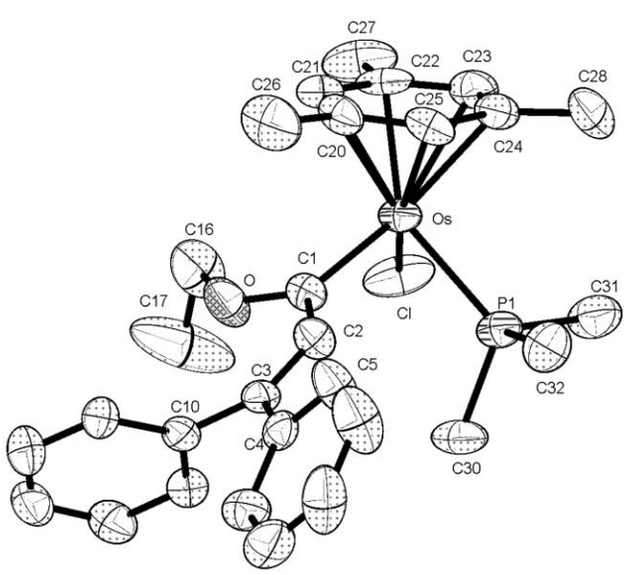


Fig. 2 An ORTEP plot of compound **8b**.

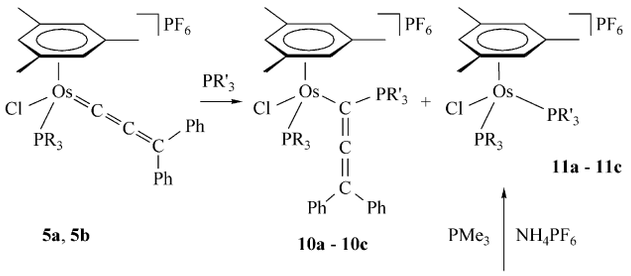
Table 2 Selected bond lengths (Å) and angles (°) for compound **8b**

Os–C(1)	1.985(6)	Os–C(23)	2.315(6)
Os–P(1)	2.344(2)	Os–C(24)	2.295(6)
Os–Cl	2.406(2)	Os–C(25)	2.207(7)
Os–C(20)	2.238(6)	C(1)–O	1.315(7)
Os–C(21)	2.262(6)	C(1)–C(2)	1.469(8)
Os–C(22)	2.287(6)	C(2)–C(3)	1.358(8)
C(1)–Os–P(1)	89.0(2)	O–C(1)–C(2)	109.6(5)
C(1)–Os–Cl	95.2(2)	C(1)–C(2)–C(3)	130.8(6)
Cl–Os–P(1)	80.66(7)	C(2)–C(3)–C(4)	121.1(6)
Os–C(1)–C(2)	121.9(5)	C(2)–C(3)–C(10)	123.3(6)
Os–C(1)–O	127.9(5)	C(1)–O–C(16)	123.8(6)

piano-stool configuration with metal-centred bond angles of 80.66(7)° [Cl–Os–P(1)], 89.0(2)° [C(1)–Os–P(1)] and 95.2(2)° [C(1)–Os–Cl]. The coordination around the carbene carbon atom C(1) is strictly planar, the sum of the respective bond angles being almost exactly 360° (Table 2). The C(1)–O distance of 1.315(7) Å is shorter than that anticipated for a carbon–oxygen single bond which is in agreement with the general bonding scheme for Fischer-type carbene complexes.[15] While the Os–C(1) bond length [1.985(6) Å] is nearly identical to that in the corresponding ruthenium compound $[Ru(\eta^6\text{-}C_6Me_6)\{=C(OMe)CH=CPh_2\}(PMe_3)Cl]PF_6$ [1.98(1) Å],[16] it is slightly longer than in the osmium carbene $[Os(\eta^6\text{-}C_6H_6)\{=C(CH_2)_3O\}(PMe^tBu_2)I]PF_6$ [1.953(2) Å],[2] probably due to the electron delocalization in the Os=C–C=C fragment. Since the two planes [Os,C(1),O,C(2)] and [C(3),C(4),C(5)] are nearly co-planar [the corresponding dihedral angle being 14.1(7)°], we conclude that at least one phenyl group is also part of the delocalized π-electron system. The distances between the metal centre and the carbon atoms of the mesitylene ring are somewhat shorter than in **5a** and in the Schrock-type alkylidene complex $[Os(\eta^6\text{-mes})\{=C(p\text{-}C_6H_4Me)_2\}(PPh_3)Cl]PF_6$.[1] The longest Os–$C_{mes}$ bond lengths [Os–C(23) and Os–C(24)] are found *trans* to C(1) and the shortest [Os–C(20) and Os–C(25)] *trans* to chloride, both data reflecting the *trans* influence of the respective ligands.

Since the mechanistic scheme for the formation of cationic alkoxy(vinyl)carbene-metal compounds from allenylidene-metal precursors and alcohols involves a short-lived M–C(OR)=C=CR_2 species as an intermediate,[9] we attempted to generate such a neutral allenyl complex by deprotonation of **8a** (see Scheme 4). Treatment of **8a** in THF with NaH results in a change of colour from red to yellow and gives, after removal of the solvent and recrystallization of the residue from benzene–hexane, a yellow solid which is extremely air-sensitive. Although owing to the lability of the compound no correct elemental analysis could be obtained, the ^{1}H NMR spectrum leaves no doubt that the alkoxy-substituted allenyl complex **9** is formed. Characteristic data supporting the proposed structure of **9** are the singlet resonance for the OCH_3 protons at δ 3.55 (which is shifted up-field by *ca.* 0.8 ppm compared to **8a**) and the doublet for the trimethylphosphine protons at δ 1.50. The ^{31}P NMR spectrum of **9** displays a signal at δ −38.7 which also appears at higher field compared to **8a**.

The results about the reactivity of the osmium allenylidenes **5a** and **5b** toward PMe_3 and PPh_3 are summarized in Scheme 5. Prior to our work it was already known that tertiary phosphines react with cationic allenylideneruthenium compounds either by attack at the α-carbon or the γ-carbon atom of the M=C=C=C chain.[17,18] We have found that addition of PMe_3 or PPh_3 to a solution of **5a** or **5b** in dichloromethane at −78 °C results in a quick change of colour from violet to brown and gives, after partial removal of the solvent and precipitation of the product with hexane, a light brown solid which in each case consists of a mixture of the phosphine-adduct **10a**,**b**,**c** and the cationic bis(phosphine) complex **11a**,**b**,**c**. The ratio of the two compounds (determined by ^{1}H NMR spectroscopy) is 4 : 1 for **10a/11a**, 6 : 1 for **10b/11b** and 5 : 1 for **10c/11c**. All attempts, by



	R	R'
10a, **11a**	Me	Me
10b, **11b**	Me	Ph
10c, **11c**	Cy	Me

Scheme 5

changing the reaction conditions, to form selectively the allenylphosphonium complexes **10a**,**b**,**c** did not succeed. Moreover, we failed to separate the two products by fractional crystallization or chromatographic techniques and could thus characterize **10a**, **10b** and **10c** only by IR and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Typical spectroscopic features, *e.g.* of the ^{13}C NMR spectrum of **10a**, are the doublet-of-doublet resonance for the metal-bound α-carbon atom at δ 70.2, the doublet resonance for the β-carbon atom at δ 209.5, and the singlet for the γ-carbon atom at δ 93.5. Similar data have been reported by Esteruelas *et al.* for the ruthenium compound [Ru(η^5-C_5H_5)-{C(PMe$_3$)=C=CPh$_2$}(CO)(P*i*Pr$_3$)]PF$_6$.[18] When we monitored the reactions of **5a** and **5b** with PMe$_3$ and PPh$_3$ in an NMR tube, we observed in no case the formation of a labile 1 : 1 adduct with the phosphine linked to the γ-carbon atom of the OsC_3 chain. By taking the relatively low nucleophilicity of PPh$_3$ into consideration, we conclude from this observation that the Os=C moiety is a centre of high electrophilicity.

The cationic bis(phosphine) complexes **11a**,**b**,**c**, generated as minor components upon treatment of **5a** and **5b** with PMe$_3$ and PPh$_3$, have been prepared on an independent route from **2a**, **2b** or **2c** and PMe$_3$ in the presence of NH_4PF_6 (see Scheme 5). In agreement with previous work from our laboratory concerning the synthesis of [Os(η^6-C_6H_6)(PMe$_3$)(PR$_3$)I]PF$_6$ [PR$_3$ = PMe$_2$Ph, PPh$_3$, P(OMe)$_3$],[19] it is preferable to use for the preparation of **11b** and **11c** instead of **2a** and PCy$_3$ or PPh$_3$ a mixture of **2b** or **2c** and PMe$_3$ as starting materials because otherwise no clean substitution occurs. Compounds **11a**,**b**,**c** are yellow air-stable solids which in nitromethane show the conductivity of 1 : 1 electrolytes. The ^{31}P NMR spectra of **11b** and **11c** display besides the signal for the PF_6^- anion two doublets, the chemical shift and ^{31}P–^{31}P coupling constants of which are similar to those of the above-mentioned benzene(iodo)osmium cations.[19]

In conclusion, the present investigations have shown that the osmium complexes **5a**–**5h** are easily accessible from the dichloro- or diiodo-metal precursors **2a**, **2b**, **2d**, **2e**, **3** or **4** and propargylic alcohols in the presence of $AgPF_6$ in THF. Although the structure of these half-sandwich-type compounds is strongly related to those of the ruthenium counterparts,[3] the osmium allenylidenes are catalytically inactive in olefin metathesis, even in ROMP of cyclooctene. These observations thus confirm the experience that in general, in the same row of the periodic table, the catalytic activity of compounds with a 4d element is significantly higher than that of analogous compounds with a 5d element as metal centre.[20]

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1a**,[4,5] **1b**,[7] **2a**–**c**,[6] **4**[21] and NaB(Ar$_F$)$_4$[22] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200, Bruker DRX 300 and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR spectrometer. Melting points were measured by DTA. The conductivity Λ was determined in nitromethane. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broadened signal; v, virtual coupling; coupling constants *J* and *N* in Hz.

Preparations

[Os(η^6-mes)(As*i*Pr$_3$)Cl$_2$] 2d. A suspension of compound **1a** (128 mg, 0.17 mmol) in benzene (10 cm^3) was treated with As*i*Pr$_3$ (102 mg, 0.50 mmol) and stirred for 3 h at room temperature. The reaction mixture was passed through a column filled with Celite (height of column 5 cm) and the filtrate was evaporated to dryness *in vacuo*. The residue was recrystallized from CH_2Cl_2–hexane to give a yellow microcrystalline solid which was separated from the mother liquor, washed with hexane (5 cm^3) and dried: yield 181 mg (91%); mp 145 °C (decomp.) (Found: C, 36.83; H, 5.56. $C_{18}H_{33}AsCl_2Os$ requires C, 36.92; H 5.68%). NMR ($CDCl_3$): δ_H (400 MHz) 5.45 (3 H, s, C_6H_3), 2.79 [3 H, sept, *J*(H,H) 7.3, AsC*H*CH$_3$], 2.24 (9 H, s, CH$_3$ of mes), 1.34 [18 H, d, *J*(H,H) 7.3, AsCHC*H*$_3$]; δ_C (100.6 MHz), 90.7 (s, *C*CH$_3$ of mes), 74.8 (s, CH of mes), 25.8 (s, As*C*HCH$_3$), 21.0 (s, AsCH*C*H$_3$), 18.8 (s, CH$_3$ of mes).

[Os(η^6-mes)(Sb*i*Pr$_3$)Cl$_2$] 2e. This compound was prepared as described for **2d** from **1a** (109 mg, 0.14 mmol) and Sb*i*Pr$_3$ (72 μL, 0.35 mmol) in benzene (10 cm^3). Light brown solid: yield 163 mg (92%), mp 126 °C (decomp.) (Found: C, 34.37; H, 5.31. $C_{18}H_{33}Cl_2OsSb$ requires C, 34.19; H, 5.26%). NMR ($CDCl_3$): δ_H (400 MHz) 5.74 (3 H, s, C_6H_3), 2.61 [3 H, sept, *J*(H,H) 7.6, SbC*H*CH$_3$], 2.27 (9 H, s, CH$_3$ of mes), 1.43 [18 H, d, *J*(H,H) 7.6, SbCHC*H*$_3$]; δ_C (100.6 MHz) 90.7 (s, *C*CH$_3$ of mes), 83.5 (s, CH of mes), 21.9 (s, SbCH*C*H$_3$), 19.4 (s, Sb*C*HCH$_3$), 18.5 (s, CH$_3$ of mes).

[Os(η^6-C_6H_6)(PCy$_3$)I$_2$] 3. This compound was prepared as described for **2d** from **1b** (418 mg, 0.40 mmol) and PCy$_3$ (280 mg, 1.00 mmol) in CH_2Cl_2 (20 cm^3). Orange solid: yield 494 mg (77%); mp 163 °C (Found: C, 35.76, H, 4.91. $C_{24}H_{39}I_2OsP$ requires C, 35.92; H, 4.90%). NMR ($CDCl_3$): δ_H (400 MHz) 5.99 (6 H, s, C_6H_6), 2.71–2.64, 2.19–2.14, 1.81–1.66, 1.42–1.18 (33 H, all m, C_6H_{11}); δ_C (100.6 MHz) 80.2 (s, C_6H_6), 39.3 [d, *J*(P,C) 25.4, C1 of C_6H_{11}], 30.7 [d, *J*(P,C) 3.0, C3,5 of C_6H_{11}], 27.3 [d, *J*(P,C) 10.2, C2,6 of C_6H_{11}], 26.4 (s, C4 of C_6H_{11}); δ_P (162.0 MHz) −23.3 (s).

[Os(η^6-mes)(=C=C=CPh$_2$)(PMe$_3$)Cl]PF$_6$ 5a. A solution of **2a** (787 mg, 1.73 mmol) and HC≡CCPh$_2$(OH) (394 mg, 1.89 mmol) in THF (15 cm^3) was treated slowly with a solution of $AgPF_6$ (434 mg, 1.72 mmol) in THF (5 cm^3) and stirred for 45 min at room temperature. A change of colour from orange to deep violet occurred. The reaction mixture was filtered, the filtrate was evaporated to dryness *in vacuo*, and the oily residue was dissolved in CH_2Cl_2 (10 cm^3). The solution was passed through a column filled with Celite (height of column 10 cm) and the filtrate was concentrated to *ca.* 2 cm^3 *in vacuo*. Upon addition of hexane (15 cm^3) a violet solid precipitated, the crystallization of which was completed by irradiating the mixture in an ultrasound bath for 5 min. The mother liquor was decanted, the violet solid was washed with hexane (2 × 5 cm^3) and dried: yield 1.107 g (85%); mp 114 °C (decomp.) (Found: C, 42.68; H, 3.98. $C_{27}H_{31}ClF_6OsP_2$ requires C, 42.83; H, 4.13%). Λ 75 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C=C) 1943 cm^{-1}. NMR (CD_3NO_2): δ_H (200 MHz) 7.98 (4 H, m, *ortho*-H of C_6H_5), 7.88 (2 H, m, *para*-H of C_6H_5), 7.46 (4 H, m, *meta*-H of C_6H_5), 6.00 (3 H, s, C_6H_3), 2.43 (9 H, s, CH$_3$ of mes), 1.79 [9 H, d, *J*(P,H) 11.4, PMe$_3$]; δ_C (100.6 MHz) 252.3 [d, *J*(P,C) 19.4, Os=*C*=C=C], 196.8

(s, Os=C=*C*=C), 161.0 (s, Os=C=C=*C*), 148.8 (s, *ipso*-C of C_6H_5), 133.0, 130.8, 130.7 (all s, C_6H_5), 117.8 [d, *J*(P,C) 2.8, *C*CH_3 of mes], 94.9 [d, *J*(P,C) 2.7, CH of mes], 19.2 (s, CH_3 of mes), 16.9 [d, *J*(P,C) 44.4, P*C*H_3]; δ_P (162.0 MHz) −27.2 (s, PMe_3), −144.2 [sept, *J*(P,F) 706.4, PF_6^-].

[Os(η⁶-mes)(=C=C=CPh₂)(PCy₃)Cl]PF₆ 5b. This compound was prepared as described for **5a** from **2b** (293 mg, 0.44 mmol), HC≡CCPh_2(OH) (100 mg, 0.48 mmol) and $AgPF_6$ (112 mg, 0.44 mmol) in THF (15 cm^3). Violet solid: yield 368 mg (87%); mp 131 °C (decomp.) (Found: C, 52.52; H, 6.28. $C_{42}H_{55}ClF_6OsP_2$ requires C, 52.47; H, 5.77%). *Λ* 81 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1952 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 8.03 (4 H, m, *ortho*-H of C_6H_5), 7.90 (2 H, m, *para*-H of C_6H_5), 7.50 (4 H, m, *meta*-H of C_6H_5), 6.08 (3 H, s, C_6H_3), 2.42 (9 H, s, CH_3 of mes), 2.27–1.19 (33 H, m, C_6H_{11}); δ_C (100.6 MHz) 258.1 [d, *J*(P,C) 15.3, Os=*C*=C=C], 200.3 (s, Os=C=*C*=C), 161.7 (s, Os=C=C=*C*), 148.1 (s, *ipso*-C of C_6H_5), 133.2, 131.4, 130.8 (all s, C_6H_5), 116.4 (s, *C*CH_3 of mes), 94.1 (s, CH of mes), 38.5 [d, *J*(P,C) 26.2, C1 of C_6H_{11}], 31.2 [d, *J*(P,C) 10.2, C3,5 of C_6H_{11}], 28.2 [d, *J*(P,C) 11.4, C2,6 of C_6H_{11}], 26.9 (s, C4 of C_6H_{11}), 19.1 (s, CH_3 of mes); δ_P (162.0 MHz) 8.7 (s, PCy_3), −144.3 [sept, *J*(P,F) 708.3, PF_6^-].

[Os(η⁶-mes)(=C=C=CPh₂)(PPh₃)Cl]PF₆ 5c. This compound was prepared as described for **5a** from **2c** (52 mg, 0.08 mmol), HC≡CCPh_2(OH) (21 mg, 0.10 mmol) and $AgPF_6$ (20 mg, 0.08 mmol) in THF (10 cm^3). Violet solid: yield 58 mg (77%); mp 122 °C (decomp.) (Found: C, 53.26; H, 3.78. $C_{42}H_{37}ClF_6OsP_2$ requires C, 53.47; H, 3.95%). *Λ* 71 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1951 cm^{-1}. NMR (acetone-d_6): δ_H (400 MHz) 7.86, 7.70–7.35 (25 H, br m, C_6H_5), 6.03 (3 H, s, C_6H_3), 2.25 (9 H, s, CH_3 of mes); δ_C (100.6 MHz) 254.3 [d, *J*(P,C) 20.3, Os=*C*=C=C], 195.9 (s, Os=C=*C*=C), 161.8 (s, Os=C=C=*C*), 147.9 (s, *ipso*-C of C–C_6H_5), 135.5 [d, *J*(P,C) 8.9, *meta*-C of P–C_6H_5], 133.0, 130.9, 130.6 (all s, C–C_6H_5), 130.2 [d, *J*(P,C) 10.2, *para*-C of P–C_6H_5], 129.4 [d, *J*(P,C) 11.4, *ortho*-C of P–C_6H_5], 119.4 [d, *J*(P,C) 2.5, *C*CH_3 of mes], 95.7 (s, CH of mes), 18.8 (s, CH_3 of mes), signal of *ipso*-C of P–C_6H_5 not exactly located; δ_P (162.0 MHz) 4.7 (s, PPh_3), −144.1 [sept, *J*(P,F) 708.4, PF_6^-].

[Os(η⁶-mes){=C=C=C(C₆H₄-*p*-OMe)₂}(PCy₃)Cl]PF₆ 5d. This compound was prepared as described for **5a** from **2b** (81 mg, 0.12 mmol), HC≡CC(C_6H_4-*p*-$OMe)_2$(OH) (40 mg, 0.15 mmol) and $AgPF_6$ (31 mg, 0.12 mmol) in THF (10 cm^3). Violet solid: yield 83 mg (68%); mp 167 °C (decomp.) (Found: C, 52.00; H, 6.03. $C_{44}H_{59}ClF_6OsP_2$ requires C, 51.73; H 5.82%). *Λ* 89 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1960 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 8.07, 7.07 [4 H each, both d, *J*(H,H) 9.1, C_6H_4], 5.89 (3 H, s, C_6H_3), 3.92 (6 H, s, OCH_3), 2.40 (9 H, s, CH_3 of mes), 2.10–1.08 (33 H, m, C_6H_{11}); δ_C (100.6 MHz) 239.6 [d, *J*(P,C) 16.5, Os=*C*=C=C], 175.4 (s, Os=C=*C*=C), 163.3 (s, Os=C=C=*C*), 156.5 (s, *ipso*-C of C_6H_4), 140.0, 135.7, 116.2 (all s, C_6H_4), 112.4 (s, *C*CH_3 of mes), 90.7 (s, CH of mes), 56.7 (s, OCH_3), 38.4 [d, *J*(P,C) 26.7, C1 of C_6H_{11}], 31.2 (br s, C3,5 of C_6H_{11}), 28.1 [d, *J*(P,C) 10.2, C2,6 of C_6H_{11}], 27.0 (s, C4 of C_6H_{11}), 19.0 (s, CH_3 of mes); δ_P (162.0 MHz) 7.4 (s, PCy_3), −144.3 [sept, *J*(P,F) 706.3, PF_6^-].

[Os(η⁶-mes)(=C=C=Ph₂)(As*i*Pr₃)Cl]PF₆ 5e. This compound was prepared as described for **5a** from **2d** (88 mg, 0.15 mmol), HC≡CCPh_2(OH) (35 mg, 0.17 mmol) and $AgPF_6$ (38 mg, 0.15 mmol) in THF (12 cm^3); time of reaction 30 min. Violet solid: yield 101 mg (76%); mp 87 °C (decomp.) (Found: C, 44.40; H, 4.42. $C_{33}H_{43}AsClF_6Os$ requires C, 44.77; H, 4.90%). *Λ* 81 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1961 cm^{-1}. NMR (CD_3NO_2): δ_H (200 MHz) 8.00 (4 H, m, *ortho*-H of C_6H_5), 7.90 (2 H, m, *para*-H of C_6H_5), 7.46 (4 H, m, *meta*-H of C_6H_5), 6.12 (3 H, s, C_6H_3), 2.84 (3 H, m, AsC*H*CH_3), 2.42 (9 H, s, CH_3 of mes), 1.32 [9 H, d, *J*(H,H) 6.9, AsCHC*H*$_3$], 1.18 [9 H, d, *J*(H,H) 7.3, AsCHC*H*$_3$]; δ_C (50.3 MHz) 254.7 (s, Os=*C*=C=C), 199.6 (s, Os=C=*C*=C), 162.8 (s, Os=C=C=*C*), 148.5 (s, *ipso*-C of C_6H_5), 133.2, 131.2, 130.6 (all s, C_6H_5), 114.8 (s, *C*CH_3 of mes), 92.5 (s, CH of mes), 29.6 (s, As*C*HCH_3), 20.8, 20.7 (both s, AsCH*C*H_3), 19.0 (s, CH_3 of mes).

[Os(η⁶-mes)(=C=C=CPh₂)(Sb*i*Pr₃)Cl]PF₆ 5f. This compound was prepared as described for **5a** from **2e** (70 mg, 0.11 mmol), HC≡CCPh_2(OH) (25 mg, 0.12 mmol) and $AgPF_6$ (28 mg, 0.11 mmol) in THF (10 cm^3). Violet solid: yield 75 mg (73%); mp 112 °C (decomp.) (Found: C, 42.43; H, 4.47. $C_{33}H_{43}ClF_6OsPSb$ requires C, 42.52; H 4.65%). *Λ* 76 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1950 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 8.07 (4 H, m, *ortho*-H of C_6H_5), 7.87 (2 H, m, *para*-H of C_6H_5), 7.42 (4 H, m, *meta*-H of C_6H_5), 6.12 (3 H, s, C_6H_3), 2.78 (3 H, m, SbC*H*CH_3), 2.45 (9 H, s, CH_3 of mes), 1.40, 1.29 [9 H each, both d, *J*(H,H) 7.3 Hz, SbCHC*H*$_3$]; δ_C (100.6 MHz) 254.1 (s, Os=*C*=C=C), 199.9 (s, Os=C=*C*=C), 161.6 (s, Os=C=C=*C*), 148.5 (s, *ipso*-C of C_6H_5), 133.2, 131.4, 130.6 (all s, C_6H_5), 113.0 (s, *C*CH_3 of mes), 90.9 (s, CH of mes), 22.9 (s, Sb*C*HCH_3), 21.8, 21.7 (both s, SbCH*C*H_3), 19.4 (s, CH_3 of mes).

[Os(η⁶-C₆H₆)(=C=C=CPh₂)(PCy₃)I]PF₆ 5g. This compound was prepared as described for **5a** from **3** (88 mg, 0.11 mmol), HC≡CCPh_2(OH) (27 mg, 0.13 mmol) and $AgPF_6$ (28 mg, 0.11 mmol) in THF (10 cm^3). Violet solid: yield 86 mg (77%); mp 164 °C (decomp.) (Found: C, 46.27; H, 5.03. $C_{39}H_{49}F_6IOsP_2$ requires C, 46.34; H, 4.89%). *Λ* 56 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1958 cm^{-1}. NMR (CD_3NO_2): δ_H (200 MHz) 8.04 (4 H, m, *ortho*-H of C_6H_5), 7.89 (2 H, m, *para*-H of C_6H_5), 7.52 (4 H, m, *meta*-H of C_6H_5), 6.54 (6 H, s, C_6H_6), 1.91–1.23 (33 H, m, C_6H_{11}); δ_C (100.6 MHz) 256.7 [d, *J*(P,C) 15.3, Os=*C*=C=C], 196.6 (s, Os=C=*C*=C), 167.1(s, Os=C=C=*C*), 147.8 (s, *ipso*-C of C_6H_5), 134,2, 132.6, 130.6 (all s, C_6H_5), 95.8 [d, *J*(P,C) 2.8, C_6H_6], 40.8 [d, *J*(P,C) 26.3, C1 of C_6H_{11}], 31.6 [d, *J*(P,C) 4.2, C3,5 of C_6H_{11}], 28.0 [d, *J*(P,C) 11.1 Hz, C2,6 of C_6H_{11}], 26.9 (s, C4 of C_6H_{11}); δ_P (162.0 MHz) 10.5 (s, PCy_3), −144.3 [sept, *J*(P,F) 706.3, PF_6^-]. MS (FAB): *m*/*z* 867 (M^+ + 1).

[Os(η⁶-*p*-cymene)(=C=C=CPh₂)(PCy₃)Cl]PF₆ 5h. This compound was prepared as described for **5a** from **4** (101 mg, 0.15 mmol), HC≡CCPh_2(OH) (35 mg, 0.17 mmol) and $AgPF_6$ (38 mg, 0.15 mmol) in THF (12 cm^3). Violet solid: yield 118 mg (81%); mp 106 °C (decomp.) (Found: C, 52.48; H, 6.33. $C_{43}H_{57}ClF_6OsP_2$ requires C, 52.94; H, 5.89%). *Λ* 64 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(C=C=C) 1949 cm^{-1}. NMR (CD_3NO_2): δ_H (200 MHz) 8.01 (4 H, m, *ortho*-H of C_6H_5), 7.88 (2 H, m, *para*-H of C_6H_5), 7.50 (4 H, m, *meta*-H of C_6H_5), 6.65, 6.58, 6.11, 6.06 [1 H each, all d, *J*(H,H) 5.9, C_6H_4], 2.75 [1 H, sept, *J*(H,H) 7.0, C*H*CH_3 of *p*-cym], 2.45–1.18 (33 H, m, C_6H_{11}), 2.39 (3 H, s, CH_3 of p-cym), 1.33, 1.31 [3 H each, both d, *J*(H,H) 7.0, CHC*H*$_3$ of *p*-cym]; δ_C (100.6 MHz) 255.0 [d, *J*(P,C) 15.2, Os=*C*=C=C], 196.8 (s, Os=C=*C*=C), 161.0 (s, Os=C=C=*C*); 147.9 (s, *ipso*-C of C_6H_5), 133.2, 131.6, 130.6 (all s, C_6H_5), 121.3, 112.0 (both br s, *C*CH_3 and *C*CHCH_3 of *p*-cym), 102.0, 98.6, 89.4, 86.1 [all d, *J*(P,C) 2.8, C_6H_4], 38.3 [d, *J*(P,C) 26.7, C1 of C_6H_{11}], 32.2 (s, *C*HCH_3 of p-cym) 30.6 [d, *J*(P,C) 2.8, C3,5 of C_6H_{11}], 28.0 [d, *J*(P,C) 11.4, C2,6 of C_6H_{11}], 26.9 (s, C4 of C_6H_{11}), 23.6, 20.8 (both s, CH*C*H_3 of *p*-cym), 18.0 (s, CH_3 of *p*-cym); δ_P (162.0 MHz) 10.1 (s, PCy_3), −144.3 [sept, *J*(P,F) 708.5, PF_6^-].

[Os(η⁶-mes)(=C=C=CPh₂)(PMe₃)Cl]B(Ar_F)₄ 6a. A suspension of **5a** (53 mg, 0.07 mmol) in ether (10 cm^3) was treated with $NaB(Ar_F)_4$ (53 mg, 0.07 mmol) and stirred for 30 min at room temperature. The suspension was filtered, and the filtrate was concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of hexane (15 cm^3) led to the precipitation of a brown solid, the crystallization of which was completed by irradiating the mixture in an ultrasound bath for 5 min. The mother liquor was decanted, the remaining solid was washed with hexane (2 × 5 cm^3) and dried:

yield 81 mg (92%), mp 101 °C (decomp.) (Found: C, 48.33; H, 3.01. $C_{59}H_{43}BClF_{24}OsP$ requires C, 48.03; H, 2.94%). Λ 37 cm^2 Ω^{-1} mol^{-1}. The spectroscopic data of **6a**, with the exception of the NMR signals for the $B(Ar_F)_4^-$ anion, were practically identical with those of **5a**.

[Os(η^6-mes)(=C=C=CPh$_2$)(PCy$_3$)Cl]B(Ar$_F$)$_4$ 6b. This compound was prepared as described for **6a** from **5b** (77 mg, 0.08 mmol) and $NaB(Ar_F)_4$ (63 mg, 0.08 mmol) in ether (10 cm^3). Brown solid: yield 125 mg (93%); mp 98 °C (decomp.) (Found: C, 52.50; H, 4.19; Os, 11.16. $C_{74}H_{67}BClF_{24}OsP$ requires C, 52.91; H, 4.02; Os, 11.33%). Λ 31 cm^2 Ω^{-1} mol^{-1}. The spectroscopic data of **6b**, with the exception of the NMR signals for the $B(Ar_F)_4^-$ anion, were practically identical with those of **5b**.

[Os(η^6-mes)(=C=C=CPh$_2$)(PCy$_3$)Br]PF$_6$ 7a. A solution of **5b** (96 mg, 0.10 mmol) in acetone (10 cm^3) was treated with KBr (119 mg, 1.00 mmol) and stirred for 48 h at room temperature. The solvent was evaporated *in vacuo*, and the residue was extracted with CH_2Cl_2 (2 × 10 cm^3). The combined extracts were concentrated to *ca.* 1 cm^3 and hexane (15 cm^3) was added. A red solid precipitated which was separated from the mother liquor, washed with hexane (2 × 5 cm^3) and dried: yield 81 mg (81%); mp 120 °C (decomp.) (Found: C, 49.75; H, 5.22. $C_{42}H_{55}BrF_6OsP_2$ requires C, 50.15; H, 5.51%). Λ 63 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C=C) 1951 cm^{-1}. NMR (CD_2Cl_2): δ_H (200 MHz) 7.97 (4 H, m, *ortho*-H of C_6H_5), 7.82 (2 H, m, *para*-H of C_6H_5), 7.48 (4 H, m, *meta*-H of C_6H_5), 5.89 (3 H, s, C_6H_3), 2.39 (9 H, s, CH_3 of mes), 1.98–1.14 (33 H, m, C_6H_{11}); δ_C (50.3 MHz) 256.2 [d, J(P,C) 15.8, Os=*C*=C=C], 196.9 (s, Os=C=*C*=C), 162.0 (s, Os=C=C=*C*), 147.6 (s, *ipso*-C of C_6H_5), 132.6, 130.9, 130.1 (all s, C_6H_5), 114.9 (s, *C*CH$_3$ of mes), 93.0 (s, CH of mes), 37.7 [d, J(P,C) 26.7, C1 of C_6H_{11}], 30.6 (br s, C3,5 of C_6H_{11}), 27.6 [d, J(P,C) 9.7, C2,6 of C_6H_{11}], 26.3 (s, C4 of C_6H_{11}), 19.3 (s, CH_3 of mes); δ_P (162.0 MHz) 10.3 (s, PCy_3), −143.0 [sept, J(P,F) 711.9, PF_6^-].

[Os(η^6-mes)(=C=C=CPh$_2$)(PCy$_3$)I]PF$_6$ 7b. This compound was prepared as described for **7a** from **5b** (115 mg, 0.12 mmol) and NaI (150 mg, 1.00 mmol) in acetone (10 cm^3); time of reaction 24 h. Red solid: yield 117 mg (93%); mp 124 °C (decomp.) (Found: C, 47.80; H, 5.28. $C_{42}H_{55}F_6IOsP_2$ requires C, 47.91; H, 5.26%). Λ 70 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C=C) 1951 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 8.09 (4 H, m, *ortho*-H of C_6H_5), 7.88 (2 H, m, *para*-H of C_6H_5), 7.49 (4 H, m, *meta*-H of C_6H_5), 6.24 (3 H, s, C_6H_3), 2.55 (9 H, s, CH_3 of mes), 2.05–1.16 (33 H, m, C_6H_{11}); δ_C (100.6 MHz) 255.6 [d, J(P,C) 14.9, Os=*C*=C=C], 203.1 (s, Os=C=*C*=C), 163.9 (s, Os=C=C=*C*), 149.0 (s, *ipso*-C of C_6H_5), 133.3, 131.5, 130.7 (all s, C_6H_5), 113.6 (s, *C*CH$_3$ of mes), 95.9 (s, CH of mes), 40.3 [d, J(P,C) 25.4, C1 of C_6H_{11}], 32.5 (br s, C3,5 of C_6H_{11}), 28.1 [d, J(P,C) 10.2, C2,6 of C_6H_{11}], 26.9 (s, C4 of C_6H_{11}), 19.4 (s, CH_3 of mes); δ_P (162.0 MHz) 10.6 (s, PCy_3), −143.2 [sept, J(P,F) 706.3, PF_6^-].

[Os(η^6-mes)(=C=C=CPh$_2$)(PCy$_3$)(κ^1-O$_2$CCF$_3$)]PF$_6$ 7c. A solution of **5b** (86 mg, 0.09 mmol) in CH_2Cl_2 (10 cm^3) was treated dropwise with a solution of CF_3CO_2Ag (20 mg, 0.09 mmol) in benzene (2 cm^3). After the reaction mixture was stirred for 1 h at room temperature, the solution was filtered and the filtrate was concentrated to *ca.* 0.5 cm^3 *in vacuo*. Addition of hexane (15 cm^3) led to the precipitation of a violet solid which was separated from the mother liquor, washed with hexane (2 × 5 cm^3) and dried: yield 83 mg (89%); mp 121 °C (decomp.) (Found: C, 51.30; H 5.72. $C_{44}H_{55}F_9O_2OsP_2$ requires C, 50.86; H, 5.33%). Λ 102 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C=C) 1953, $\nu(OCO)_{asym}$ 1712, $\nu(OCO)_{sym}$ 1448 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 7.88 (4 H, m, *ortho*-H of C_6H_5), 7.80 (2 H, m, *para*-H of C_6H_5), 7.44 (4 H, m, *meta*-H of C_6H_5), 6.19 (3 H, s, C_6H_3), 2.35 (9 H, s, CH_3 of mes), 2.24–1.12 (33 H, m, C_6H_{11}); δ_C (100.6 MHz) 257.5 [d, J(P,C) 15.3, Os=*C*=C=C], 193.6 (s, Os=C=*C*=C), 163.9 (s, Os=C=C=*C*), 164.2 [q, J(C,F) 37.4 Hz, CF_3CO_2], 146.6 (s, *ipso*-C of C_6H_5), 132.2, 131.0, 130.0 (all s, C_6H_5), 113.1 (s, *C*CH$_3$ of mes), 112.9 [q, J(C,F) 291.3, *C*F$_3$CO$_2$], 90.4 (s, CH of mes), 35.5 [d, J(P,C), 25.0, C1 of C_6H_{11}], 30.3 (br s, C3,5 of C_6H_{11}), 27.4 [d, J(P,C) 11.1, C2,6 of C_6H_{11}], 26.1 (s, C4 of C_6H_{11}), 18.9 (s, CH_3 of mes); δ_F (376.5 MHz) −72.4 [d, J(P,F) 713.3, PF_6^-], −78.3 (s, CF_3CO_2); δ_P (162.0 MHz) 16.4 (s, PCy_3), −144.2 [sept, J(P,F) 713.3 Hz, PF_6^-].

[Os(η^6-mes){=C(OMe)CH=CPh$_2$}(PMe$_3$)Cl]PF$_6$ 8a. A solution of **5a** (113 mg, 0.15 mmol) in methanol (10 cm^3) was stirred for 5 h at room temperature. A smooth change of colour from violet to red occurred. The solvent was evaporated *in vacuo*, the oily residue was dissolved in CH_2Cl_2 (1 cm^3) and the solution was chromatographed on Al_2O_3 (basic, acitivity grade III, height of column 10 cm). With CH_2Cl_2–acetone (7 : 1) a red solution was eluted which was concentrated *in vacuo* to *ca.* 1 cm^3. Addition of hexane (20 cm^3) led to the precipitation of an orange-red solid which was separated from the mother liquor, washed with hexane (2 × 5 cm^3) and dried: yield 86 mg (73%); mp 131 °C (decomp.) (Found: C, 42.24; H, 4.42. $C_{28}H_{35}ClF_6OOsP_2$ requires C, 42.61; H, 4.47%). Λ 67 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C) 1542, ν(C–O) 1263 cm^{-1}. NMR (CD_3NO_2): δ_H (200 MHz) 7.35, 7.33 (4 H each, both m, C_6H_5), 7.19 (2 H, m, C_6H_5), 6.71 (1 H, s, =CH), 5.19 (3 H, s, C_6H_3), 4.37 (3 H, s, OCH_3), 2.32 (9 H, s, CH_3 of mes), 1.77 [9 H, d, J(P,H) 10.6, PMe_3]; δ_C (50.3 MHz) 276.6 [d, J(P,C) 14.0, Os=C], 149.6 (s, *C*Ph$_2$), 142.1 (s, *ipso*-C of C_6H_5), 141.2 (s, =CH), 130.6, 129.9, 129.6, 129.3, 129.2 (all s, C_6H_5), 110.0 (s, *C*CH$_3$ of mes), 83.4 [d, J(P,C) 2.8, CH of mes], 67.7 (s, OCH_3), 18.8 (s, CH_3 of mes), 16.6 [d, J(P,C) 39.4, PCH_3]; δ_P (81.0 MHz) −35.3 (s, PMe_3), −144.8 [sept, J(P,F) 707.0, PF_6^-].

[Os(η^6-mes){=C(OEt)CH=CPh$_2$}(PMe$_3$)Cl]PF$_6$ 8b. This compound was prepared as described for **8a** from **5a** (129 mg, 0.17 mmol) in ethanol–THF (9 : 1, 10 cm^3). Orange-red solid: yield 93 mg (68%); mp 145 °C (decomp.) (Found: C, 42.94; H, 4.77. $C_{29}H_{37}ClF_6OOsP_2$ requires C, 43.36; H 4.64%). Λ 87 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=C) 1543, ν(C–O) 1260 cm^{-1}. NMR (CD_3NO_2): δ_H (300 MHz) 7.45, 7.36 (4 H each, both m, C_6H_5), 7.20 (2 H, m, C_6H_5), 6.86 (1 H, s, =CH), 5.20 (3 H, s, C_6H_3), 4.86, 4.72 (1 H each, both m, OCH_2), 2.34 (9 H, s, CH_3 of mes), 1.75 [9 H, d, J(P,H) 10.6, PCH_3], 1.15 (3 H, m, CH_2CH_3); δ_C (75.5 MHz) 276.4 [d, J(P,C) 18.9, Os=C], 149.6 (s, *C*Ph$_2$), 142.0, 140.7 (both s, *ipso*-C of C_6H_5), 144.0 (s, =CH), 131.0, 130.3, 129.9, 129.7, 129.6, 129.4 (all s, C_6H_5), 109.9 [d, J(P,C) 1.8, *C*CH$_3$ of mes], 82.8 [d, J(P,C) 2.3, CH of mes], 78.3 (s, OCH_2), 18.9 (s, CH_3 of mes), 16.5 [d, J(P,C) 40.2, PCH_3], 14.7 (s, CH_2CH_3); δ_P (81.0 MHz) −36.2 (s, PMe_3), −143.6 [sept, J(P,F), 711.9, PF_6^-]. MS (FAB): m/z 659 ($M^+ + 1$).

[Os(η^6-mes){C(OMe)=C=CPh$_2$}(PMe$_3$)Cl] 9. A solution of **8a** (110 mg, 0.14 mmol) in THF (5 cm^3) was treated with NaH (4.8 mg, 0.20 mmol). After the solution was stirred for 5 min at 60 °C, it was cooled to room temperature and continuously stirred for 30 min. During this period of time, a change of colour from red to yellow occurred. The solvent was evaporated *in vacuo*, and the residue was suspended in benzene (2 cm^3). The suspension was filtered with Celite, the residue was washed with benzene (2 × 5 cm^3) and the combined solutions were concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of hexane (20 cm^3) led to the precipitation of a yellow solid, which was separated from the mother liquor, washed with hexane (2 × 5 cm^3) and dried: yield 73 mg (81%). Although the product, owing to the NMR spectra, seemed to be pure, no correct elemental analysis could be obtained. NMR ($CDCl_3$): δ_H (200 MHz) 8.31, 7.49 (2 H each, both m, C_6H_5), 7.38 (6 H, m, C_6H_5), 4.54 (3 H, s, C_6H_3), 3.55 (3 H, s, OCH_3), 1.97 (9 H, s, CH_3 of mes), 1.50 [d, J(P,H) 10.4, PCH_3]; δ_P (81.0 MHz) −38.7 (s).

[Os(η⁶-mes){C(PMe$_3$)=C=CPh$_2$}(PMe$_3$)Cl]PF$_6$ 10a and [Os(η⁶-mes)(PMe$_3$)$_2$Cl]PF$_6$ 11a. A solution of **5a** (106 mg, 0.14 mmol) in CH_2Cl_2 (10 cm^3) was cooled to −78 °C and then treated with a cooled solution (−78 °C) of PMe_3 (43 μL, 0.42 mmol) in CH_2Cl_2 (5 cm^3). After the solution was warmed to room temperature under continuous stirring, it was concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of hexane (15 cm^3) led to the precipitation of a light brown solid which was separated from the mother liquor, washed with hexane (2 × 5 cm^3) and dried. The NMR spectra confirmed that a mixture of **10a** and **11a** in the ratio of 4 : 1 was formed which could not be separated by fractional crystallization or chromographic techniques. Spectroscopic data for **10a** are as follows: IR (KBr): *ν*(C=C=C) 1880 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.26–7.09 (10 H, m, C_6H_5), 5.05 (3 H, s, C_6H_3), 2.06 (9 H, s, CH_3 of mes), 2.02 [9 H, d, *J*(P,H) 12.9, Os–PMe$_3$], 1.43 [9 H, d, *J*(P,H) 10.2, C–PMe$_3$]; δ_C (100.6 MHz) 209.5 [d, *J*(P,C) 5.5, =C=], 138.4, 138.1 (both s, *ipso*-C of C_6H_5), 129.4, 129.3, 129.2, 129.0, 128.1, 127.9 (all s, C_6H_5), 100.3 (s, *C*CH$_3$ of mes), 93.5 (br s, *C*Ph$_2$), 80.4 [d, *J*(P,C) 2.8, CH of mes], 70.2 [dd, ^{1}*J*(P,C) 27.6, ^{2}*J*(P,C) 12.5, OsC], 18.8 (s, CH_3 of mes), 15.0 [d, *J*(P,C) 55.5, Os–PCH$_3$], 93.3 [d, *J*(P,C) 52.7, C–PCH$_3$]; δ_P (162.0 MHz) 21.2 [d, *J*(P,P) 4.3, C–PMe$_3$], −39.6 [d, *J*(P,P) 4.3, Os–PMe$_3$], −144.3 [sept, *J*(P,F) 710.3, PF_6^-].

[Os(η⁶-mes)(PMe$_3$)$_2$Cl]PF$_6$ 11a. A suspension of **2a** (50 mg, 0.11 mmol) in methanol (10 cm^3) was treated stepwise with PMe_3 (11 μL, 0.11 mmol) and NH_4PF_6 (18 mg, 0.11 mmol) and then stirred for 2 h at 65 °C. After the reaction mixture was cooled to room temperature, the solvent was evaporated *in vacuo*. The residue was extracted twice with CH_2Cl_2 (2 × 5 cm^3) and the combined extracts were concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of hexane (20 cm^3) led to the precipitation of a yellow solid which was separated from the mother liquor, washed with hexane (2 × 5 cm^3) and dried: yield 58 mg (81%); mp 206 °C (decomp.) (Found: C, 27.88; H, 4.63. $C_{15}H_{30}ClF_6OsP_3$ requires C, 28.02; H, 4.70%). *Λ* 76 cm^2 Ω^{-1} mol^{-1}. NMR ($CDCl_3$): δ_H (200 MHz) 5.73 (3 H, s, C_6H_3), 2.31 (9 H, s, CH_3 of mes), 1.64 (vt, *N* 9.0, PMe_3); δ_C (50.3 MHz) 97.0 (s, *C*CH$_3$ of mes), 88.2 (s, CH of mes), 18.5 (vt, *N* 40.1, PCH$_3$), 18.4 (s, CH_3 of mes); δ_P (81.0 MHz) −44.5 (s, PMe_3), −143.3 [sept, *J*(P,F) 706.3, PF_6^-].

[Os(η⁶-mes){C(PPh$_3$)=C=CPh$_2$}(PMe$_3$)Cl]PF$_6$ 10b and [Os(η⁶-mes)(PMe$_3$)(PPh$_3$)Cl]PF$_6$ 11b. The mixture of these two compounds was prepared as described for **10a/11a** from **5a** (120 mg, 0.17 mmol) and PPh_3 (62 mg, 0.24 mmol) in CH_2Cl_2 (15 cm^3). Owing to the NMR spectra, a mixture of **10b** and **11b** in the ratio of 6 : 1 was obtained. Spectroscopic data for **10b** are as follows: IR (KBr): *ν*(C=C=C) 1862 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.61–7.49, 7.24, 6.88, 6.72 (25 H, all m, C_6H_5), 4.61 (3 H, s, C_6H_3), 2.13 (9 H, s, CH_3 of mes), 1.46 [9 H, d, *J*(P,H) 10.2, PMe_3]; δ_C (75.0 MHz) 215.2 [d, *J*(P,C) 7.6, =C=], 137.2, 136.4 (both s, *ipso*-C of C–C_6H_5), 136.7 [d, *J*(P,C) 57.5, *ipso*-C of P–C_6H_5], 135.5 [d, *J*(P,C) 8.8, *meta*-C of P–C_6H_5], 134.1 [d, *J*(P,C) 1.5, *para*-C of P–C_6H_5], 129.3, 129.2, 129.0, 128.6, 128.3, 127.9 (all s, C–C_6H_5), 129.1 [d, *J*(P,C) 12.0, *ortho*-C of P–C_6H_5], 103.2 (s, *C*CH$_3$ of mes), 100.9 (br s, *C*Ph$_2$), 73.3 (s, CH of mes), 64.3 (m, OsC), 18.5 (s, CH_3 of mes), 16.4 [d, *J*(P,C) 37.4, PCH$_3$]; δ_P (81.0 MHz) 29.8 [d, *J*(P,P) 7.6, PPh_3], −39.4 [d, *J*(P,P) 7.6, PMe_3], −143.7 [sept, *J*(P,F) 711.0, PF_6^-].

[Os(η⁶-mes)(PMe$_3$)(PPh$_3$)Cl]PF$_6$ 11b. This compound was prepared as described for **11a** from **2c** (58 mg, 0.09 mmol), PMe_3 (15 μL, 0.15 mmol) and NH_4PF_6 (24 mg, 0.15 mmol). Yellow solid: yield 93 mg (75%); mp 88 °C (decomp.) (Found: C, 43.84; H, 4.74. $C_{30}H_{36}ClF_6OsP_3$ requires C, 43.45; H, 4.38%). *Λ* 81 cm^2 Ω^{-1} mol^{-1}. NMR (CD_2Cl_2): δ_H (200 MHz) 7.48–7.28 (15 H, m, C_6H_5), 5.19 (3 H, s, C_6H_3), 2.20 (9 H, s, CH_3 of mes), 1.32 [d, *J*(P,H) 10.2, PCH$_3$]; δ_C (50.3 MHz) 135.2 [d, *J*(P,C) 9.2, *meta*-C of C_6H_5], 132.5 [d, *J*(P,C) 54.6, *ipso*-C of C_6H_5], 131.7 (s, *para*-C of C_6H_5), 128.7 [d, *J*(P,C) 10.2, *ortho*-C of C_6H_5], 102.4 (s, *C*CH$_3$ of mes), 87.3 (s, CH of mes), 18.6 (s, CH_3 of mes), 17.8 [d, *J*(P,C) 38.8, PCH$_3$]; δ_P (81.0 MHz) −7.2 [d, *J*(P,P) 30.5, PPh_3], −49.7 [d, *J*(P,P) 30.5, PMe_3], −143.8 [sept, *J*(P,F) 711.9, PF_6^-].

[Os(η⁶-mes){C(PMe$_3$)=C=CPh$_2$}(PCy$_3$)Cl]PF$_6$ 10c and [Os(η⁶-mes)(PMe$_3$)(PCy$_3$)Cl]PF$_6$ 11c. The mixture of these two compounds was prepared as described for **10a/11a** from **5b** (125 mg, 0.13 mmol) and PMe_3 (40 μL, 0.39 mmol) in CH_2Cl_2 (15 cm^3). Owing to the NMR spectra, a mixture of **10c** and **11c** in the ratio of 5 : 1 was obtained. Spectroscopic data for **10c** are as follows: IR (KBr): *ν*(C=C=C) 1860 cm^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 7.64–7.32 (10 H, m, C_6H_5), 5.42 (3 H, s, C_6H_3), 2.29 (9 H, s, CH_3 of mes), 2.30–1.19 (33 H, m, C_6H_{11}), 2.09 [9 H, d, *J*(P,H) 12.9, PMe_3]; δ_C (100.6 MHz) 140.4, 140.0 (both s, *ipso*-C of C_6H_5), 130.1, 130.0, 129.8, 129.4, 129.2 (all s, C_6H_5), 100.2 (s, *C*Ph$_2$), 99.2 [d, *J*(P,C) 2.5, *C*CH$_3$ of mes], 81.4 (s, CH of mes), 63.4 (m, OsC), 37.5 [d, *J*(P,C) 25.4, C1 of C_6H_{11}], 31.9 (br s, C3,5 of C_6H_{11}), 28.3 [d, *J*(P,C) 8.9, C2,6 of C_6H_{11}], 27.2 (s, C4 of C_6H_{11}), 19.0 (s, CH_3 of mes), 9.4 [d, *J*(P,C) 53.4, PCH$_3$], signal of =C= carbon atom not exactly located; δ_P (162.0 MHz) 35.8 [d, *J*(P,P) 4.3, PCy$_3$], −8.4 [d, *J*(P,P) 4.3, PMe_3], −143.5 [sept, *J*(P,F) 712.3, PF_6^-].

[Os(η⁶-mes)(PMe$_3$)(PCy$_3$)Cl]PF$_6$ 11c. This compound was prepared as described for **11a** from **2b** (93 mg, 0.14 mmol), PMe_3 (14 μL, 0.14 mmol) and NH_4PF_6 (22 mg, 0.14 mmol). Yellow solid: yield 86 mg (72%); mp 84 °C (decomp.) (Found: C, 42.89; H, 6.93. $C_{30}H_{55}ClF_6OsP_3$ requires C, 42.47; H, 6.54%). *Λ* 74 cm^2 Ω^{-1} mol^{-1}. NMR (CD_3NO_2): δ_H (400 MHz) 5.93 (3 H, s, C_6H_3), 2.39 (9 H, s, CH_3 of mes), 2.31–1.31 (33 H, m, C_6H_{11}), 1.74 [9 H, d, *J*(P,H) 10.0, PMe_3]; δ_C (100.6 MHz) 98.4 (s, *C*CH$_3$ of mes), 87.7 (s, CH of mes), 39.9 (m, C1 of C_6H_{11}), 30.9 (br s, C3,5 of C_6H_{11}), 28.2 [d, *J*(P,C) 9.5, C2,6 of C_6H_{11}], 26.9 (s, C4 of C_6H_{11}), 19.9 [d, *J*(P,C) 38.1, PCH$_3$], 18.9 (s, CH_3 of mes); δ_P (162.0 MHz) −12.4 [d, *J*(P,P) 32.8, PCy$_3$], −55.1 [d, *J*(P,P) 32.8, PMe_3], −143.3 [sept, *J*(P,F) 706.3, PF_6^-].

Crystallography

Single crystals of both, **5a** and **8b**, were grown from a saturated solution in dichloromethane which was layered with pentane at room temperature. Crystal data collection parameters are summarized in Table 3. Intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections (*Ψ*-scan method, minimal transmission 75.72% and 77.89%, respectively) were applied. Data reduction was performed with Enraf-Nonius CAD4 software for **5a** and **8b**. The structures were solved by the Patterson method (SHELXS-97).[23] Atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 (SHELXL-97).[24] The ethoxy-group of **8b** is disordered and found in two positions with an occupancy of 0.67 : 0.33; it was refined anisotropically with restraints.

CCDC reference numbers 172105 and 172106.

See http://www.rsc.org/suppdata/dt/b1/b108992g/ for crystallographic data in CIF or other electronic format.

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Table 3 Crystallographic data for **5a** and **8b**

Formula	$C_{27}H_{31}ClF_6OsP_2$ **5a**	$C_{29}H_{37}ClF_6OOsP_2$ **8b**
M	757.11	803.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	8.424(3)	10.164(3)
b/Å	14.521(2)	16.615(2)
c/Å	23.448(8)	18.957(7)
β/°	99.04(1)	101.36(1)
V/Å^3	2833(1)	3139(1)
T/K	193(2)	193(2)
Z	4	4
D_c/g cm^{-3}	1.775	1.700
λ(Mo-Kα)/Å	0.71073	0.71073
μ/mm^{-1}	4.764	4.307
No. of reflections measured	5483	5943
No. of unique reflections	4957 [R(int) = 0.0414]	5525 [R(int) = 0.0242]
$R1$ [a]	0.0524	0.0376
$wR2$ [b]	0.1240	0.0748
Residual electron density/e Å^{-3}	1.423/−0.851	0.790/−0.686

[a] $R = \Sigma|F_o - F_c|$ [for $F_o > 2\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0394P)^2 + 18.5126P]$ **5a**, $[\sigma^2(F_o^2) + (0.0186P)^2 + 7.2093P]$ **8b**, where $P = [F_o^2 + 2F_c^2]/3$; for all data reflections, respectively.

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