

Synthesis, characterization and molecular structures of allenylidene, vinylidene–alkylidene complexes containing $[\text{CpOs}(\text{PPh}_3)_2]^+$ fragment

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Received 10 November 2003; accepted 12 November 2003

Abstract

The reaction of $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ with diphenylpropargylic alcohol $\text{HC}\equiv\text{CCPh}_2(\text{OH})$ in the presence of ammonium hexafluorophosphate leads to the formation of cationic osmium allenylidene complex $[\text{CpOs}(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**1**), but when the dimethylpropargylic alcohol $\text{HC}\equiv\text{CCMe}_2(\text{OH})$ was used as a substrate, a dicationic osmium vinylidene–alkylidene complex of the formula $[(\text{CpOs})_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4][\text{PF}_6]_2$ (**2**) was obtained. The structures of these complexes have been determined by X-ray diffraction. Complex **1** crystallizes in monoclinic space group $P2_1/c$ with $a = 13.4083(6)$ Å, $b = 19.5700(9)$ Å, $c = 20.3806(9)$ Å and $\beta = 100.3620(10)^\circ$. Complex **2** crystallizes in triclinic space group $P\bar{1}$ with $a = 13.0396(11)$ Å, $b = 15.2420(13)$ Å, $c = 21.6406(19)$ Å and $\alpha = 72.5290(10)^\circ$, $\beta = 75.1960(10)^\circ$, $\gamma = 85.6360(10)^\circ$.

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Keywords: Osmium; Allenylidene; Vinylidene; Alkynols; Cyclopentadienyl

1. Introduction

The current interest in complexes containing unsaturated carbon chains arises mainly due to their potential to form molecular wires [1] and other nanoelectric devices [2]. The use of transition metal allenylidene complexes in organic synthesis is also well documented [3]. The chemistry of the metal allenylidene complexes ($\text{M}=\text{C}=\text{C}=\text{CR}_2$) has been known for last two decades [4] [5]. The first example of a stable allenylidene complex $[\text{CpRu}(\text{C}=\text{C}=\text{CPh}_2)(\text{PMe}_3)_2]^+$, was obtained by the activation of dimethylpropargylic alcohol with $[\text{CpRuCl}(\text{PMe}_3)_2]$ in methanol [6] and this method has found widespread application for synthesis of allenylidene complexes of other elements. In comparison with related iron and ruthenium complexes [7], the chemistry of the $\text{Os}(\eta^5\text{-Cp})$ unit is little known field [8] due to the lack of

convenient synthetic precursors [9] and the kinetic stability of CpOsL_3 complexes [8]. Recently, few reports are available on the allenylidene complexes containing $[\text{CpOs}(\text{P}^i\text{Pr}_3)_2]$ fragment [10], but the chemistry of more classical $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ remains relatively unexplored.

Our current interest in the cyclopentadienylosmium complex [11] bearing triphenylphosphines prompted us to investigate its reaction with alkynols. In this article, we describe the synthesis and structure of new allenylideneosmium(II) compound $[\text{CpOs}(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**1**) and a diosmium vinylidene–alkylidene complex $[(\text{CpOs})_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4][\text{PF}_6]_2$ (**2**) analogous to ruthenium complexes.

2. Experimental section

^1H , ^{13}C and ^{31}P NMR spectra were recorded on Bruker 300 MHz spectrometer using Me_4Si and H_2PO_4 (85%) respectively as internal standards. IR spectra were

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recorded using Nicolet Impact Spectrophotometer. UV–vis spectra were obtained from Beckman DU 650 Spectrophotometer. The alcohols $\text{HC}\equiv\text{CCPh}_2(\text{OH})$ and $\text{HC}\equiv\text{CCMe}_2(\text{OH})$ were obtained from Lancaster and used as received. $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ was prepared according to literature procedure [12].

3. Synthesis of the complexes

Complexes $[\text{CpOs}(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**1**) and $[(\text{CpOs})_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4][\text{PF}_6]_2$ (**2**) were prepared by the following procedure.

The mixture of $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ (100 mg, 0.117 mmol), alkynols (0.312 mmol) and NH_4PF_6 (52 mg, 0.320 mmol) were refluxed in 45 ml methanol under dry nitrogen atmosphere for 6 h. The whole solution was left at 0 °C overnight whereby unreacted starting complex crystallized out which were removed by filtration. The filtrate was then rotary evaporated to dryness in vacuo. The residue was extracted with dichloromethane and filtered through short silica gel column to remove the insoluble white precipitate. Subsequent concentration and addition of the excess hexane gave **1** as red brown solid and **2** as red–purple solid.

$[\text{CpOs}(\text{C}=\text{C}=\text{CPh}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**1**) Yield: 60 mg, 83%. ^1H NMR (CDCl_3 , δ): 7.81 (t, 2H, $J_{\text{H-H}} = 9$ Hz), 7.64 (d, 4H, $J_{\text{H-H}} = 6$ Hz), 7.38–7.27 (m, 10H), 7.14–6.98 (m, 24H), 5.31 (s, 5H, Cp). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): –0.66 (s), –143 (Sept). IR (KBr pellet): 1924 $\nu_{(\text{C}=\text{C}=\text{C})}$, 844 $\nu_{(\text{PF}_6)}$. UV–vis (CH_2Cl_2): $\lambda_{\text{max}} = 474$ nm, $\epsilon = 1.2 \times 10^4$. Anal. Calc. for $\text{C}_{57}\text{H}_{45}\text{C}_{13}\text{F}_6\text{Os}_1\text{P}_3$: C, 55.50; H, 3.67. Found: C, 55.82; H, 3.46.

$[(\text{CpOs})_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4][\text{PF}_6]_2$ (**2**). Yield: 80 mg, 68%. ^1H NMR (CDCl_3 , δ): 7.70–6.90 (m, ph), 6.3 (s, 1H, vinyl), 5.44 (s, 5H, Cp), 4.95 (s, 5H, Cp), 2.34 (s, 6H, CH_3), 1.07–1.00 (m, 4H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): –0.74, –6.27 (s), –143 (Sept). IR (KBr pellet): 1573 $\nu_{(\text{C}=\text{C})}$, 844 $\nu_{(\text{PF}_6)}$. UV–vis (CH_2Cl_2): $\lambda_{\text{max}} = 498$ nm,

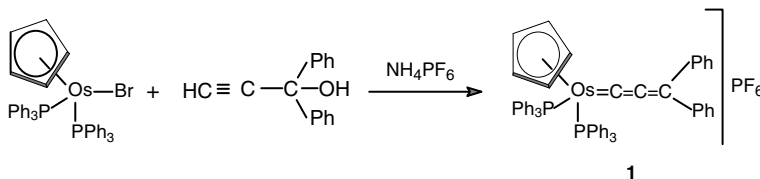
$\epsilon = 1.3 \times 10^4$. Anal. Calc. for $\text{C}_{92}\text{H}_{82}\text{F}_{12}\text{O}_2\text{Os}_2\text{P}_6$: C, 54.87; H, 4.10. Found: C, 54.91; H, 4.29.

4. Results and discussion

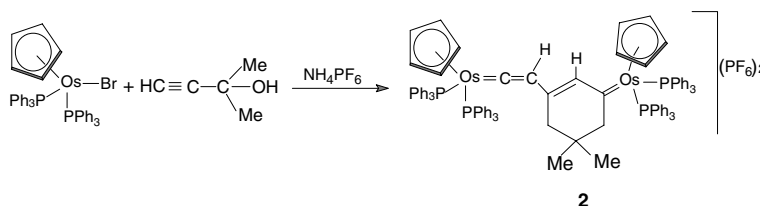
Treatment of $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ with excess $\text{HC}\equiv\text{CC}(\text{OH})\text{Ph}_2$ in refluxing methanol in the presence of NH_4PF_6 affords after 6 h the cationic allenylidene-osmium complex $[\text{CpOs}\{\text{C}=\text{C}=\text{C}(\text{Ph})_2\}(\text{PPh}_3)_2]\text{PF}_6$ (**1**) in a fairly good yield (Scheme 1). Esteruelas and co-workers [13] have observed the splitting of the Os– P^iPr_3 bond by $\text{HC}\equiv\text{CC}(\text{OH})\text{Ph}_2$ using pentane or toluene to obtain a closely related but neutral complex $[\text{CpOsCl}\{\text{C}=\text{C}=\text{C}(\text{Ph})_2\}(\text{P}^i\text{Pr}_3)_2]$, however we do not observe the spitting of Os– PPh_3 under similar reaction conditions.

Complex **1** is stable in air and is readily soluble in most of the polar solvents. The formation of the allenylidene chain is confirmed by the appearance of $\nu_{(\text{C}=\text{C}=\text{C})}$ absorption (asymmetric stretching vibration) as a strong band at 1924 cm^{-1} in the IR spectrum. The ^1H NMR spectrum of the complex **1** showed as expected a single sharp signal for Cp ring at 5.31 ppm and the phenyl protons appeared in the aromatic region in the range of 7.81–6.99 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this complex exhibited a single sharp peak at –0.66 ppm indicating the chemical equivalence of both phosphines while the starting complex $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ showed the same at –3.85 ppm [11]. In addition, a septet at –143 ppm was also observed for PF_6^- ion.

In contrast to the above reaction, $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ reacts with $\text{HC}\equiv\text{CC}(\text{OH})\text{Me}_2$ in a different way and the product isolated was a diosmium vinylidene–alkylidene complex of the formulation $[\text{Os}_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4(\text{Cp})_2][\text{PF}_6]_2$ (**2**) (Scheme 2) apparently resulting from the dimerization of the expected dimethylallenylidene complexes $[\text{CpOs}\{\text{C}=\text{C}=\text{C}(\text{Me})_2\}(\text{PPh}_3)_2]\text{PF}_6$.



Scheme 1.

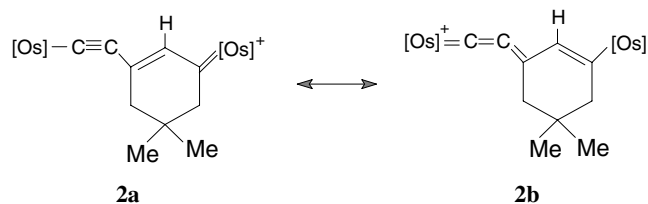


Scheme 2.

The complex **2** was obtained due to the formation of two carbon–carbon bonds between two $C=C=CMe_2$ ligands with concomitant proton shifts resulting in the cyclization and finally giving the $C_{10}H_{12}$ moiety. We believed that the mechanism of the formation of **2** would apparently follow the mechanism proposed by Selegue for ruthenium analogue [6b].

1H NMR spectrum of the complex **2** showed two distinct singlets for the two Cp's rings at 5.44 and 4.95 ppm respectively and the phenyl and vinyl protons appear in the aromatic region in the range of 7.81–6.99 ppm. ^{31}P { 1H } NMR spectrum shows two signals, which is consistent with the inequality of the phosphorus atoms coordinated to the two osmium centers. The appearance of medium intensity band at 1573 cm^{-1} in the IR spectrum confirm the presence of the $\nu_{C=C}$ [14] of the vinylidene moiety. Unfortunately, we are unable to observe the corresponding signals for C_α and C_β carbons of the ligand in ^{13}C { 1H } NMR spectra of these complexes.

The visible spectral data for **1**, **2** and **2a** (after addition of Et_3N) are presented in experimental section. Complexes **1** and **2** show sharp unsymmetrical metal-to-ligand charge-transfer (MLCT) bands at 474 and 498 nm, respectively. Upon addition of triethylamine to solution of **2** in dichloromethane, the color of the solution immediately become deep blue violet and the MLCT band shifts to 584 nm suggesting the formation of new species that can be regarded as the resonance hybrid of alkynyl-alkylidene **2a** and allenylidene-vinyl **2b** complex. This is further confirmed by the appearance of a new band at 1977 cm^{-1} in the IR spectrum.



5. Crystal structures of the complexes

In order to confirm the structures suggested by the spectroscopic evidences, molecular structure of these complexes were determined using single crystal X-ray study. The summary of the single-crystals X-ray structure analyses are shown in Table 1, and the selected bond lengths and bond angles are presented in Tables 2 and 3 respectively. The ORTEP drawing of the complexes **1** and **2** are shown in Figs. 1 and 2 respectively.

The geometry around the osmium center of **1** is close to octahedral, with cyclopentadienyl ligand occupying the three coordinate sites. The angles subtended by P1–Os–C1, P2–Os–C1 and P1–Os–P2 bonds showed a slight

Table 1
Crystal data summary and structure refinement for complexes **1** and **2**

| | | |
|--|--|--|
| Empirical formula | $C_{57}H_{45}Cl_3F_6Os_1P_3$ | $C_{92}H_{82}F_{12}O_2Os_2P_6$ |
| Formula weight | 1233.38 | 2013.80 |
| T (K) | 293(2) | 98(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | monoclinic | triclinic |
| Space group | $P21/c$ | $P\bar{1}$ |
| a (Å) | 13.4083(6) | 13.0396(11) |
| b (Å) | 19.5700(9) | 15.2420(13) |
| c (Å) | 20.3806(9) | 21.6406(19) |
| α (°) | 90 | 72.5290(10) |
| β (°) | 100.3620(10) | 75.1960(10) |
| γ (°) | 90 | 85.6360(10) |
| Volume (Å ³) | 5260.7(4) | 3966.5(6) |
| Z | 4 | 2 |
| D_{calc} (Mg/m ³) | 557 | 1.686 |
| Absorption coefficient (mm ⁻¹) | 2.726 | 3.401 |
| $F(000)$ | 2452 | 2000 |
| θ range for data collection (°) | 1.98 to 28.31 | 1.02 to 28.36 |
| Index ranges | $-17 \leq h \leq 17,$ $-25 \leq k \leq 26,$ $-27 \leq l \leq 26$ | $-17 \leq h \leq 17,$ $-20 \leq k \leq 20,$ $-27 \leq l \leq 28$ |
| Reflections collected | 45,511 | 36,541 |
| Independent reflections | 12,418 | 18,408 |
| Completeness to θ | $[R_{\text{int}} = 0.0219]$ 28.31° 94.8% | $[R_{\text{int}} = 0.0267]$ 28.36° 92.8% |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data/restraints/parameters | 12,418/3/631 | 15,206/0/1029 |
| Goodness-of-fit | 1.032 | 1.043 |
| R_1, wR_2 [$I > 2\sigma(I)$] | 0.0414, 0.1211 | 0.0267, 0.0444 |
| R indices (all data) | $R_1 = 0.0500,$ $wR_2 = 0.1278$ | $R_1 = 0.0338,$ $wR_2 = 0.0896$ |
| Largest different peak/hole (e Å ⁻³) | 1.031/–1.757 | 2.810/–1.196 |

Table 2
Selected bond lengths and angles for the complex $[CpOs\{C=C=C(Ph)_2\}(PPh_3)_2]PF_6$ (**1**)

| Bond lengths (Å) | | Bond angles (°) | |
|------------------|------------|-----------------|-----------|
| Os–C01 | 2.280(5) | C1–Os–P1 | 97.76(13) |
| Os–C02 | 2.269(5) | C1–Os–P2 | 89.53(14) |
| Os–C03 | 2.249(5) | P1–Os–P2 | 96.02(4) |
| Os–C04 | 2.254(5) | Os–C1–C2 | 170.2(4) |
| Os–C05 | 2.281(5) | C1–C2–C3 | 172.4(5) |
| Os–C1 | 1.897(4) | C2–C3–C71 | 121.7(5) |
| Os–P1 | 2.3514(11) | C2–C3–C81 | 118.0(5) |
| Os–P2 | 2.3271(11) | | |
| C1–C2 | 1.258(6) | | |
| C2–C3 | 1.350(6) | | |

deviation from the ideal value of 90°. The average bond distance of osmium to the carbon atoms of the cyclopentadienyl ligand is 2.266 Å. A bond distance of 1.897 Å for Os–C1 is in consistent with the double bond character as evidence from the other allenylidene osmium complexes, for example $[CpOs\{C=C=C(Ph)_2\}]$

Table 3
Selected bond lengths and angles for the complex $[(\text{CpOs})_2(\text{PPh}_3)_4(\mu\text{-C}_{10}\text{H}_{12})][\text{PF}_6]_2$ (**2**)

| Bond lengths (Å) | | Bond angles (°) | |
|----------------------|------------|-----------------|------------|
| Os1–P10 | 2.3472(14) | P3–Os1–P10 | 100.62(5) |
| Os1–P3 | 2.3240(14) | C37–Os1–P3 | 95.13(17) |
| Os1–C37 | 1.988(6) | C37–Os1–P10 | 89.72(16) |
| Os1–Cen ^a | 1.9189 | Os1–C37–C38 | 125.5(4) |
| Os2–P4 | 2.3591(14) | Os1–C37–C36 | 128.8(4) |
| Os2–P8 | 2.3758(14) | C31–Os2–P4 | 85.38(17) |
| Os2–C31 | 1.825(5) | C31–Os2–P8 | 101.47(17) |
| C31–C32 | 1.337(8) | Os2–C31–C32 | 167.9(5) |
| C32–C33 | 1.439(7) | C31–C32–C33 | 125.6(5) |
| Os2–Cen ^b | 1.9609 | C32–C33–C34 | 117.8(5) |
| | | C32–C33–C38 | 112.7(5) |

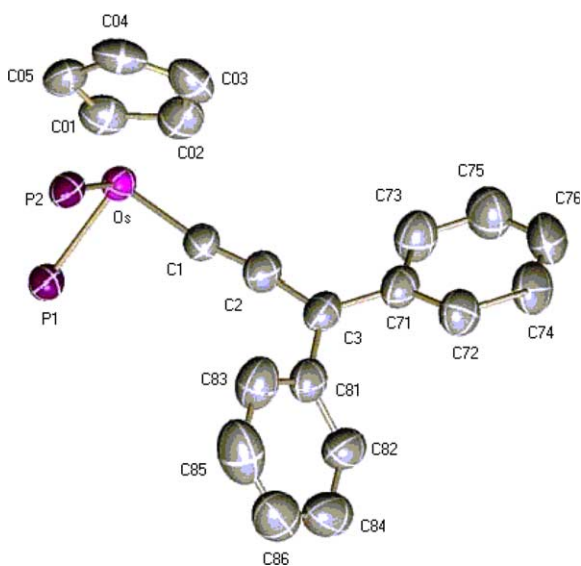


Fig. 1. Molecular structure of the complex $[\text{CpOs}\{\text{C}=\text{C}=\text{C}(\text{Ph})_2\}(\text{PPh}_3)_2]\text{PF}_6$ (**1**). All the hydrogens and the phenyl groups of phosphines are omitted for clarity.

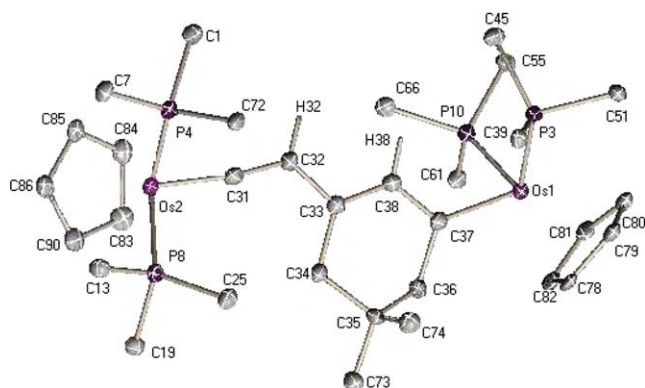
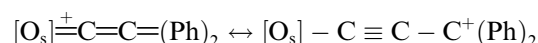


Fig. 2. Molecular structure of the complex $[(\text{CpOs})_2(\text{PPh}_3)_4(\mu\text{-C}_{10}\text{H}_{12})][\text{PF}_6]_2$ (**2**). All the hydrogens except H32 and the phenyl carbons (except ipso carbons) of phosphines are omitted for clarity.

$(\text{P}^i\text{Pr}_3)_2]\text{PF}_6$ [1.875 Å], $[(\eta^5\text{-C}_9\text{H}_7)\text{Os}\{\text{C}=\text{C}=\text{C}(\text{Ph})_2\}(\text{PPh}_3)_2]\text{PF}_6$ [1.895 Å], $[(\eta^6\text{-mes})\text{Os}(\text{C}=\text{C}=\text{C}(\text{Ph})_2)(\text{PMe}_3)\text{Cl}]\text{PF}_6$ [1.90 Å] [15]. The bond angles of Os–C1–C2 (170.2 Å) and C1–C2–C3 (172.4 Å) showed a deviation from the linear arrangement of the allenylidene chain. The C1–C2 bond length of 1.258 Å is nearly as short as carbon–carbon triple bond (1.20–1.21 Å) [16]. The C2–C3 bond length is not typical of an allene $\text{C}(\text{sp})\text{--C}(\text{sp}^2)$ double bond [16] and the observed value is very similar to that observed for $[(\eta^5\text{-C}_9\text{H}_7)\text{M}\{\text{C}=\text{C}=\text{C}(\text{Ph})_2\}(\text{PPh}_3)_2]\text{PF}_6$ (M = Ru, Os) [17]. The observed carbon–carbon distances in the allenylidene chain are not of expected for carbon–carbon double bond lengths [18], indicating a substantial contribution of the canonical forms as shown below.



In complex **2**, two typical $[\text{CpOs}(\text{PPh}_3)_2]$ moieties are bonded to a bridging $\text{C}_{10}\text{H}_{12}$ ligand. The Os2–C31–C32–C33 group comprises a vinylidene linkage, as suggested by a short Os2–C31 bond of 1.825 Å and a nearly linear bond angle of Os2–C31–C32 [167.9 (5)]. An allenylidene bond with a bond length of 1.899 Å links the second Os1 and C37 of the cyclohexene ring. As in the case of complex **1**, the geometry around the two-osmium atoms is slightly distorted octahedral. All the geometrical parameters are found to be in a close agreement with its ruthenium analogue [6b]. The peculiar nature of the crystals of **2** is that the residual electron density peaks, not within the bonding distance of any other atom, were refined as an oxygen molecule with a distance of 1.1 Å between the two oxygen atoms. Similar observation was observed in the case of ruthenium analogue [6b] except only one oxygen atom was found. It is presumably part of two water molecules although no associated protons were located.

6. X-ray structure analysis of the complexes

Suitable single crystals for X-ray analysis of complex **1** were grown from slow diffusion of diethylether in concentrated solution of **1** in chloroform and **2** were grown with same method using hexane and dichloromethane. The X-ray intensity data were measured at 98(2) K for **1** and 293(2) K for **2** on a Bruker Smart Apex CCD system equipped with graphite monochromator and a Mo $\text{K}\alpha$ fine-focus sealed tube operated at 1600 W power (50 kV, 32 mA). Intensities were extracted and then corrected for Lorentz and polarization effects through the SAINT program. The structures were solved and refined using the Bruker SHELXTL Software Package [19]. Data were corrected for absorption effects using the multiscan technique (SADABS) [20].

7. Conclusions

New osmium complexes $[\text{CpOs}(\text{=C=C=CPh}_2)(\text{PPh}_3)_2][\text{PF}_6]$ (**1**) and $[(\text{CpOs})_2(\mu\text{-C}_{10}\text{H}_{12})(\text{PPh}_3)_4][\text{PF}_6]_2$ (**2**) were obtained by the reaction of $[\text{CpOs}(\text{PPh}_3)_2\text{Br}]$ with the alkynols $\text{HC}\equiv\text{CCR}_2(\text{OH})$ ($\text{R} = \text{Ph, Me}$). These complexes were fully characterized with single crystal X-ray diffraction study.

8. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 219956 for complex **1** and 219955 for complex **2**, respectively. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

Acknowledgements

KMR thanks the DST (DST SERC: SP/S1/F-22/98), New Delhi for financial support. RL thanks the UGC for financial support in the form of DRS program.

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