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# Helical racemate architecture based on osmium(II)-polypyridyl complexes: Synthesis and structural characterisation

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**Abstract**

New polypyridyl osmium(II) complexes $[Os(\kappa^3\text{-tptz})(EPh_3)_2Cl]BF_4$ (E = P, **1**; As, **2**) with group 15 donor ligands are reported. Structural studies on the representative complex $[Os(\kappa^3\text{-tptz})(PPh_3)_2Cl]BF_4$ revealed formation of helical racemates with sidewise stacking of right and left-handed anti-parallel helical strands. Salient structural features and DNA binding studies along with binding constant [$6.6 \times 10^3$ $M^{-1}$] and site size [0.12] of the complex **1** with *calf thymus* (ct) DNA by absorption spectroscopy are described.


*Keywords:* Osmium(II)-polypyridyl complexes; Group 15 donor ligands; X-ray; Weak interactions; DNA binding constant; Helical racemates

## 1. Introduction

The investigations of polypyridyl transition metal complexes are of particular interest because of their potential use in many areas [1,2]. Self-assembled molecular helices are found in many biologically important macromolecules [3]. Formation of the helicates is governed by choice of the ligand, metal core and sometimes by reaction conditions [4]. A linear combination of two complex units lead to helicates but the binding to the metal centers in these units, determines twisting or sidewise stacking of the units. Vander Waals interaction play a vital role in the stabilization of such huge architectures. Further, it has been shown that transition metal complexes containing planar polypyridyl ligands are of significant importance in DNA binding studies [5b,5c]. Recently, we have been interested in the synthesis and characterization of metallo-ligands/synthons based on organometallic systems containing polypyridyl ligands [5a]. We have reported a new series of complexes $[Ru(\kappa^3\text{-L})(EPh_3)_2Cl]BF_4$ (E = P, As and L = tpy, tptz) containing both group 15 and polypyridyl ligands and have shown that these could be employed as precursor in the synthesis of other ruthenium complexes and that they behave as metallo-intercalators [5b,5c]. To examine the effect of the metal core and uncoordinated sites on the reactivity and DNA binding activity of the complexes, we have prepared analogous osmium complexes $[Os(\kappa^3\text{-tptz})(EPh_3)_2Cl]BF_4$ (E = P, As). Due to the presence of uncoordinated nitrogen donor sites on tptz ligand in these complexes, they may behave as potential metallo-ligands. Absorption titration studies on the osmium complexes with ct DNA indicated a moderate interaction with calf thymus DNA presumably in an intercalative manner between the base pairs of the DNA helix. The complexes under investigation present the first example of osmium complexes containing both group 15 and polypyridyl ligands [6]. In this short communication, we present preliminary results on the synthetic, spectral, structural including weak interactions studies and DNA binding behavior of the osmium complexes

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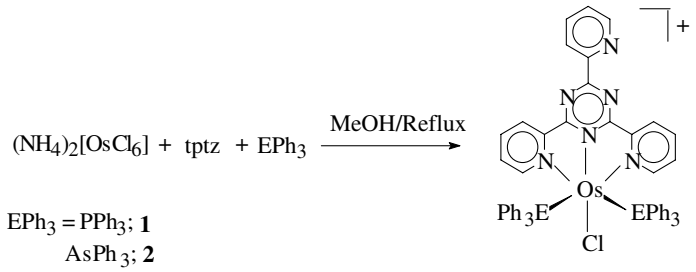
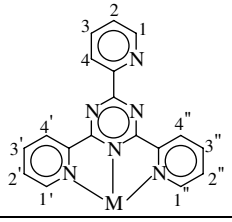



Scheme 1.

Table 1
$^1$H NMR data for complexes **1** and **2** relative to free tptz ligand

| Free tptz ligand | Complex **1** | Complex **2** |
|---|---|---|
| $\delta$ 8.98 (d, $3H_{1,1',1''}$) | $\delta$ 9.18 (d, $1H_1$) | $\delta$ 9.21 (d, $1H_1$) |
| $\delta$ 7.58 (t, $3H_{2,2',2''}$) | $\delta$ 8.19 (t, $1H_2$) | $\delta$ 8.27 (t, $1H_2$) |
| $\delta$ 8.01 (t, $3H_{3,3',3''}$) | $\delta$ 8.80 (t, $1H_3$) | $\delta$ 8.96 (t, $1H_3$) |
| $\delta$ 8.91 (d, $3H_{4,4',4''}$) | $\delta$ 9.08 (d, $1H_4$) | $\delta$ 9.04 (d, $1H_4$) |
| | $\delta$ 8.66 (d, $2H_{4',4''}$) | $\delta$ 8.72 (d, $2H_{4',4''}$) |
| | $\delta$ 8.09 (t, $2H_{3',3''}$) | $\delta$ 8.12 (t, $2H_{3',3''}$) |
| | $\delta$ 7.86 (t, $2H_{2',2''}$) | $\delta$ 7.59 (t, $2H_{2',2''}$) |
| | $\delta$ 9.59 (d, $2H_{1',1''}$) | $\delta$ 9.62 (d, $2H_{1',1''}$) |




with calf thymus DNA along with the binding constant '$K_b$' and site size value '$s$'.

## 2. Results and discussion

Reactions of ammonium hexachloro osmate(II) with 2,4,6-tris(2-pyridyl)1,3,5-triazine (tptz) in the presence of $EPh_3$ (E = P; **1** and As; **2**) under refluxing conditions, afforded a new series of cationic complexes $[Os(\kappa^3\text{-tptz})(EPh_3)_2Cl]^+$ in good yields (Scheme 1). The complexes were isolated as their tetrafluoroborate salts [7].

The cationic complexes $[Os(\kappa^3\text{-tptz})(EPh_3)_2Cl]^+$ possessing $\kappa^3$ bonded tptz, two tertiary phosphines or arsines and a labile chloro group have the potential to exhibit rich chemistry. Further, due to the presence of

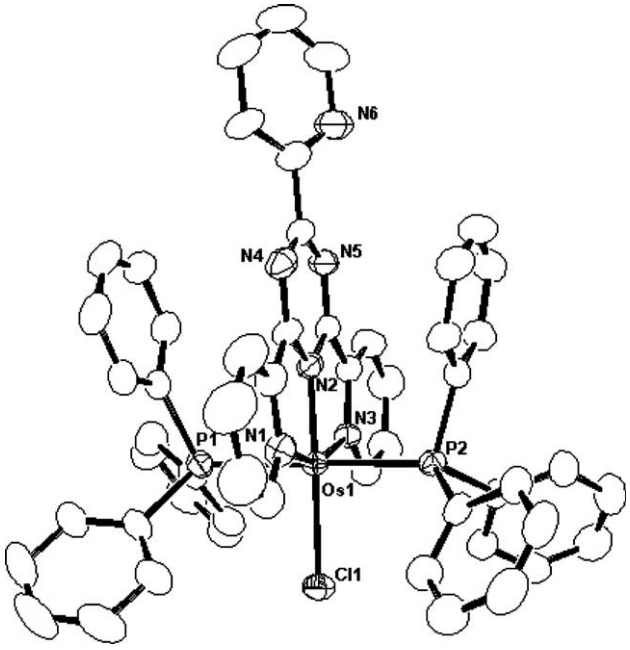



Fig. 1. X-ray crystal view for the complex **1**.

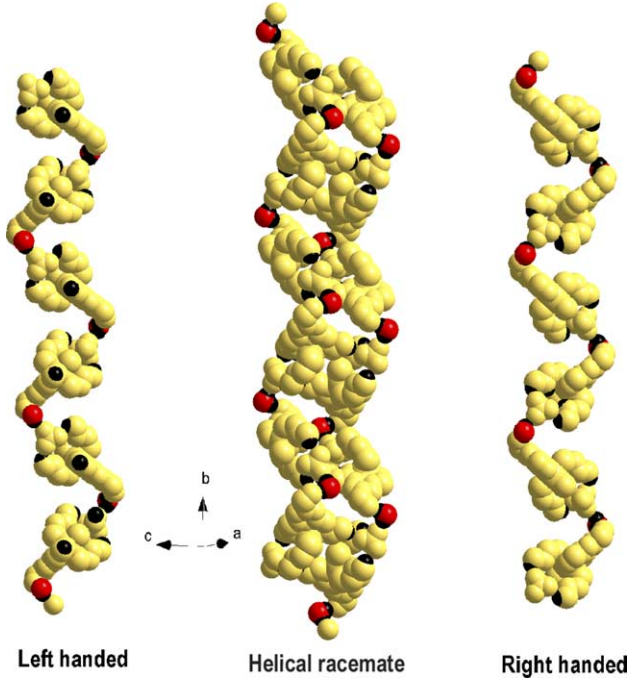



Fig. 2. Helical racemate architecture of complex **1**.

uncoordinated donor sites on tptz, these have the potential to behave as metallo-ligands and could find application in the synthesis of homo/hetero bi/poly nuclear systems. Like, analogous ruthenium complexes it reacted with NaCN and sodium diethyldithiocarbamate to give analogous substitution products as $[Ru(\kappa^3\text{-tptz})(PPh_3)(CN)_2]$ and $[Ru(\kappa^3\text{-tptz})(PPh_3)(dtc)]^+$, respectively [5b]. The structural identity of complexes **1** and **2** were established by a set of well-resolved signals in the $^1H$ NMR spectra of the complexes in $CDCl_3$ (Table 1). All the protons of the coordinated tptz ligands are shifted downfield with respect to that of the free ligand in both the complexes. The spectra were fully assigned with the help of $^1H$–$^1H$ COSY and data are resembled with the proposed structure. $^{31}P$ NMR of the complex **1** contained a singlet at $\delta$ −22.35 ppm. The presence of a singlet strongly supported the idea that the $^{31}P$ nuclei are equivalent and indicated that the $PPh_3$ groups are *trans* disposed.

Complex **1** crystallizes in the monoclinic space group $P2_1/c$ [8]. It consists of a macro cationic $[Os(\kappa^3\text{-tptz})(PPh_3)_2Cl]^+$ part, its neutrality is achieved by $[BF_4]^-$ and a water molecule is present in the crystal lattice. The osmium core is in a +2 oxidation state and is octahedrally coordinated, with three coordination sites occupied with the tptz ligand [Os–N(1) 2.105(3); Os–N(2) 1.935(3); Os–N(3) 2.092(3) Å], two for the *trans*-$PPh_3$ groups [P(1)–Os–P(2) 178.96(4); Os–P(1) 2.4097(11); Os–P(2) 2.4220(11) Å] and one for the chloro group [Os–Cl 2.4559(11) Å] which is *trans* to the nitrogen atom of the central triazine ring [N(2)–Os–Cl 177.08(10)] (Fig. 1) [9]. An interesting right and left-handed helical strand has been revealed in the crystal structure of the complex **1**. Crystal packing of the complex shows an extended helical superstructure (Fig. 2), where the stacked association of helical domains with opposite direction of growth and different arrangements of the metal complex, (Fig. 3(a)) by a series of two

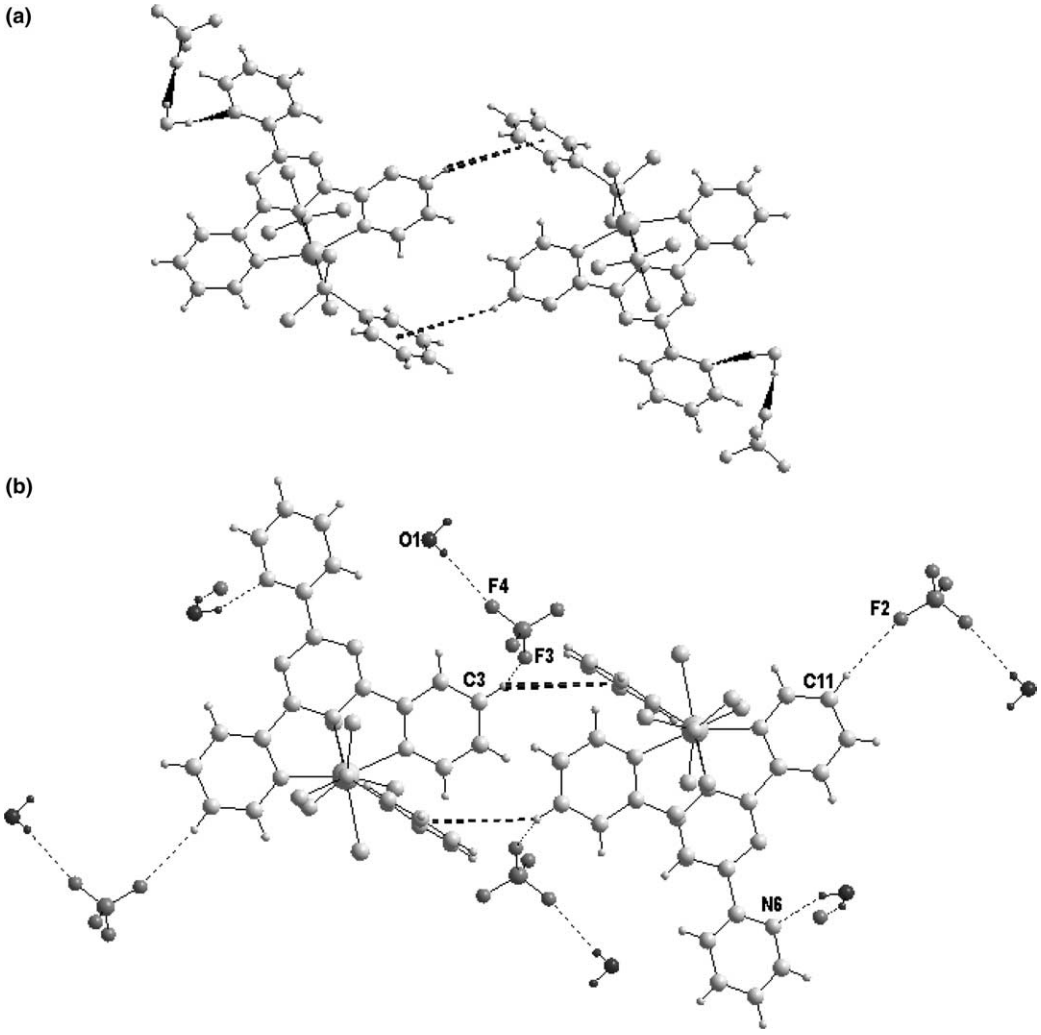



Fig. 3. (a) Opposite configuration of the metal complex unit for the complex **1** resulted via various intermolecular interactions. (b) Various interactions C–H...X (X = F and $\pi$) involved in the stabilization of helical recimate for the complex **1**.

equivalent pairs of intermolecular interaction generates a racemate of helical architecture [9c]. The two strands alternates up and down. One potential driving force for such stacking (Fig. 3a & b) is the various C–H···π(2.807 Å) interactions involving phenyl rings of $PPh_3$ and C–H···F (of $BF_4^-$) interactions [C3–H3···F3 2.560; C11–H11···F2 2.548 Å] involving the pyridyl ring of the ligand and the counter anion, which exists between adjacent strands (Table 2) [10]. It is also evident that the water molecule present in the crystal lattice plays an important role in the stabilization of these helical superstructures by acting as a linker between the complex units [O–H···N6 2.211; O–H···F4 2.326 Å]. It is noteworthy that due to the lack of void space in these densely packed complex molecules, the water molecules prefers to act as linker instead of occupying the voids [11]. The independent and anti-parallel behavior of these strands can be correlated with the opposite arrangement of the linkers (water molecule and counter anion $BF_4^-$) as well as the metal complex in both the strands. The pitch of the helix is calculated to be 24.915(8) Å containing four metal centers (two of each strand) per turn for both right- and left-handed strands [12]. The individual complex unit possibly in a $C_2$-symmetric state (with few distortion), loses this state upon the generation of such huge architecture and gains an unsymmetric $C_1$ state for the recemate.

Extensive studies have been conducted to exploit the mode of interaction of metal complexes with DNA [13]. It has been shown that both intercalation and surface binding are the most acceptable binding modes for non-planar octahedral complexes. Another non-classical mode is partial intercalation where the planar chromophore does not intercalate fully. In such cases the role of ancillary ligands becomes prominent, as these may prevent deep intercalation between the base pairs due to steric hindrance [13c]. In the present case, we have followed DNA interaction studies by an absorption titration method [5]. Buffer A (5 mM Tris–HCl, pH 7.1, 50 mM NaCl) was used for absorption titration. Fig. 4 depicts the absorption isotherm obtained for complex **1** with *calf thymus* DNA. Data were obtained after equilibration of the absorption titration of a fixed amount of the complex **1** (50 μM) with increasing amounts of *calf thymus* DNA (0–100 μM) at pH 7.1. The binding constant ('$K_b$') and base pair sites ('*s*') for complex **1** with *calf thymus* DNA were analyzed quantitatively by noting its decay in absorbance with increasing concentration of *calf thymus* DNA, following the model of Bard and Thorp for non-cooperative and non-specific binding [14]. The calculated value of $K_b$ and *s* for complex **1** are $6.6 \times 10^3$ $M^{-1}$ and 0.12, respectively. ($s < 1$ is comparable with other reports, $s = 0.02$) [13b,15]. The observed value of $K_b$ and *s* for the osmium complex is lower than that of observed for the analogous ruthenium complexes, Os(tptz) < Ru(tptz) [5b].

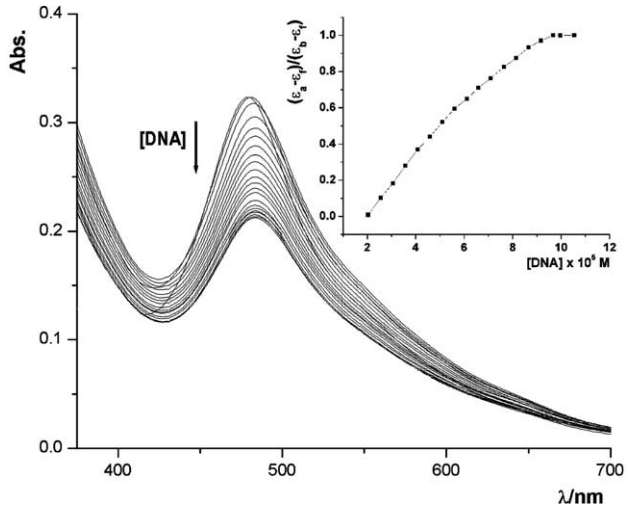



Fig. 4. Absorption spectra of $[Os(\kappa^3\text{-tptz})Cl(PPh_3)_2]^+$ (50 μM), in buffer A in the presence of increasing amount of CT DNA (0–100 μM). Inset represents plot of $(\varepsilon_a-\varepsilon_f)/(\varepsilon_a-\varepsilon_f)$ vs. [DNA]μM for $[\mathbf{1}]^+$. The best-fit data for the absorption titration [$K_b = 6.6 \times 10^3$ $M^{-1}$ ($s = 0.12$)].

Table 2
Relevant weak interaction parameters for complex **1**

| X–H···Y | *d* H···Y (Å) | *D* X–H···Y (Å) | *θ* X–H···Y (°) |
|---|---|---|---|
| O(1)–H(101)···N(6) | 2.21 | 2.9953 | 156 |
| O(1)–H(102)···F(4) | 2.33 | 3.0097 | 155 |
| C(11)–H(11)···F(2) | 2.55 | 3.4587 | 166 |
| C(20)–H(20)···Cl(1) | 2.80 | 3.6527 | 153 |
| C(32)–H(32)···Cl(1) | 2.70 | 3.4003 | 133 |
| C(44)–H(44)···Cl(1) | 2.71 | 3.5544 | 152 |
| C(54)–H(54)···Cl(1) | 2.68 | 3.5263 | 151 |

The extracted binding constant for this complex shows moderate binding with *calf thymus* DNA and this may be due to steric hindrance caused by bulky phosphines, which block further intercalation of the planar part of the tptz ligand between the base pairs. The absorption spectra exhibited 65% hypochromism and a bathochromic shift of 5 nm suggesting partial intercalation of the planar part of tptz ligand in the complex **1** is probably the mode of interaction [5b]. Further, the presence of an isobestic point at 278 nm strengthened the above fact.

## 3. Conclusions

We have shown that the Os(II) polypyridyl complexes $[Os(\kappa^3\text{-tptz})(EPh_3)_2Cl]^+$ presents an excellent example of an three-dimensional recemate of right and left-handed anti-parallel stacked helical strands, where such a self assembled process was assisted by counter ions and the water molecule of crystal lattice. We have also detailed on interaction study with *calf thymus* DNA and found a weak interaction. More detailed investigations towards reactivity of the complexes leading to substitu-

tion products, biocatalytic aspects, and self-assembling processes are in progress.

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## Appendix A. Supplementary data

$^1H$–$^1H$ COSY spectra, Tables including bond parameters and full scale UV-Visible titration spectra for complex **1** are available as supporting materials. Crystallographic data for the complex **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 245835 in CIF format. 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.uk or www://ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.03.051.

## References

[1] (a) J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995;
(b) N.H. Dam-rauer, G. Cerullo, A. Yeh, T.R. Boussie, C.V. Shank, J.K. McCusker, Science 275 (1997) 54;
(c) C. Metcalfe, S. Spey, H. Adams, J.A. Thomas, J. Chem. Soc., Dalton Trans. (2002) 4732;
(d) S. Rau, B. Schafer, S. Schebesta, A. Grüßing, W. Poppitz, D. Walther, M. Dauti, W.R. Browne, J.G. Vos, Eur. J. Inorg. Chem. (2003) 1503;
(e) J.D. Soper, J.M. Mayer, J. Am. Chem. Soc. 125 (2003) 12217.

[2] (a) W.R. Browne, C.M. O'Connor, H.P. Hughes, R. Hage, O. Walter, M. Doering, J.F. Gallagher, J.G. Vos, J. Chem. Soc., Dalton Trans. (2002) 4048;
(b) T. Steiner, Angew, Chem., Int. Ed. 41 (2002) 48;
(c) Y. Wang, J. Yu, M. Guo, R. Xu, Angew. Chem., Int. Ed. 42 (2003) 4089;
(d) K.E. Erkkila, D.T. Odom, J.K. Barton, Chem. Rev. 99 (1999) 2777.

[3] T.J. Katz, Angew. Chem., Int. Ed. 39 (2000) 1921.

[4] (a) C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. 97 (1997) 2005;
(b) C.-Y. Su, Y.-P. Cai, C.-L. Chen, F. Lissner, B.-S. Kang, W. Kaim, Angew. Chem. 114 (2002) 3519.

[5] (a) M. Chandra, A.N. Sahay, D.S. Pandey, R.P. Tripathi, J.K. Saxena, V.J.M. Reddy, M.C. Puerta, P. Valerga, J. Orgnomet. Chem. 689 (2004) 2256;
(b) S. Sharma, M. Chandra, D.S. Pandey, Eur. J. Inorg. Chem. (2004) 3555;
(c) S. Sharma, S.K. Singh, M. Chandra, D.S. Pandey, J. Inorg. Biochem. 99 (2005) 458.

[6] (a) M.H.V. Huynh, D.G. Lee, P.S. White, T.J. Meyer, Inorg. Chem. 40 (2001) 3842;
(b) P. Paul, B. Tyagi, A.K. Bilakhiya, P. Dastidar, E. Suresh, Inorg. Chem. 39 (2000) 14;
(c) P. Paul, Proc. Indian Acad. Sci. (Chem. Sci.) 114 (2002) 269.

[7] (a) Synthesis of $[Os(\kappa^3\text{-tptz})(PPh_3)_2Cl]BF_4 \cdot H_2O$ (**1**): A methanolic solution of ammonium hexachloro osmate(II) (0.430 g, 1.0 mmol) was added to a refluxing solution of triphenylphosphine (1.578 g, 6.0 mmol) in methanol (50 mL) and the resulting solution was refluxed for 1 h. Tptz (0.312 g, 1.0 mmol) was added to the resulting suspension and the contents of the flask were again refluxed for 8–10 h. The dark purple solution was cooled at room temperature and was filtered to remove any solid residue. The filtrate was reduced to one fourth of its volume under pressure. A saturated solution of ammonium tetrafluoroborate dissolve in methanol was added to the resulting concentrated solution and left for slow crystallization in the refrigerator at ~4 °C. A microcrystalline product was obtained and which was separated by filtration and washed repeatedly with methanol ($2 \times 10$ mL) and diethyl ether ($2 \times 10$ mL) and dried under vacuum. X-ray suitable block shaped crystals were grown by diffusion technique from dichloromethane and pet ether (60–80 °C) Yield: 0.874 g (76%). Anal. Calc. for $BC_{54}ClF_4H_{44}N_6OP_2Os$: C, 55.48; H, 3.77; N, 7.19. Found: C, 55.64; H, 3.69; N, 7.24. *m/z* (observed, relative intensity, assignments): 1063, 65, [M + 1]; 800, 80, [M − $PPh_3$ + 1]; 764, 48, [M − $PPh_3$ − Cl + 1]; 500, 10, [M − $PPh_3$ − Cl − $PPh_3$ + 1]. $^1H$ NMR ($\delta$ ppm, $CDCl_3$): 9.59 (d, 2H, $J = 5.4$), 9.18 (d, 1H, $J = 7.5$), 9.08 (d, 1H, $J = 7.5$), 8.80 (t, 1H, $J = 7.8$), 8.66 (d, 2H, $J = 7.8$), 8.19 (t, 1H, $J = 6.0$), 8.09 (t, 2H, $J = 7.5$), 7.86 (t, 1H, $J = 6.3$) and 7.29–7.17 ppm (br.m, 15H, aromatic protons of $PPh_3$). $^{31}P$ NMR ($\delta$ ppm, $CDCl_3$): −22.35 (s). UV–Vis {$CH_2Cl_2$, $\lambda_{max}$ nm ($\varepsilon$ $M^{-1}\,cm^{-1}$)}: 476 ($6.1 \times 10^3$), 346 ($5.7 \times 10^3$), 290 ($1.4 \times 10^4$), 252 ($2.3 \times 10^4$);
(b) Synthesis of [Synthesis of $[Os(\kappa^3\text{-tptz})(AsPh_3)_2Cl]BF_4$ (**2**): It was prepared following the above procedure, except using triphenylarsine (1.830 g, 6.0 mmol) in place of triphenylphosphine. Yield: 0.913 g (74%). Anal. Calc. for $BC_{54}ClF_4H_{42}N_6As_2Os$: C, 56.25; H, 3.82; N, 7.29. Found: C, 56.42; H, 3.67; N, 7.32. *m/z* (observed, relative intensity, assignments): 1047, 59 [M + 1], 842, 64 [M − $AsPh_3$ + 1], 806, 35, [M − $AsPh_3$ − Cl + 1]. $^1H$ NMR ($\delta$ ppm, $CDCl_3$): 9.62 (d, 2H, $J = 5.4$), 9.21 (d, 1H, $J = 7.6$), 9.04 (d, 1H, $J = 7.5$), 8.96 (t, 1H, $J = 7.7$), 8.72 (d, 2H, $J = 7.8$), 8.27 (t, 1H, $J = 6.2$), 8.12 (t, 2H, $J = 7.5$), 7.95 (t, 2H, $J = 6.2$) and 7.30–7.2 (br.m, 15H, aromatic protons of $AsPh_3$). UV–Vis {$CH_2Cl_2$, $\lambda_{max}$ nm ($\varepsilon$, $M^{-1}\,cm^{-1}$)}: 481 ($5.8 \times 10^3$), 351(sh), 292(sh), 257(sh).

[8] Crystal data for **1**: $BC_{54}ClF_4H_{42}N_6P_2Os \cdot H_2O$, $M = 1167.35$, purple cubes ($0.40 \times 0.20 \times 0.20$ mm), monoclinic, $P2_1/c$, $a = 12.3610(6)$, $b = 24.915(3)$, $c = 16.2820(11)$ Å, $\alpha = 90$, $\beta = 100.993(5)$, $\gamma = 90°$, $V = 4922.4(7)$ Å$^3$, $Z = 4$, $D_{calc} = 1.575$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 2.772 mm$^{-1}$, $\lambda = 0.70930$ Å. Collected reflection 8977, 8649 are unique [$R_{int} = 0.0268$], final $R_1 = 0.0302$, $wR_2 = 0.0620$ [$I > 2\sigma(I)$], and GOF = 1.042 (for all data, $R_1 = 0.0586$, $wR_2 = 0.0684$). The function minimized for complex **1** was $\sum w(F_o - F_c)^2$ where $w^{-1} = [\sigma^2(F_0^2) + (0.0271P)^2 + 3.7619P]$, where $P = (F_o^2 + 2F_c^2)/3$.

[9] (a) A.D. Ryabov, V.S. Soukharev, L. Alexandrova, R. Le Lagadec, M. Pfeffer, Inorg. Chem. 42 (2003) 6598;
(b) S.K. Leung, J.S. Huang, N. Zhu, C.M. Che, Inorg. Chem. 42 (2003) 7266;
(c) B.F. Abrahams, S.R. Batten, H. Hamit, B.F. Hoskins, R. Robson, Chem. Commun. (1996) 1313.

[10] (a) S.J. Carlson, T.-B. Lu, R.L. Luck, Inorg. Chem. Commun. 6 (2003) 455;
(b) G.R. Desiraju, Acc. Chem. Res. 35 (2002) 565;
(c) H. Suezawa, T. Yoshida, S. Ishihara, Y. Umezawa, M. Nishio, Cryst. Eng. Commun. 5 (2003) 514.
[11] (a) D.L. Reger, R.F. Semeniuc, V. Rassolov, M.D. Smith, Inorg. Chem. 43 (2004) 537;
(b) J. Xu, T.N. Parac, K.N. Raymond, Angew. Chem., Int. Ed. Engl. 38 (1999) 2878.
[12] R. Custelcean, M.D. Ward, Angew. Chem., Int. Ed. Engl. 41 (2002) 1724.
[13] (a) N. Gupta, N. Grover, G.A. Neyhart, W. Liang, P. Singh, H.H. Thorp, Angew. Chem., Int. Ed. Engl. 31 (1992) 1048;
(b) R.B. Nair, E.S. Teng, S.L. Kirkland, C.J. Murphy, Inorg. Chem. 37 (1998) 139;
(c) A.M. Pyle, J.P. Rehmann, R. Meshoyrer, C.V. Kumar, N.J. Turro, J.K. Barton, J. Am. Chem. Soc. 111 (1989) 3051.
[14] (a) M.T. Carter, M. Rodriguez, A.J. Bard, J. Am. Chem. Soc. 111 (1989) 8901;
(b) S.R. Smith, G.A. Neyhart, W.A. Karlsbeck, H.H. Thorp, New J. Chem. 18 (1994) 397.
[15] (a) J.-G. Liu, Q.-L. Zhang, X.-F. Shi, L.-N. Ji, Inorg. Chem. 40 (2001) 5045;
(b) A. Frodl, D. Herebian, W.S. Sheldrick, J. Chem. Soc., Dalton Trans. (2002) 3664.