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Journal of Organometallic Chemistry 690 (2005) 3105–3110

Journal of Organometallic Chemistry

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

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Received 11 December 2004; revised 10 March 2005; accepted 14 March 2005
Available online 23 May 2005

**Abstract**

New polypyridyl osmium(II) complexes [Os($\kappa^3$-tptz)($EPh_3$)$_2$Cl]$BF_4$ (E = P, **1**; As, **2**) with group 15 donor ligands are reported. Structural studies on the representative complex [Os($\kappa^3$-tptz)($PPh_3$)$_2$Cl]$BF_4$ 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.
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*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($\kappa^3$-L)($EPh_3$)$_2$Cl]$BF_4$ (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($\kappa^3$-tptz)($EPh_3$)$_2$Cl]$BF_4$ (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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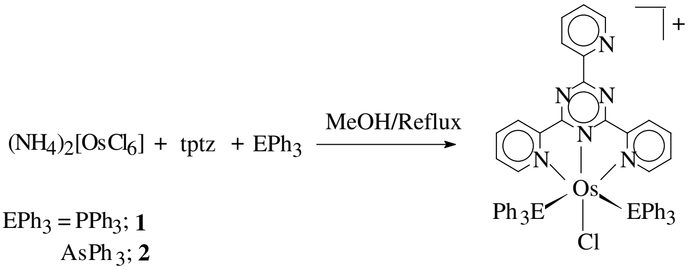
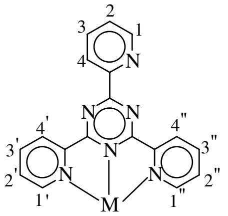
doi:10.1016/j.jorganchem.2005.03.051



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

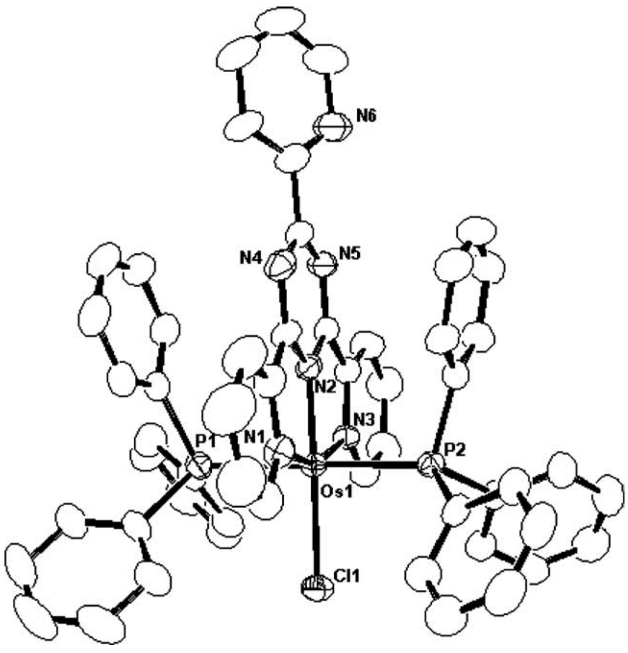


Fig. 1. X-ray crystal view for the complex **1**.

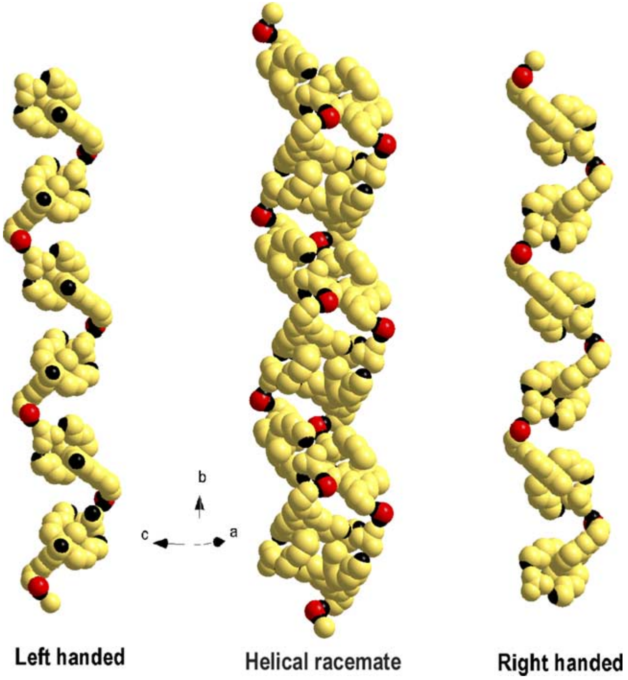


Fig. 2. Helical racemate architecture of complex **1**.