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Synthesis and reactivity studies of cyclopentadienyl bis(triphenylphosphine)osmium(II) complexes. Crystal and molecular structure of [CpOs(PPh$_3$)(phen)]BF$_4$

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Abstract

Reaction of [CpOs(PPh$_3$)$_2$Br] (**1**) with acetonitrile ligand or monodentate anions yielded complexes of the type [CpOs(PPh$_3$)$_2$(CH$_3$CN)]$^+$ (**2**), [CpOs(PPh$_3$)$_2$X], X = CN (**3**) and NCS (**4**). Treatment of **1** with NaNO$_2$–HCl in the presence of NH$_4$BF$_4$ yielded the dicationic complex [CpOs(PPh$_3$)$_2$(NO)](BF$_4$)$_2$ (**5**). Reactions of the complex [CpOs(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (**2**) with chelating ligands L$_2$ yielded cationic complexes of the type [CpOs(L$_2$)(PPh$_3$)]BF$_4$, where L$_2$ = 2,2′-bipyridine (bipy) (**6**), 1,10-phenanthroline (phen) (**7**). These compounds were characterized by ^{1}H NMR, ^{31}P NMR and IR spectral data. The X-ray crystal structure of the complex [CpOs(PPh$_3$)(phen)]BF$_4$ has been determined.

Keywords: Cyclopentadienyl; Osmium; Chelating ligands; Bipyridine; Phenanthroline

1. Introduction

Cyclopentadienyl ruthenium half sandwich complexes are the most extensively studied class of cyclopentadienyl chemistry among the transition metal complexes. The spectrum of reactivity and chemical properties to date for this system is remarkable, especially considering the limited number of synthetic precursors, viz. [CpRu(PPh$_3$)$_2$Cl] and [CpRu(CO)$_2$Cl] [1]. Recently, more convenient routes have been developed by use of easily exchangeable ligands [2]. However, not much work has been carried out in the case [CpOs(PPh$_3$)$_2$Br], which could be due to lower kinetic lability of the phosphines compared to its ruthenium analogue. For instance, in the case of ruthenium, the substitution of two triphenylphosphines by chelating diphos ligands takes place readily in boiling benzene or toluene, whereas the same reaction requires boiling decaline for several hours in case of its osmium analogue [3]. But it was observed that the dissociation of the M–X bond takes place readily in polar solvents such as methanol for both cases [4].

We recently reported the reactions of [(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$(CH$_3$CN)]$^+$ and [(η^5-C$_9$H$_7$)Ru(PPh$_3$)$_2$(CH$_3$CN)]$^+$ with bipy and phen and presented their results [5]. In this paper, we would like to report a few substitution reactions at Os–Br and Os–P bonds. In methanol, bromide was replaced by other anions to give neutral complexes of the type [CpOs(PPh$_3$)$_2$X] and in acetonitrile, the cationic complex [CpOs(PPh$_3$)$_2$(NCCH$_3$)]$^+$ was isolated. Reaction of [CpOs(PPh$_3$)$_2$(NCCH$_3$)]BF$_4$ with chelating ligands L$_2$ by refluxing in toluene followed by methanol yielded cationic complexes [CpOs(L$_2$)(PPh$_3$)]BF$_4$, where L$_2$ = bipy and phen. The molecular structure of [CpOs(PPh$_3$)(phen)]BF$_4$ has been solved by X-ray crystallography.

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2. Experimental

All solvents were dried and distilled by standard methods. All chemicals were obtained from commercial sources. Infrared spectra were recorded as KBr pellets (CsI for complex **5**) using a Perkin–Elmer model-983 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external tetramethylsilane. ^{31}P {^{1}H} NMR chemical shifts are recorded relative to H_3PO_4 (85%). Elemental analyses were performed by the Regional Sophisticated Instrumentation Centre (RSIC), NEHU, Shillong.

2.1. Preparation of [CpOs(PPh$_3$)$_2$Br] (1)

This compound was prepared by following a literature procedure [6].

^{1}H NMR ($CDCl_3$, δ): 7.25 (m, 30H, Ph), 4.31 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): −3.85 (s).

2.2. Preparation of [CpOs(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (2)

A mixture of [CpOs(PPh$_3$)$_2$Br] (100 mg, 0.116 mmol) and NH_4BF_4 (25 mg, 0.24 mmol) was refluxed in acetonitrile (20 ml) under nitrogen atmosphere. The insoluble starting material slowly dissolved and the color changed to very pale yellow solution after 1 h. The solvent was then evaporated under reduced pressure. The residue was extracted with acetone, filtered and the volume of the filtrate was reduced. Subsequent addition of hexane yielded a cream colored product. The compound recrystallised from dichloromethane–diethylether giving grey needle shaped crystals.

Yield: 86 mg, 82%. *Anal.* Found: C, 56.88; H, 4.20; N, 1.56. Calc. for $C_{43}H_{38}BF_4NP_2Os$: C, 56.89; H, 4.21; N, 1.54%. ^{1}H NMR ($CDCl_3$, δ): 7.34–7.01 (m, 30 H, Ph), 4.66 (s, 5H, Cp), 2.41 (s, 3H, CH_3). ^{31}P{^{1}H} NMR (δ): 2.11 (s). IR (KBr): 2282 (m, ν_{CN}), 1082 (s, br, ν_{BF}).

2.3. Preparation of [CpOs(PPh$_3$)$_2$CN] (3)

A mixture of [CpOs(PPh$_3$)$_2$Br] (200 mg, 0.233 mmol) and 600 mg of KCN was refluxed in methanol (20 ml) for 3 h. A pale yellow solution was evaporated to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 and excess KCN was filtered off. Addition of excess hexane into the CH_2Cl_2 solution yielded the product as a colorless crystalline solid.

Yield: 120 mg, 64%. *Anal.* Found: C, 62.55; H, 4.36; N, 1.69. Calc. for $C_{42}H_{35}NP_2Os$: C, 62.59; H, 4.37; N, 1.73%. ^{1}H NMR ($CDCl_3$, δ): 7.33 (m, 30H, Ph), 4.46 (s, 5H, Cp). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 2.76 (s).IR (KBr, ν_{CN}): 2063 (s).

2.4. Preparation of [CpOs(PPh$_3$)$_2$(NCS)] (4)

This complex was prepared in a similar manner to that of complex **3**. Here KSCN was used instead of KCN. The compound is yellow in color.

Yield: 60 mg, 64%. *Anal.* Found: C, 59.99; H, 4.16; N, 1.59. Calc. for $C_{42}H_{35}NP_2SOs$: C, 60.20; H, 4.21; N, 1.67%. IR (KBr, ν_{NCS}): 2108 (s).

2.5. Preparation of [CpOs(PPh$_3$)$_2$(NO)](BF$_4$)$_2$ (5)

The mixture of [CpOs(PPh$_3$)$_2$Br] (100 mg, 0.116 mmol) and 1 ml HCl was refluxed in EtOH (30 ml) for 1 h. Then $NaNO_2$ (168 mg, 2.434 mmol) in water (1 ml) was added, the whole mixture turns into a homogeneous yellowish clear solution which was filtered while hot. NH_4BF_4 (aq) was added to the filtrate which was then left overnight resulting in the formation of a yellow precipitate that was collected by centrifuge.

Yield = 60 mg, 52.6%. *Anal.* Found: C, 49.98; H, 3.00; N, 1.45. Calc. for $C_{41}H_{35}B_2F_8NOP_2Os$: C, 50.07; H, 3.07; N, 1.42%. ^{1}H NMR ($CDCl_3$, δ): 7.51–7.05 (m, 30H, Ph), 6.23 (s, 5H, Cp). ^{31}P{^{1}H} NMR (δ): −2.06 (s). IR (CsI): 1845 (s, ν_{NO}), 1062 (s, br,ν_{BF}).

2.6. Preparation of [CpOs(PPh$_3$)(bipy)]BF$_4$ (6)

A mixture of [CpOs(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (100 mg, 0.110 mmol) and 2,2′-bipyridine (55 mg, 0.354 mmol) was refluxed in toluene (30 ml) for 12 h and the solvent was removed in a rotary evaporator to dryness. Then methanol (30 ml) was added, the solution turned a deep red color and was refluxed for 10 h. Methanol was removed in a rotary evaporator under reduced pressure. The residue was dissolved in dichloromethane and loaded onto a silica gel column (hexane) where 20 ml of dichloromethane was first run to this column. The red band of the compound was eluted with a mixture of CH_2Cl_2 and methanol (3:1). The solution was evaporated to dryness, dissolved in acetone (~ 1 ml) and addition of excess hexane precipitated the product as a dark red crystals.

Yield: 30 mg, 35.8%. *Anal.* Found: C, 52.00; H, 3.56; N, 3.50. Calc. for $C_{33}H_{28}BF_4N_2POs$: C, 52.11; H, 3.71; N, 3.68%. ^{1}H NMR ($CDCl_3$, δ): 9.29 (d), 7.87 (d), 7.68 (t), 7.40–6.70 (m), 4.90 (s, Cp). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 16.65 (s). IR (KBr, ν_{BF}): 1089 (s, br). UV–Vis (λ_{max} in CH_3CN) = 392 nm.

2.7. Preparation of [CpOs(PPh$_3$)(Phen)]BF$_4$ (7)

This compound was prepared in similar manner to the preparation of **6** except 1,10-phenanthroline was used instead of 2,2′-bipyridine.

Yield: 36 mg, 41.6%. *Anal.* Found: C, 53.55; H, 5.56; N, 3.50. Calc. for $C_{35}H_{28}BF_4N_2POs$: C, 53.57; H, 3.59;

N, 3.57%. ^{1}H NMR (acetone-d_6 δ): 9.91 (d, 2H), 8.39 (d, 2H) 8.03 (s, 2H) 7.63 (d, 2H), 7.30–6.92 (m, 17H), 5.21 (s, 5H, Cp). ^{31}P{^{1}H} NMR (δ): 22.60 (s). IR (KBr): 1089 (s, br, ν_{BF}); UV–Vis (λ_{max}, in CH_3CN) = 375 nm.

2.8. Crystallographic analysis

Single crystals suitable for x-ray analysis were grown by slow diffusion of hexane into acetone solution. X-ray intensity data were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromatic Mo Kα radiation ($\lambda = 0.71069$ Å) at a temperature of 293 K. Indexing was performed from a series of 1° oscillation images with exposures of 100 s per frame. A hemisphere of data was collected using 6° oscillation angles with exposures of 100 s per frame and a crystal-to-detector distance of 82 mm. Oscillation images were processed using BIOTEX [8], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the TEXSAN [9] program package for further processing and structure solution on a Silicon Graphics O_2 computer. A total of 22223 reflections were measured over the ranges $5.02 \leq 2\theta \leq 54.96°$, $-23 \leq h \leq 23$, $-10 \leq k \leq 12$, $-24 \leq l \leq 24$ yielding 6737 unique reflections ($R_{int} = 0.0395$). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB [10] (minimum and maximum transmission 0.655, 1.000) Table 1.

The structure was solved by direct methods (SIR-92 [11]). Refinement was by full-matrix least-squares based on F^2 using SHELXL-93 [12]. All reflections were used during refinement (F^2 values that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + 0.0516P^2 + 9.8409P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a 'riding' model. Refinement converged to $R_1 = 0.0488$ and $wR_2 = 0.1114$ for 6050 reflections for which $F > 4\sigma(F)$ and $R_1 = 0.0563$, $wR_2 = 0.1166$ and GOF = 1.134 for all 6737 unique, non-zero reflections and 398 variables. The maximum Δ/σ in the final cycle of least squares was 0.002 and the two most prominent peaks in the final difference Fourier were +1.170 and −1.262 e Å^{-3}.

Fig. 1 is an ORTEP [13] representation of the molecule with 30% probability thermal ellipsoids displayed.

3. Results and discussion:

The reaction of the complex [$CpOs(PPh_3)_2Br$] with anions take place by refluxing in methanol yielding complexes of the type [$CpOs(PPh_3)_2X$] via the solvated compound [$CpOs(PPh_3)_2(MeOH)$]$^+$ as shown in Scheme 1. Complex **2** was obtained by refluxing **1** in acetonitrile in the presence of NH_4BF_4.

Table 1
Summary of structure determination of compound [$CpOs(PPh_3)(phen)$]BF_4

Formula	$OsC_{35}BH_{28}PN_2F_4$
Formula weight	784.57
Crystal class	monoclinic
Space group	$P2_1/n$ (no. 14)
Z	4
Unit cell dimensions	
a (Å)	18.2243(2)
b (Å)	9.49800(10)
c (Å)	19.0352(2)
β (°)	113.8630(10)
V (Å^3)	3013.22(6)
μ (cm^{-1})	43.38
Crystal size (mm)	0.35 × 0.32 × 0.10
D_{calc} (g cm^{-3})	1.729
F(000)	1536
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
2θ range (°)	5.02–54.96
hkl collected	$-23 \leq h \leq 23$; $-10 \leq k \leq 12$; $-24 \leq l \leq 24$
No. reflections measured	22223
No. unique reflections	6737 ($R_{int} = 0.0395$)
No. observed reflections	6050 ($F > 4\sigma$)
No. reflections used in refinement	6737
No. parameters	398
R indices ($F > 4\sigma$) [a]	$R_1 = 0.0488$, $wR_2 = 0.1114$
R indices (all data)	$R_1 = 0.0563$, $wR_2 = 0.1166$
GOF [b]	1.134
Final difference peaks (e Å^{-3})	+1.170, −1.262

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2\}^{1/2}$.

[b] GOF = $\{\Sigma\, w(F_o^2 - F_c^2)^2/(n-p)\}^{1/2}$, where n = the number of reflections and p = the number of parameters refined.

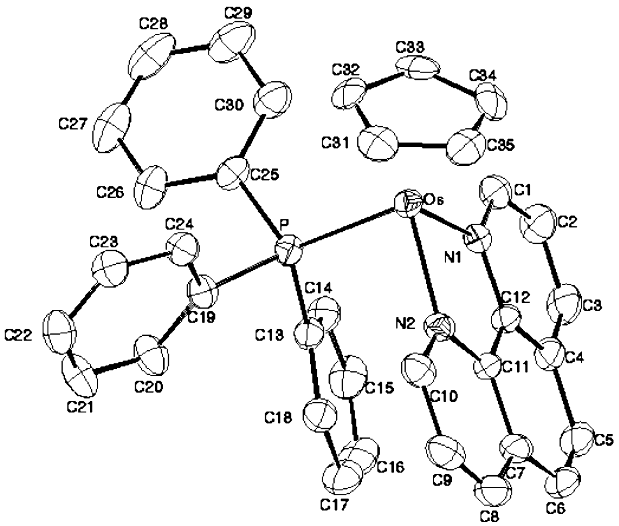

Fig. 1. ORTEP drawing of compound **7** with 30% probability thermal ellipsoids. Hydrogen atoms and BF_4 omitted for clarity.

All these complexes are colorless to pale yellow colored and soluble in most organic solvents. Complex **2** displays a characteristic IR band at 2282 cm^{-1} due to

$$[CpOs(PPh_3)_2Br] \xrightarrow{CH_3CN} [CpOs(PPh_3)_2\,(CH_3CN)]^+\ (\mathbf{2})$$

$$[CpOs(PPh_3)_2Br] \longrightarrow [CpOs(PPh_3)_2(MeOH)]^+ \xrightarrow{X^-} [CpOs(PPh_3)_2X]$$

X= CN (**3**), NCS (**4**)

Scheme 1.

ν_{CN} of CH_3CN. This compound has been isolated as the tetraphenylborate salt [3]. The ^1H NMR spectrum of the complex exhibited the resonance of the CH_3 protons of coordinated acetonitrile as a singlet at δ 2.41 [lit. δ 1.33 (t)]. The IR spectra of complexes **3** and **4** showed strong bands at 2063 and 2108 cm^{-1} for ν_{CN} and ν_{NCS} respectively [4a].

The reaction of **1** with $NaNO_2$ and HCl (aq) in ethanol yielded a yellow compound which was characterized as $[CpOs(PPh_3)_2(NO)](BF_4)_2$ (**5**). This compound showed a strong ν_{NO} band at 1848 cm^{-1} indicating a linear Os–NO bond [7]. The ^1H NMR spectrum of this complex exhibited a resonance for the deshielded Cp protons at 6.23 ppm, a very significant shift compared to the starting complex **1** (4.31 ppm) that indicates a good π-accepting ability of the nitrosyl ligand. However, the same reaction conditions in the case of the ruthenium analogue resulted in the dissociation of one triphenylphosphine forming $[CpRu(PPh_3)(NO)Cl]BF_4$ [7]. The integration of the ^1H NMR spectrum, the absence of band in the range of 200–300cm^{-1} (Os–Br) in the far IR spectrum and the analytical data suggested the compound to be $[CpOs(PPh_3)_2NO](BF_4)_2$ (**5**). Moreover, only a slight shift of phosphorus resonance in the ^{31}P NMR was observed in comparison to the starting complex. We feel that there would be significant shift in the position of the phosphorus peak in the ^{31}P NMR if one triphenylphosphine had been replaced from the metal centre. The formation of the dication of $[CpOs(PPh_3)_2NO](BF_4)_2$ has been reported previously via a different route [14].

Treatment of $[CpOs(PPh_3)_2Br]$ (**1**) with excess of ligands L_2 such as 2,2′-bipyridine or 1,10-phenanthroline in methanol, toluene or benzene under refluxing condition even after 2 days does not give the expected compounds. However, the reaction of $[CpOs(PPh_3)_2(CH_3CN)]BF_4$ (**2**) with bipy and phen yielded cationic complexes of the type $[CpOs(PPh_3)(L_2)]BF_4$, which were isolated as dark red compounds.

$$[CpOs(PPh_3)_2(CH_3CN)]BF_4 \overset{i\ \text{and}\ ii}{\rightarrow} [CpOs(PPh_3)(L_2)]BF_4$$

where i = toluene; ii = methanol; L_2 = bipy (**6**) and phen (**7**).

A downfield shift of the cyclopentadienyl protons in comparison to the starting complex was observed in the ^1H NMR spectra. The parent complex $[CpOs(PPh_3)_2(CH_3CN)]BF_4$, (**2**) showed the resonance for the cyclopentadienyl protons at 4.66 ppm while complexes **6** and **7** exhibited the resonance for the same at δ 4.91 and 5.21 ppm, respectively. This indicates that there is a significant deshielding after substituting CH_3CN and one PPh_3 with chelating N,N′-donor heterocyclic ligands. The ^1H NMR spectra of these complexes also showed a multiplet in the range of 7.0–9.5 ppm due to the phenyl protons of triphenylphosphine and of the heterocyclic N,N′-donor ligands. The ^{31}P NMR spectra of the **6** and **7** exhibited a single sharp resonance at 16.65 ppm and 22.60 ppm respectively while the starting complex $[CpOs(PPh_3)_2CH_3CN]BF_4$ showed the same at 2.11 ppm. These distinct downfield shifts were observed because of the dissociation of one triphenylphosphine from the metal centre. The downfield shift of complex **7** is slightly more compared to complex **6** due to steric bulkiness of the phenanthroline ligand.

3.1. The structure of $[CpOs(PPh_3)(phen)]BF_4$

The structure of complex **7** is shown in Fig. 1. The bond lengths and bond angles are listed in Table 2. The osmium atom is bonded to a phenanthroline ligand, triphenylphosphine ligand and cyclopentadienyl group through the five-membered ring. The cyclopentadienyl group is clearly bonded in a pentahapto fashion to the metal. Two of the Os–C bond lengths, those involving the C(32) and C(33) are shorter (2.176 and 2.193 Å) than the other three C(31), C(34) and C(35) carbon atoms (2.210, 2.215 and 2.211 Å). The average Os–C bond

Table 2
Selected bond lengths (Å) and bond angles (°) in the compound $[CpOs(PPh_3)(phen)]BF_4$

Bond lengths			
Os–N1	2.090(5)	N2–C10	1.345(8)
Os–C33	2.193(6)	C31–C32	1.418(11)
Os–C34	2.215(6)	C34–C35	1.375(13)
P–C25	1.835(7)	B–F3	1.371(12)
N1–C12	1.373(7)	Os–C32	2.176(6)
C31–C35	1.413(11)	Os–C35	2.211(6)
C33–C34	1.431(12)	P–C13	1.831(7)
B–F4	1.352(12)	N1–C1	1.347(8)
Os–N2	2.092(5)	N2–C11	1.372(8)
Os–C31	2.210(6)	C32–C33	1.409(11)
Os–P	2.318(2)	B–F2	1.263(12)
P–C19	1.844(7)	B–F1	1.423(14)
Bond angles			
N1–Os–N2	77.2(2)	C12–N1–Os	115.6(4)
C13–P–Os	113.1(2)	F2–B–F4	119.3(11)
C1–N1–Os	128.1(4)	F4–B–F1	103.4(10)
C19–P–Os	118.7(2)	N1–Os–P	88.86(14)
F2–B–F1	106.0(10)	C11–N2–Os	115.5(4)
F4–B–F3	109.5(8)	C10–N2–Os	126.6(5)
N2–Os–P	89.02(13)	F2–B–F3	111.7(10)
C25–P–Os	116.1(2)	F3–B–F1	105.8(9)

distance being 2.201 Å, slightly longer than the parent complex [CpOs$(PPh_3)_2$Br] (2.177 Å) [6].

The Os–P bond length is 2.318 Å which also is slightly longer than the average Os–P distance (2.293 Å) [6]. The two Os–N bonds are almost equal, 2.090 and 2.092 Å, and also are little longer compared to the Os–N bond lengths observed for osmium–phenanthroline complexes which fall within a range of 2.066–2.1 Å [15]. The geometry of complex **7** is octahedral about the metal center assuming the cyclopentadienyl ligand occupies three coordinate sites. This is evident by the near 90° bond angles between N(1)–Os–P (88.86°) and N(2)–Os–P (89.02°).

4. Conclusions

The reactions of [CpOs$(PPh_3)_2$Br] with monodentate anions and neutral ligands were described and they do not seems to differ much from their ruthenium analogues except in the formation of [CpOs$(PPh_3)_2$NO]$^{+2}$ (**5**). We also observed that the complex [CpOs$(PPh_3)_2$-$(CH_3CN)]^+$ was a better precursor for the preparation of [CpOs$(PPh_3)(L_2)]^+$ compared to [CpOs$(PPh_3)_2$Br]. The molecular structure of the complex [CpOs(PPh_3)-(phen)]BF_4 was established by single X-ray crystallography.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194247 for complex **7**. 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).

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