CHAPTER 2

Reactivity study of cyclopentadienyl osmium(II) bisphosphine azido complexes with activated alkynes and nitriles: isolation of osmium triazolato and tetrazolato complexes by 1,3 dipolar addition.

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Reactivity study of cyclopentadienyl osmium (II) bisphosphine azido complexes with activated alkynes and nitriles: isolation of osmium triazolato and tetrazolato complexes by 1,3 dipolar addition*.

Abstract:

The cyclopentadienyl osmium(II) complexes \([(\eta^5-C_5H_5)Os(PPh_3)_2X] [X = Br (1), CH_3CN (2)]\) reacts with sodium azide (NaN_3) to yield the corresponding azido complex of the type \([(\eta^5-C_5H_5)Os(PPh_3)_2N_3] (3)\). The azido complex thus generated undergoes [3+2] dipolar cycloaddition reaction with activated alkynes such as diethylacetylenedicarboxylate and dimethylacetylenedicarboxylate to yield triazolato complexes \([(\eta^5-C_5H_5)Os(PPh_3)_2\{N_3C_2(CO_2R)_2\}] [R = -CH_2CH_3 (4) and -CH_3 (5)]. The complex 3 also reacts with nitriles such as tetracyanoethylene (TCE), fumaronitrile and p-nitrobenzonitrile to yield complexes of the type \([(\eta^5-C_5H_5)Os(PPh_3)_2\{N_4C(C_6H_4-p-NO_2))\} (8). These complexes were fully characterized on the basis of microanalyses, FT-IR and NMR spectroscopic data. Molecular structure of the representative complex \([(\eta^5-C_5H_5)Os(PPh_3)_2\{N_3C_2(CO_2CH_2CH_3)_2\}] (4) was determined by single crystal X-ray analysis.

Keywords: Osmium complexes, cyclopentadienyl, dimethylacetylenedicarboxylate, diethylacetylenedicarboxylate, fumaronitrile, tetracyanoethylene, p-nitrobenzonitrile.

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2.1 Introduction

The $\sigma$-donor and $\pi$-acceptor abilities of the cyclopentadienyl ligands stabilize transition metal complexes in low and high oxidation states. The half sandwich cyclopentadienyl ruthenium and osmium biphosphine complexes viz., $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5-C_5H_5)Os(PPh_3)_2Br]$ (1), have generated a great deal of interest for the last few decades due to high reactivity [1] and catalytic activity [2]. However, the chemistry of $[(\eta^5-C_5H_5)Os(PPh_3)_2Br]$ (1) is less research in compared to its analogue ruthenium complexes [3]. This could be due to the lack of convenient osmium synthetic precursor [4] and the higher kinetic stability of the cyclopentadienyl osmium $((\eta^5-C_5H_5)OsL_3)^+$ compounds in comparison with the related cyclopentadienyl ruthenium complexes [5]. Our interest arises due to catalytic potential in organic reactions, which is particularly important for synthesizing heterocyclic compounds [6]. In addition, tetrazoles are not only important in precursors to a variety of nitrogen containing heterocycles [7] but also to diverse application in pharmaceuticals [8], explosives [9] and corrosion inhibitors [10]. The presence of a coordinated azide in certain metal complexes has been reported to react with electron-poor nitriles [11] and isonitriles [12] under relatively mild conditions to produce metal-nitrogen and metal-carbon bonded tetrazoles respectively. Similar reactions with alkynes produce triazolates, whereas alkenes react very slowly and mostly afford an impure product [13]. Similarly, it has been reported that azido complexes react with carbon disulfides to produce thiothiatriazolate [14]. A number of azido complexes have been found to react with organic isothiocyanates and alkyl thiocyanates to give tetrazolinethionates and 5-(thioalkyl) tetrazolates respectively [15].
Recently cyclopentadienyl ruthenium triazolato and tetrazolato complexes have been reported [16]. We recently reported the triazolato complexes of the type \([\eta^6\text{-arene}]\text{Ru(LL)}\{\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2}\] and \([\eta^5\text{-indenyl}]\text{Ru(LL)}\{\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2}\] (LL = \(\beta\)-diketonates, dppe, dppm) which result from the reaction of \([\eta^6\text{-arene}]\text{Ru(\mu-N}_3\text{)(LL)}\] and \([\eta^5\text{-indenyl}]\text{Ru(2LL)(N}_3\text{)}\] respectively with various substituted acetylenes [17]. The study revealed two important observations, these are:- (i) \(\eta^5\text{-indenyl ruthenium(II)}\) complexes containing bulky triphenylphosphine ligands did not undergo 1, 3 cycloaddition and (ii) in our study, the ethoxy substituted complex exclusively produces the isomer with the metal bonded to the terminal nitrogen atom (N1) of triazolato ring. To understand the role of steric factors in 1,3 -dipolar cyclo-addition reactions, we carried out the reaction between activated alkynes / nitriles and cyclopentadienyl osmium azido complex \([\eta^5\text{-C}_5\text{H}_5]\text{Os(PPh}_3\text{)}_2\text{N}_3\] (3). The work presented here is an elaborate study on cycloaddition reaction of cyclopentadienyl osmium azido complexes.

2.2 Experimental Section

All solvents were dried in appropriate drying agents and distilled prior to use [22]. Osmium tetraoxide (Arora Matthey Limited), dimethylacetylenedicarboxylate, diethylacetylenedicarboxylate, tetracyano-ethylene (TCE), fumaronitrile (Aldrich) and \(p\)-nitrobenzonitrile (Across) were used as received. \(^1\text{H}\) NMR spectra were recorded on an AMX-400 MHz spectrometer at 400.13 (\(^1\text{H}\), or 100.61 MHz (\(^13\text{C}\)) and 161.97 (\(^31\text{P}\)) with SiMe\(_4\) or 85% H\(_3\)PO\(_4\) as references and coupling constants were given in Hertz. Infrared spectra were recorded as a KBr pellets on a Perkin-Elmer Model 983 spectrometer. Elemental analyses were carried out at the Sophisticated Analytical Instrumentation facility (SAIF), NEHU - Shillong, using a Perkin-Elmer 2400 CHN/S.
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analyzer. The precursor complexes \([(\eta^5-C_5H_5)Os(PPh_3)_2Br] (1)\) and \([(\eta^5-C_5H_5)Os(PPh_3)_2CH_3CN][PF_6] (2)\) were prepared by following a literature method [21].

2.3 Synthesis of the complex \([(\eta^5-C_5H_5)Os(PPh_3)_2N_3] (3)\)

Two routes were used to prepare for this complex:

(Caution: Reactions with azide salts and their complexes should perform with extreme care)

Route (a): A solution of \([(\eta^5-C_5H_5)Os(PPh_3)_2Br] (1) (100 mg, 0.12 mmol)\) and \(NaN_3 (50 mg, 0.75 mmol)\) in ethanol (30 ml) was refluxed for ca., 5 hrs. During the period of reaction, the color of the solution progressively changed from pale yellow to an orange colored. The solution was concentrated to ca. 5 ml and left at room temperature for overnight; a pale green crystalline compound was deposited on the beaker. The crystalline compound was collected and washed with cold ethanol (3 x 10 ml) and air dried.

Route (b): A mixture of \([(\eta^5-C_5H_5)Os(PPh_3)_2(CH_3CN)][BF_4] (2) (100 mg, 0.10 mmol)\) and \(NaN_3 (20 mg, 0.31 mmol)\) in ethanol (30 ml) was refluxed for ca., 3 hrs. The solvent was removed under reduced pressure; the solid residue was extracted with dichloromethane and filtered to remove NaCl and excess \(NaN_3\). The filtrate on concentration to ca. 5 ml and addition of excess hexane gave a pale green crystalline solid of compound (3), and washed with cold ethanol (3 x 10 ml).

Yield: 72 mg, 84.61 %

Elemental analyses: (%): Calc.C_{41}H_{35}P_2N_3Os: C 59.2; H 4.2; N 5.1; found: C 59.75; H 4.87; N 5.64.

IR (KBr, cm\(^{-1}\)): 2034 (\nu_{N_3})

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1H NMR (CDCl₃, δ): 7.82-7.01 (m, 30H, Ph); 4.47 (s, 5H, C₅H₅).

13C ¹H NMR (CDCl₃, δ): 133.5-127.6 (Ph), 79.7 (C₅H₅).

31P ¹H NMR (CDCl₃, δ): 1.15.

2.4 Synthesis of [η⁵-C₅H₅]Os(PPh₃)₂[N₃C₂(CO₂C₂H₅)₂] (4)

General Procedure:

Diethylacetylenedicarboxylate (175 mg, 1.23 mmol) and dichloromethane (20 ml) were added to a round bottom flask charged with the corresponding azido complex (3) (100 mg, 0.12 mmol). The reaction mixture was stirred at room temperature for ca. 15 hrs. The solvent was evaporated under reduced pressure to ca. 5 ml. To this solution was added 30 ml of hexane, whereby the compound precipitated out as a light yellow solid. The solid compound was collected by centrifuge and washed with hexane (2 x 20 ml) and dried under vacuum to yield the N(2)-bound triazole complex [(η⁵-C₅H₅)Os(PPh₃)₂[N₃C₂(CO₂C₂H₅)₂] (4)

Yield: 85 mg, 62.69 %.

Elemental analyses: (%) for C₄₀H₃₅N₃P₂O₄Os. Calc.: C 59.3; H 4.5; N 4.2; found: C 59.9; H 4.1; N 4.8.

IR (KBr, cm⁻¹): 1724 (νC=O), 1433 (νN=N), 1245 (νC-O).

1H NMR (CDCl₃, δ): 7.45-7.03 (m, 30H; Ph); 4.51 (s, 5H, C₅H₅); 3.23 (q, 2H, -OCH₂CH₃); 1.94 (t, 3H, OCH₂CH₃).

31P ¹H NMR (CDCl₃, δ): 1.15 (s).
2.5 Synthesis of \( [(\eta^5-C_5H_5)Os(PPh_3)_2(N_2C_2(CO_2CH_3)_2)] \) (5)

This complex was prepared in a similar manner to that of the preparation of complex 4, except the ligand dimethylacetylenedicarboxylate \([C_2(CO_2Me)_2]\) was used instead of \([C_2(CO_2C_2H_5)_2]\) to yield a light yellow complex (5).

- **Yield:** 85 mg, 64.52 %

Elemental analyses: (%) for C_{47}H_{41}N_{3}P_{2}O_{4}S. Calc.: C 58.6; H 4.3; N 4.4; found: C 58.1; H 4.8; N 4.2.

- **IR (KBr, cm\(^{-1}\))**: 1735 (vC=O), 1439 (vN=N).

- **\(^1\)H NMR (CDCl\(_3\), \(\delta\))**: 7.45-7.03 (m, 30H, Ph); 4.51 (s, 5H, C\(_5\)H\(_5\)); 3.06 (s, 3H, OCH\(_3\)).

- **\(^{13}\)C \{\(^1\)H\} NMR (CDCl\(_3\), \(\delta\))**: 162.9 (CO\(_2\)); 135.2 \{C(CO\(_2\)CH\(_3\))\}; 133.8 (Ph); 82.81 (C\(_5\)H\(_5\)); 51.4 (OCH\(_3\)).

- **\(^{31}\)P \{\(^1\)H\} NMR (CDCl\(_3\), \(\delta\))**: 1.19 (s).

2.6 Synthesis of \( [(\eta^5-C_5H_5)Os(PPh_3)_2N_4C\{CN\}C=C(CN)\}_2] \) (6)

Dichloromethane (20 ml) was added to a round bottom flask charged with complex 3 (100 mg, 0.12 mmol) and tetracyanoethylene (0.60 mmol). The reaction mixture was stirred at room temperature for ca. 36 hrs. The solvent was evaporated under reduced pressure to ca. 5 ml. To the solution was added 20 ml of n-hexane, whereby a deep blue compound was precipitated. The precipitate was filtered, washed with n-hexane (2 x 10 ml) and dried under vacuum to yield \( [(\eta^5-C_5H_5)Os(PPh_3)_2N_4C\{CN\}C=C(CN)\}_2] \) (6).

- **Yield:** 83 mg, 64.0 %

Elemental analyses: (%) for C\(_{47}\)H\(_{35}\)N\(_7\)P\(_2\)Os. Calc.: C 59.4; H 3.7; N 10.3; found: C 58.9; H 3.2; N 9.8.

- **IR (KBr, cm\(^{-1}\))**: 2227, 2183 (s, vC=N), 1430 (s, vN=N).
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\[ ^1\text{H NMR (CDCl}_3, \delta): 7.73-6.96 \text{ (m, 30H, Ph); 4.05 (s, 5H, C}_5\text{H}_5). \]

\[ ^{13}\text{C} \{^1\text{H} \} \text{ NMR (CDCl}_3, \delta): 154.2 \{\text{C(CN)}_2\}, 139.4 \{\text{C(CN)}\}, 132.1-126.4 \text{ (Ph), 125.3 (C=N), 112.6, 110.4, 108.5 (CN), 81.4 (s, C}_5\text{H}_5). \]

\[ ^{31}\text{P} \{^1\text{H} \} \text{ NMR (CDCl}_3 \delta): 1.26 (s). \]

2.7 Synthesis of \([\eta^5\text{-C}_5\text{H}_5\text{Os(PPh}_3)_2\text{N}_3\text{C}_2\text{HCN}] (7)\]

The mixture of azido complex \([\eta^5\text{-C}_5\text{H}_5\text{Os(PPh}_3)_2\text{N}_3]\) (3) (100 mg, 0.12 mmol) and fumaronitrile \([\text{C}_2\text{H}_2(\text{CN})_2]\) (0.60 mmol) was stirred at room temperature for 36 hrs in dichloromethane (20 ml), then the solution was concentrated to ca. 5 ml. To this solution was added 30 ml of n-pentane, whereby the compound precipitated as a deep green solid. The solid compound was centrifuged, collected and washed with n-pentane (2 x 10 ml) to yield the complex \([\eta^5\text{-C}_5\text{H}_5\text{Os(PPh}_3)_2\text{N}_3\text{C}_2\text{HCN}] (7)\) and further dried under vacuum.

Yield: 86 mg; 72.1 %

Elemental analyses: (%) for \(\text{C}_{46}\text{H}_{36}\text{N}_6\text{P}_2\text{O}_5\). Calc.: \(\text{C} 59.7; \text{H} 3.9; \text{N} 9.1\); found: \(\text{C} 59.0; \text{H} 4.1; \text{N} 8.7\).

IR (KBr, cm\(^{-1}\)): 2221 (s, \(\nu\text{C}=\text{N}\)), 1433 (s, \(\nu\text{N}==\text{N}\)).

\[ ^1\text{H NMR (CDCl}_3, \delta): 7.50-7.13 \text{ (m, 30H, Ph); 6.2 (s, 1H, CH); 4.05 (s, 5H, C}_5\text{H}_5). \]

\[ ^{13}\text{C} \{^1\text{H} \} \text{ NMR (CDCl}_3, \delta): 137.2 \{\text{C(CN)}\}, 136.02 (\text{CH}); 132.1-126.4 (\{^1\text{H} \} \text{ Ph), 113.8 (CN); 82.8 (s, C}_5\text{H}_5). \]

\[ ^{31}\text{P} \{^1\text{H} \} \text{ NMR (CDCl}_3 \delta): 1.25. \]

2.8 Synthesis of \([\eta^5\text{-C}_5\text{H}_5\text{Os(PPh}_3)_2\text{N}_3\text{C}(\text{C}_6\text{H}_4-\text{-p-NO}_2)] (8)\]

The mixture of azido complex \([\eta^5\text{-C}_5\text{H}_5\text{Os(PPh}_3)_2\text{N}_3]\) (3) (100 mg, 0.12 mmol) and para-nitrobenzonitrile \((\text{NO}_2\text{-C}_6\text{H}_4\text{-C}==\text{N})\) (0.60 mmol) in dichloromethane (20 ml) was
stirred at room temperature for one week, and the solution was concentrated to ca. 5 ml. To this solution was added 30 ml of n-pentane, whereby the compound precipitated as a deep green solid. The solid compound was centrifuged, collected and washed with n-pentane (2 x 20 ml) to yield the complex \([\eta^5-C_5H_5]Os(PPh_3)_2N_4C(C_6H_4-p-NO_2)\] (16) and dried under vacuum.

Yield: 75 mg, 71.0 %

Elemental analyses: (%) for C_{48}H_{39}N_5O_2P_2Os. Calc.: C 59.4; H 4.0; N 7.2; found: C 58.9; H 4.7; N 7.9.

IR (KBr, cm⁻¹): 1475 (vN=O), 1430 (vN=N).

\(^1\)H NMR (CDCl₃, δ): 4.82 (s, 5H, C₅H₅); 7.0-7.56 (m, 30H, Ph); 8.3 (d, J₁₁-H = 5.92Hz, 1H); 9.3 (d, J₁₂-H = 5.6Hz, 1H).

\(^{13}\)C \(^1\)H NMR (CDCl₃, δ): 36.02 (CH); 132.1-126.4 (Ph); 82.0 (C₅H₅).

\(^{31}\)P \(^1\)H NMR (CDCl₃, δ): 1.19 (s)

Results and discussion

2.9 Preparation of azido complex \([(\eta^5-C_5H_5)Os(PPh_3)_2N_3]\)

Treatment of the complexes \([(\eta^5-C_5H_5)Os(PPh_3)_2Br]\) (1) and \([(\eta^5-C_5H_5)Os-(PPh_3)_2-(CH_3CN)]BF_4\) (2) with an excess of sodium azide (NaN₃) in ethanol under refluxed condition for 5 hrs, affords a pale yellow product of cyclopentadienyl osmium azido complex \([(\eta^5-C_5H_5)Os(PPh_3)_2N_3]\) (3) in good yield (Scheme 2.1). The azido complex 3 is air stable and soluble in polar solvents such as CH₂Cl₂, CHCl₃ and acetone, also stable in solution. The infrared spectrum of the complex exhibits a strong band at 2034 cm⁻¹ due to terminal azido group (Figure 2.1). The \(^{31}\)P NMR spectrum of the complex 3 displays a singlet at δ 1.15 corresponds to triphenylphosphines. The \(^1\)H NMR spectrum
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of the complex 3 displays a singlet resonance at δ 4.47, assigned to the protons of cyclopentadienyl group. The cyclopentadienyl protons showed a down field position in compared to the starting complex (δ 4.31) is presume as due to the increased steric factor on the metal centre of the complex (3). Also the spectrum displays a multiplet in the range of δ 7.82-7.01 corresponds to the protons of the triphenylphosphines.

Figure 2.1: Infrared spectrum of Figure 2.2: Infrared spectrum of

\[ [(\eta^5-C_5H_5)Os(PPh_3)_2N_3] (3) \] \[ [(\eta^5-C_5H_5)Os(PPh_3)_2(N_3C_2(CO_2C_6H_5)_2)] (4) \]

2.9.1 Reaction of complex 3 with diethylacetylenedicarboxylate:

Azido complex \[ [(\eta^5-C_5H_5)Os(PPh_3)_2N_3] (3) \] is treated with excess of diethylacetylenedicarboxylate in dichloromethane and stirred at room temperature for 15 hrs, and results in a light yellow solid compound 4 in good yield. The formation of the complex can be readily confirmed by the disappearance of characteristic azide peak
and the subsequent appearance of a sharp peaks at 1724 and 1433 cm\(^{-1}\) corresponds to the characteristic stretching frequency of C=O and N=N respectively (Figure 2.2). The formation of the complex is supported by the single crystal X-ray analysis. The proton NMR spectrum shows a quartet at \(\delta 3.23\), triplet at \(\delta 1.94\), and singlet \(\delta 4.51\) for the ten ethoxy protons and five protons of cyclopentadienyl group. It has been reported that the triazole anion could be coordinated by a metal centre through either its N(1) or N(2) nitrogen atoms [18]. Evidence obtained to date indicates that either two isomers N(1) and N(2) are formed simultaneously. In our case, the N(2) bound isomer is produced exclusively. The \(^1\)H NMR spectrum is also displays multiplet in the aromatic region due to phenyl groups of triphenylphosphines.

2.9.2 Reaction of complex 3 with dimethylacetylenedicarboxylate

Treatment of complex 3 with excess of dimethylacetylenedicarboxylate in dichloromethane at room temperature for 15 hrs affords 4,5-bis(methoxycarbonyl)-1,2,3-triazolato complex 5 in good yield. The infrared spectrum shows sharp peaks at 1724 and 1433 cm\(^{-1}\) which are assigned to the stretching frequencies of C=O and N=N of the complex. The proton NMR spectrum displays a singlet at \(\delta 3.06\) and \(\delta 4.51\) corresponds to methoxy and cyclopentadienyl protons. \(^{31}\)P NMR resonance of the complex 5 appears at \(\delta 1.19\) which is comparable to the starting complex (3). The complex is soluble in polar solvents but insoluble in non-polar solvents, and is air stable.
2.9.3 Reaction of complex 3 with tetracyanoethylene (TCE):

The azido complex 3 is reacted with excess of tetracyanoethylene (TCE) in dichloromethane at room temperature. The reaction mixture is turned to deep green colouration after one hour and continued to stirring up to 36 hrs to ensure complete reaction. This affords the tetrazolato complex \([(\eta^5-C_5H_5)Os(PPh_3)_2N_4C{(CN)C=\ C(CN)N}_2}] (6) in good yield. The infrared spectrum exhibited a sharp peaks at 2925 cm\(^{-1}\), 2197 cm\(^{-1}\) and 1430 cm\(^{-1}\) assigned to the stretching frequencies of C=\(\equiv\)N and N=N groups (Figure 2.3), agreeable to the reported values [17]. The \(^1\)H NMR spectrum shows a singlet at \(\delta\) 4.05 for cyclopentadienyl group, the up field chemical shift of this
compound is due to more electron density on the metal centre. Multiplets observed at the aromatic region correspond to the protons of the triphenylphosphines.

![Figure 2.3: IR spectrum of [(η⁵-C₅H₅)Os(PPh₃)₂N₄C{(CN)C=C(CN)₂}] (6)](image)

$^{31}$P NMR resonance of this complex displays singlet at δ 1.26. The formation of complex 6 can also be confirmed by the disappearance of terminal azide peak, which is observed at 2057 cm⁻¹ and the appearance of stretching frequency of C=NS group. In general, most of the tetrazoles are prepared from the corresponding nitriles by reaction of sodium azide and ammonium chloride [19]. Our effort to get single crystals for X-ray analysis was not succeed.

### 2.9.4 Reaction of complex 3 with fumaronitrile:

Treatment of complex 3 with excess of fumaronitrile at room temperature affords a chocolate coloured 4-cyano-1, 2, 3-triazolato complex [(η⁵-C₅H₅)Os(PPh₃)₂ {N₃C₂HCN}] (7) in good yield. The infrared spectrum of the complex shows as a sharp peaks at 2221 and 1433 cm⁻¹ assignable to the stretching frequency of C≡N and N≡N
groups. The $^1$H NMR spectrum displays a characteristic singlet resonance at $\delta$ 6.2 assigned to the proton (-CH) of triazole group and a singlet resonance at $\delta$ 4.05 attributed to the protons of cyclopentadienyl ligand (Figure 2.4). The $^{31}$P NMR resonance of this complex appears at $\delta$ 1.25 for two triphenylphosphine groups. The complex is soluble in dipolar solvents such as acetone, chloroform, methanol etc., and air stable. The cycloaddition reaction of fumaronitrile to coordinated azide can take place via C=C or C=N bond. In addition, the reaction of coordinated azide in Ni (II) with CH$_2$=CHCN gave triazolinato complex [18]. A pathway via direct cyclization of HC≡CCN with azide resulting in the formation of triazalato has been reported [20]. The formation of this complex can also be readily confirmed by the disappearance of the azide peak at 2037 cm$^{-1}$, and the simultaneous appearance of the peak for C≡N group. Our effort to get single crystals for x-ray analysis is not successful.

![Figure 2.4: $^1$H NMR spectrum of [CpOs(PPh$_3$)$_2$N$_3$C$_2$HCN] (7)](image)

2.9.5 Reaction of complex 3 with p-nitrobenzonitrile:

Treatment of complex 3 with five fold excess of p-nitrobenzonitrile at room temperature for one week gives a deep green coloured complex \([(\eta^5$-C$_5$H$_5$)Os(PPh$_3$)$_2\]$}
{N₄C(C₆H₄-p-NO₂)} (8), in good yield. The formation of the complex is enviable from the appearance of -NO₂ peak at 1474 cm⁻¹ and the disappearance of the terminal azide peak (Figure 2.6). The ¹H NMR spectrum shows a singlet peak at δ 4.82 assigned to the protons of cyclopentadienyl ligand which is very down field to the chemical shift of the starting complex (δ 4.47) (Figure 2.7). The p-nitrobenzonitrile ligand exhibited two doublets at δ 9.3, δ 8.2 which correspond to the 1,2 and 3,4 protons of benzyl group.

![Triazolato complex](image)

Figure 2.5: Triazolato complex [{η⁵-C₅H₅}Os(PPh₃)₂N₄C(C₆H₄-p-NO₂)] (8) with numbering scheme.

The phenyl protons of PPh₃ group displays in the aromatic region. Moreover, only a slight shift of phosphorus resonance (δ 1.19) in the ³¹P NMR was observed in comparison to the starting complex (δ 1.15). The complex is a deep green colour solid, soluble in polar solvents such as acetone, dichloromethane; chloroform and methanol etc., and is air stable.
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2.9.6 Crystal structure

Crystal structure determination of the compound \([(\eta^5-C_5H_5)Os(PPh_3)_2N_4C(C_6H_4-p-NO_2)]\) (4) has been carried out. Details of crystallographic data collection parameters are summarized in table 1. ORTEP diagram of the complex with atom labelling scheme are shown in figure 2.8 and 2.9. ORTEP 2.7 exhibits clear view of the molecule due to removal of phenyl groups of triphenylphosphine. In this complex the
osmium atom is \( \pi \)-bonded to the cyclopentadienyl group in \( \eta^5 \)-fashion with the distance between osmium atom and the centroid of the cyclopentadienyl being 1.66 Å which is similar to the ruthenium analogues. The geometry around the osmium atom is a distorted octahedral assuming the cyclopentadienyl ligand which occupies three facial coordination sites. The remaining coordination sites are occupied by the P atom of triphenylphosphines and an N-atom of the coordinated triazolato group. The complex 4 adopts the well-known piano stool geometry with P and N atoms forming the legs. The planar five-membered triazolato ring is coordinated to Os via N(2). The N(1)-N(2) and N(2)-N(3) bond distances are 1.331 (4) Å and 1.343 (3) Å respectively (Table 2.2), which are comparable to the reported values of its ruthenium analogues [17]. The Os-P(1) and Os-P(2) bond lengths are 2.323 Å and 2.326 Å which are slightly longer than the average Os-P distance (2.293 Å) [21].

![Figure 2.8: ORTEP diagram of complex 4 with 30% probability thermal ellipsoids displayed and H atoms being omitted for clarity.](image)
Figure 2.9: ORTEP diagram of complex 4 with 30% probability thermal ellipsoids displayed without phenyl groups of phosphines and H atoms being omitted for clarity.

2.9.7 Single-crystal X-ray structures analyses

Crystals suitable for X-ray diffraction study were grown by slow diffusion of diethylether into dichloromethane solution of the complex 4. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-Kα radiation (α = 0.71069 Å) at a temperature of 143 K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 seconds. A total of 410 rotation images were collected with a crystal to detector distance of 35 mm, a 2 θ swing angle of -12°, rotation widths of 0.5° and exposures of 20 seconds. Rotation images were processed using Crystal Clear [23] producing a listing of unaveraged F^2 and α (F^2) values which were then passed to the crystal structure [24] program package for further processing and structure solution on a Dell Pentium III computer. A total of 21130 reflections were measured over the ranges 5.08 ≤ 2θ ≤ 54.98°, -15 ≤ h ≤ 16, -26 ≤ k ≤ 32, -17 ≤ l ≤ 17 yielding 9051 unique reflections (R_{int} = 0.0193). The
intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB [23] (minimum and maximum transmission 0.836, 1.000). The structure was solved by direct methods (SIR97) [25]. Refinement was by full-matrix least squares based on F^2 using SHELXL-97 [26]. All reflections were used during refinement (F^2's that were experimentally negative were replaced by F^2 = 0). The weighting scheme used was w = 1/[σ^2(F_0^2) + 0.0112P^2 + 0.0000P] where P = (F_0^2 + 2F_c^2)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to R_I = 0.0214 and wR_2 = 0.0387 for 7407 reflections for which F > 4σ(F) and R_I = 0.0286, wR_2 = 0.0404 and GOF = 0.914 for all 9051 unique, non-zero reflections and 535 variables. The maximum Δ/σ in the final cycle of least squares was 0.003 and the two most prominent peaks in the final difference Fourier were +1.579 and -0.923 e/Å^3. Crystallographic details are summarized in table 2.1. The figure 2.8 and 2.9 were drawn with ORTEP -II [27] representation of the molecule with 30% probability thermal ellipsoids displayed.

2.9.8 Concluding remarks: This study described the 1,3-dipolar addition of [η^5-C_3H_5]Os(PPh_3)_2N_3] complex with activated alkynes and nitriles to generate cyclopentadienyl osmium triazolato and tetrazolato complexes in spite of complex having bulky triphenylphosphine groups. Where as its analogue ruthenium complexes [(η^5-C_3H_5)Ru(PPh_3)_2N_3] and [(η^5-indenyl)Ru(PPh_3)_2N_3] do not undergo such type of addition reaction, this could be due to bulkiness of triphenylphosphine. It may be due to the larger size of the osmium atom in compared to its analogue ruthenium yielded these complexes. Unlike p-cymene ruthenium triazolato complexes, central nitrogen atom of triazolato ring is bonded to the osmium metal in these complexes. These reactions
indicated that size of the central metal atom played a very important role in 1,3 dipolar-
cycloaddition reaction. Another fascinating point is that in contrast to ruthenium
complexes, the less steric complexes of the type [(η⁵-C₅H₅)Os(dppe)N₃] and [(η⁵-
C₅H₅)Os(dppm)N₃] complexes did not undergo cyclo-addition reactions with
diethylacetylenedicarboxylate and dimethylacetylene dicarboxylate, investigation is
under process.

Table 2.1: Summary of structure determination for [(η⁵-
C₅H₅)Os(PPh₃)₂N₃C₂(CO₂C₂H₅)₂] (4).

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C₄₀H₄₅N₃P₂O₄Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC. Number</td>
<td>649330</td>
</tr>
<tr>
<td>Formula weight</td>
<td>992.02</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>143 K</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2₁/n (no.14)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.4947(7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>24.8362(13)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.7755(8)</td>
</tr>
<tr>
<td>β (°)</td>
<td>99.558(2)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>4215.5(4)</td>
</tr>
<tr>
<td>μ</td>
<td>31.50 cm⁻¹</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density (mg/cm³)</td>
<td>1.563</td>
</tr>
<tr>
<td>Radiation Å</td>
<td>Mo-kα (λ=0.71069)</td>
</tr>
</tbody>
</table>

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Table 2.2: Selected bond lengths and angles of [(η⁵-C₅H₅)Os(PPh₃)₂N₃C₂(CO₂C₂H₅)₂]

(4)

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(1)-P(2)</td>
<td>2.3263(6)</td>
</tr>
<tr>
<td>N(1)-N(2)-N(3)</td>
<td>114.9(2)</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.302(3)</td>
</tr>
<tr>
<td>N(3)-N(2)-Os(1)</td>
<td>118.20(14)</td>
</tr>
<tr>
<td>N(2)-N(3)</td>
<td>1.343(3)</td>
</tr>
<tr>
<td>N(1)-N(2)-Os(1)</td>
<td>126.7(2)</td>
</tr>
<tr>
<td>N(1)-Os(1)</td>
<td>2.078(3)</td>
</tr>
<tr>
<td>N(2)-N(3)-C(1)</td>
<td>104.8(2)</td>
</tr>
</tbody>
</table>
\[ \begin{align*}
N(3)-C(1) & \quad 1.343(3) \\
N(1)-C(2) & \quad 1.346(3) \\
C(1)-C(3) & \quad 1.502(4) \\
C(2)-C(6) & \quad 1.478(3) \\
Os(1)-Centroid of Cp & \quad 1.66
\end{align*} \]

References


