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# $\begin{array}{l} Imidazole \rightarrow imidazolidine. \ Preparation \ by \ reduction \\ of \ [Os(H)(CO)(PPh_3)_2(PyaiR)]^{+/0} \ with \ NaBH_4 \ and \ characterisation \\ of \ the \ products \ (PyaiR = 1-alkyl-2-\{3'-(pyridylazo)\}imidazole) \end{array}$

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#### Abstract

The reaction of 2-(3'-pyridylazo)imidazole (PyaiH) or 1-alkyl-2-(3'-pyridylazo)imidazole (PyaiR) with  $[Os(H)(Cl)(CO)(PPh_3)_3]$  in THF or MeCN has synthesized stable red coloured  $[Os(H)(CO)(PPh_3)_2(Pyai)]$  (**2a**) or  $[Os(H)(CO)(PPh_3)_2(PyaiR)](PF_6)$  (**2b–2d**). While the reaction of PyaiR and  $[Os(H)(Cl)(CO)(PPh_3)_3]$  in dry *n*-heptane has separated shining green compound and has been identified azoanion radical,  $[Os(Cl)(CO)(PPh_3)_2(PyaiR^{-})]$  (**4b–4d**). The reaction performance in *n*-hexane or toluene is very poor. Upon addition of  $Cl_2$  in MeCN to  $CH_2Cl_2$  solution of **2** or **4** the colour has changed sharply to red-violet and has isolated  $[Os(Cl)(CO)(PPh_3)_2(PyaiR)]^+$ (**3**). The reaction of **2** in ethanol with NaBH<sub>4</sub> suspension under dinitrogen has reduced coordinated imidazole group to imidazolidine (**5**). One of the structures of azo-imidazolidinate-hydrido-osmium–carbonyl,  $[Os(H)(CO)(PPh_3)_2(PyaiH_2)]$  (**5**a), is characterized by X-ray diffraction study. Other spectroscopic studies (IR, UV–Vis, NMR) are used to identify the structure of all the complexes. Electrochemistry shows two consecutive anodic peaks ( $E_{pa}$ ) and suggest irreversible oxidations Os(III)/Os(II), Os(IV)/Os(III) along with azo reductions. © 2006 Elsevier B.V. All rights reserved.

Keywords: Pyridylazoimidazole; Azo-anion radical; Imidazolidine; X-ray structure; Electrochemistry

#### 1. Introduction

Progress in polypyridine metal complexes [1,2] has encouraged syntheses of complexes of other N-heterocycles [3]. Imidazole and imidazole containing ligands are chosen because of their chemical and biological ubiquity [4]. We have been engaged in the design of azo-functionalised imidazole ligands those carry azoimine, -N=N-C=N-, function [5]. Azo group is  $\pi$ -acidic, responsible for photochromism, pH-responsive and shows redox activity to the molecules. For the last several years we have been engaged in the transition metal chemistry of arylazoimidazoles [5–9]. Ruthenium–carbonyl complexes of azoheterocycles have attracted recent interest [10,11]. Osmium–carbonyl complexes are relatively less explored [12] than ruthenium. In

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this context we are interested to synthesize azoheterocyclic osmium complexes. Metal-carbonyls are efficient system to stabilize M-H bonds. Transition metal hydrides are good candidates to catalyze hydrogenations. The strength of  $L_nM-H$  bonds depends on the electronegativity of the metal center and the nature of ligand [13]. Hydridic starting materials  $[M(H)(Cl)(CO)(PPh_3)_3]$  (M = Ru, Os) has inherent reducing equivalent and has been used to generate radical anion by M-H bond cleavage [11,12] (Eq. (1)). Arylazoheterocycle (L) is reduced to  $[M(X)(CO)(PPh_3)_2(L^{-})]$  under extremely dry oxygen free condition. The hydrido complexes are turned to dihydrogen complexes ( $\eta^2$ -H<sub>2</sub>) upon addition of acid and capable to synthesize different substituted complexes as well as some interesting compounds by inserting unsaturated molecules (like RC=CH, CO<sub>2</sub>, CS<sub>2</sub>,  $ArN_{2}^{+}$ ) [13,14].

In this work we account on the reaction of [Os(H)(Cl)-(CO)(PPh<sub>3</sub>)<sub>3</sub>]with 2-(3'-pyridylazo)imidazoles (PyaiH) and

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1-alkyl-2-(3'-pyridylazo)imidazoles (PyaiR). Both non-radical (2, 3) and radical (4) carbonyl complexes are characterized by spectroscopic studies. We observe a novel reaction of carbonyl complexes in the presence of reducing agent, NaBH<sub>4</sub> in ethanol in which imidazole -CH=CH- is reduced to -CH(H)-CH(H)- instead of the reduction of -N=N- function (Eq. (2)) in the chelated ligand. These complexes (5) are spectroscopically and structurally established.

#### 2. Results and discussion

#### 2.1. Synthesis and formulation

Two different reaction conditions have been employed to synthesize two classes of compounds. In dry THF under dinitrogen atmosphere the reaction of 2-(3'-pyridylazo)imidazole (PyaiH, **1a**) or 1-alkyl-2-(3'-pyridylazo)imidazoles (PyaiR where R = Me (**1b**), Et (**1c**), CH<sub>2</sub>Ph (**1d**)) and [Os(H)(Cl)(CO)(PPh<sub>3</sub>)<sub>3</sub>] has synthesized [Os(H)-(CO)(PPh<sub>3</sub>)<sub>2</sub>(Pyai)] (**2a**) (imidazole N(1)–H in PyaiH is dissociated to generate Pyai<sup>-</sup>) or [Os(H)(CO)(PPh<sub>3</sub>)<sub>2</sub>-(PyaiR)](PF<sub>6</sub>) (**2b–2d**). The reaction in dry MeCN is equally good.

The reaction of  $[Os(H)(Cl)(CO)(PPh_3)_3]$  and PyaiR in boiling *n*-heptane under dinitrogen atmosphere has synthesized a bright green anion radical compound  $[Os(Cl)-(CO)(PPh_3)_2(PyaiR)]$  (4b-4d).

$$-N = N - \stackrel{'M-H'}{\longrightarrow} [-N - N - ]^{-}$$
(1)

$$-CH=CH-\xrightarrow{'Os-H',NaBH_4} -CH(H)-CH(H)$$
(2)

However, the reaction of  $[Os(H)(Cl)(CO)(PPh_3)_3]$  with PyaiH under identical condition in dry *n*-heptane has isolated brown-red intractable solid. Because of insolubility of the compound we could not proceed to analyse the complex. The composition has been supported by microanalytical data (see Section 3). We have carried out this reaction in dry *n*-hexane and toluene and the reaction is ended with the isolation of very small amount (<5% in *n*-hexane and 15% in toluene) of green anion radical. The observation suggests that *n*-heptane is suitable solvent to carry out this reaction. Protic or non-protic nature of the solvent has definite role to control path of the reaction. It is not known how much protonic impurity, such as water, is contained in toluene, *n*-hexane or *n*-heptane used in the experiments, it is likely that an inadvertently contained trace amount of water may facilitate the scavenging of anion radical. In THF or MeCN presence of trace amount of water impurity may be the reason to remove anion radical and to select second route to synthesize non-radical complexes. Heat capacity of the solvent is also playing typical role for percentage conversion of the reaction.

Upon addition of few drops of  $Cl_2$  saturated MeCN solution to red solution of  $[Os(H)(CO)(PPh_3)_2(Pyai/PyaiR)]^{0/+}$ (2) or green solution of  $[Os(Cl)(CO)(PPh_3)_2(PyaiR^{-})]$  (4) in presence of excess of  $NH_4PF_6$ ) in dichloromethane has yielded red-violet  $[Os(Cl)(CO)(PPh_3)_2(Pyai/PyaiR)]^{0/+}$  (3).

$$[Os(H)(Cl)(CO)(PPh_{3})_{3}] + PyaiH/PyaiR$$

$$\xrightarrow{\text{reflux, THF}} [Os(H)(CO)(Pyai/PyaiR)(PPh_{3})_{2}]^{0/+} (1)$$
(2)

$$[Os(H)(Cl)(CO)(PPh_3)_3] + PyaiR$$

$$\xrightarrow{\text{reflux, n-Heptane/N_2}} [Os(H)(CO)(PPh_3)_2(PyaiR)] (2)$$

2 or 
$$4 \xrightarrow{\text{Cl}_2 \text{ in MeCN}} [\text{Os}(\text{Cl})(\text{CO})(\text{Pyai/PyaiR})(\text{PPh}_3)_2]^{0/+}$$
  
(3)

The solution conductivity data in MeCN show that 2b-2d and 3b-3d are 1:1 electrolyte ( $\Lambda_{\rm M} = 95 - -110 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^{-1}$ ) while 2a and 3a are non-conducting. The complexes 2 and 3 are diamagnetic. The room temperature magnetic moments of anion radical complexes (4b: 1.90; 4c: 1.92; 4d: 1.88  $\mu_{\rm B}$ ) correspond to the presence of one unpaired electron (S = 1/2). Powder EPR spectra are approximately axial and the 'g' values are nearer to 2 (4b: 1.990, 1.942; 4c: 1.991, 1.955; 4d: 1.88, 1.945) (Fig. 1). The spectra do not exhibit nitrogen hyperfine structure. This is not unusual [11,15] because the <sup>14</sup>N coupling constant in azo- $\pi^*$  radicals is small and difficult to observe. We are not capable to isolate 4a in good solid state at ambient condition and have not been characterized.

#### 2.2. Spectra and bonding

The complexes **2** and **3** show a sharp stretch at 1910–1945 cm<sup>-1</sup> (Table 1) which is corresponding to v(CO) and



Fig. 1. Powder EPR spectrum of  $[Os(H)(CO)(PPh_3)_2(PyaiEt^{-})]$  (4b) in the X-band (9.11 GHz) at 298 K. Intrument setting: power, 28 dB; modulation, 100 kHz; sweep center.3200 G; sweep width, 1000 G; sweep time 240 s.

Table 1	
UV-Vis spectral <sup>a</sup> and cyclic voltammetric d	ata <sup>b</sup>

Compound	$v(CO) (cm^{-1})$	UV–Vis spectral data <sup>a</sup> $\lambda_{max}$ , nm (10 <sup>-3</sup> $\varepsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	Cyclic voltammetric data <sup>b</sup>		
			$E_{\mathbf{M}}^{1}$	$E_{\mathbf{M}}^{2}$	Ligand reductions
2a	1912	480 (8.82), 370 (10.28), 275 (15.32)	0.65 (160)	1.20 (170)	$-0.80$ (170), $-1.45^{d}$
2b	1914	520 (6.24),385 (9.62), 278 (12.76)	0.60 (160)	1.22 (200)	$-0.84(180), -1.50^{d}$
2c	1918	525 (3.76), 380 (11.56), 310 (8.06)	0.66 (160)	1.20 (200)	$-0.82(140), -1.45^{d}$
2d	1935	530 (3.10), 375 (9.45), 300 (6.14)	0.70 (170)	1.30 (180)	$-0.85(140), -1.42^{d}$
3a	1928	510 (6.28), 385 (8.72), 282 (13.32)	0.72 (150)	1.22 (160)	$-0.80(150), -1.32^{d}$
3b	1934	562 (4.42), 395 (8.22), 295 (10.36)	0.75 (140)	1.28 (170)	$-0.72(140), -1.26^{d}$
3c	1935	576 (3.06), 390 (7.75), 300 (8.28)	0.80 (160)	1.30 (170)	$-0.78(180), -1.48^{d}$
3d	1947	582 (2.33), 385 (8.40), 312 (5.66)	0.82 (140)	1.35 (180)	$-0.70(140), -1.45^{d}$
4b	1883	690 (1.24), 440 (3.54), 375 (6.24), 310 (10.74)			-0.65(140)
4c	1888	695 (1.56), 448 (2.25), 394 (6.05), 282 (11.25)			-0.60(160)
4d	1897	705 (1.46), 480 (3.86), 370 (5.62), 285 (12.48)			-0.57 (150)
5a	1911	492 (3.64), 410 (3.17), 368 (3.86), 320 (2.52)	0.48 (140)	1.10 (180)	$-0.83(150), -1.63^{d}$
5b	1913	544 (4.04), 420 (4.28), 324 (6.24)	0.50 (160)	1.02 (200)	$-0.88$ (180), $-1.60^{d}$
5c	1916	560 (4.16), 450 (6.44), 370 (3.92)	0.52 (160)	1.00 (240)	$-0.80(140), -1.55^{d}$
5d	1928	570 (2.24), 455 (6.44), 372 (7.26)	0.58 (170)	1.15 (180)	$-0.85$ (140), $-1.62^{d}$

<sup>a</sup> Solvent CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Solvent Gr<sub>2</sub>er<sub>2</sub>. <sup>b</sup> Solvent MeCN, Pt-disk working electrode, Ag/AgCl reference electrode, Pt wire auxiliary electrode, [*n*Bu<sub>4</sub>N][CIO<sub>4</sub>] supporting electrolyte.  $E_{\rm M}^{\rm l} = 0.5E_{\rm pa} + E_{\rm pc}$ , V for Os(III)/Os(II) couple,  $E_{\rm M}^{\rm 2}$  for Os(IV)/Os(III) couple in unit of V,  $\Delta E_{\rm p} = |E_{\rm pa} - E_{\rm pc}|$ , mV.

<sup>d</sup>  $E_{pc}$ (cathodic-peak-potential),  $E_{pa}$  (anodic-peak-potential).

is in support of presence of Os–CO bond [10,14]. Other characteristic stretching are v(N=N) and v(C=N) at 1370–1400 and 1560–1580 cm<sup>-1</sup>, respectively. The v(N=N) is significantly shifted to lower frequency region compared to free ligand value (1415–1425 cm<sup>-1</sup>) [16] and is in support of back donation, dOs(II)  $\rightarrow \pi^*(azo)$ . The radical anion complexes, [Os(Cl)(CO)(PPh\_3)<sub>2</sub>(PyaiR<sup>-+</sup>)] (**4b**– **4d**) exhibit v(CO) at 1880–1900 cm<sup>-1</sup> which is shifted to lower frequency [17], region by 20–60 cm<sup>-1</sup> with reference to non-radical red complex, **3**. The v(Os–H) is a weak band at ca. 2035–2100 cm<sup>-1</sup> and is characteristic of complexes **2**. The v(CO) of **3** is shifted to higher frequency by 15– 20 cm<sup>-1</sup> than **2**. This is corroborated with the absence of  $\sigma$ -donation of Os–H to Os–CO motif.

The electronic spectra of **2** in MeCN show two high intense transition in 270–300 and 370–390 nm and these are assigned to ligand-centred charge transfer transitions [16]. An intense broad band at 480–525 nm (Table 2 and Fig. 2), absent in free ligand, is assigned to  $d\pi(Os) \rightarrow \pi^*(azoimine)$  transition [5,6]. The solution spectra of **3** show blue shift by 10–30 nm. The complexes **4** display moderate intense ( $\varepsilon \sim 1200-1600 \text{ M}^{-1} \text{ cm}^{-1}$ ) band at 690– 710 nm in benzene solution. On comparing with reported results [11,12,17] it is assumed an intraligand excitation

Table 2 <sup>1</sup>H NMR data recorded in CDCl<sub>3</sub> at 298 K

Compounds	δ, (ppm) (J/Hz)									
	4-H	5-H	7-H <sup>b</sup>	9-H <sup>a</sup>	10-H <sup>c</sup>	11-H <sup>a</sup>	N(1)-R	Os–H <sup>c</sup>	PPh <sub>3</sub> _Protons <sup>d</sup>	
2a	7.15 <sup>a</sup> (6.0)	7.06 <sup>a</sup> (6.0)	8.55	7.62 (9.0)	7.42 (9.0)	8.36 (6.0)		-9.10 (22.0)	7.25-7.40	
2b	$7.16^{a}$ (6.0)	$7.04^{a}$ (6.0)	8.60	7.68 (9.0)	7.46 (9.0)	8.34 (6.0)	4.24 <sup>e</sup>	-9.15 (20.0)	7.25-7.45	
2c	$7.22^{a}$ (6.0)	$7.12^{a}$ (6.0)	8.62	7.50 (9.0)	7.42 (9.0)	8.34 (6.0)	4.53 (9.0), 1.51 (8.0) <sup>f</sup>	-9.16 (20.0)	7.20-7.40	
2d	$7.22^{a}$ (6.0)	$7.10^{\rm a}$ (6.0)	8.60	7.60 (9.0)	7.46 (9.0)	7.38 (6.0)	5.74 <sup>g</sup>	-9.25 (20.0)	7.20-7.35	
3a	7.20 (6.0)	$7.10^{a}$ (6.0)	8.60	7.68 (9.0)	7.52 (9.0)	8.42 (6.0)			7.20-7.40	
3b	$7.24^{\rm a}$ (6.0)	7.11 <sup>a</sup> (6.0)	8.71	7.81 (9.0)	7.58 (9.0)	8.46 (6.0)	4.36 <sup>e</sup>		7.25-7.40	
3c	$7.36^{a}$ (6.0)	$7.18^{a}$ (6.0)	8.84	7.67 (9.0)	7.54 (9.0)	8.42 (6.0)	$4.76(9.0), 1.62(8.0)^{f}$		7.30-7.45	
3d	$7.38^{a}$ (6.0)	$7.22^{\rm a}$ (6.0)	8.78	7.72 (9.0)	7.54 (9.0)	7.46 (6.0)	5.96 <sup>g</sup>		7.20-7.40	
5a	$4.18^{\circ}$ (8.0)	$3.87^{c}$ (8.0)	8.60	7.68 (9.0)	7.52 (9.0)	8.39 (6.0)		-11.25 (20.0)	7.20-7.35	
5b	$4.24^{c}$ (8.0)	3.91 <sup>c</sup> (8.0)	8.64	7.72 (9.0)	7.53 (9.0)	8.42 (6.0)	4.28 <sup>e</sup>	-11.34 (20.0)	7.30-7.45	
5c	$4.26^{\circ}(7.5)$	$3.88^{\circ}$ (7.5)	8.68	7.57 (9.0)	7.48 (9.0)	8.37 (6.0)	4.57 (9.0), 1.53 (8.0) <sup>f</sup>	-11.34 (22.0)	7.25-7.40	
5d	4.25° (8.0)	$3.92^{\circ}$ (8.0)	8.65	7.66 (9.0)	7.56 (9.0)	7.48 (6.0)	5.78 <sup>g</sup>	-11.38 (22.0)	7.20–7.40	

<sup>a</sup> Doublet.

<sup>b</sup> Singlet.

<sup>c</sup> Triplet.

<sup>d</sup> Multiplet.

<sup>e</sup>  $\delta(N(1)-Me)$ , singlet.

 $^{\rm f}$   $\delta(N(1)\text{-}CH_2)\text{-}CH_3$  quartet and sextet.

 $^{g}$   $\delta(N(1)-CH_{2}Ph)$ .

<sup>&</sup>lt;sup>c</sup> Shoulder.



Fig. 2. UV–Vis spectra of  $[OsH(CO)(PPh_3)_2(PyaiEt)]PF_6$  (2c) (···),  $[Os(Cl)(CO)(PPh_3)_2(PyaiEt)]PF_6$  (3c) (–),  $[OsH(CO)(PPh_3)_2(PyaiEtH_2)]$ - $PF_6$  (–oo–) (5c) in acetonitrile,  $[Os(Cl)(CO)(PPh_3)_2(PyaiEt^-)]$  (4c) (–––) in benzene and fluorescence spectrum of  $[Os(Cl)(CO)(PPh_3)_2(PyaiEt)]$  (4c) (–––) in benzene.

of the anion radical electron from the azo-anion to the imidazolyl and/or pyridine motif. This band is rapidly diminishing upon addition of  $\rm NH_4PF_6$  in dichloromethane–acetonitrile solution or a drop of acetic acid and finally merged with the spectrum of nonradical complex. This supports radical quenching via protonation.

The anion radical compounds, **4**, are fluorescent active (Fig. 2). Excitation of benzene solution at 360 nm show intense emission at 480–510 nm (quantum yield,  $\phi$  varies 0.012–0.022). The non-radical complexes, **2** and **3**, are nonfluorescent. This supports indirectly the excitation of anion-radical electron which is of  $(\pi, \pi^*)$  type. Upon addition of Cl<sub>2</sub> (in MeCN) emission is vanished instantaneously and shifts absorption maxima from green to red (excluding the possibility of Os(II)  $\rightarrow$  Os(III)). This may be due to radical quenching and formation of nonradical compound.

The <sup>1</sup>H NMR spectra of the complexes are carried out in CDCl<sub>3</sub>. The proton numbering pattern is shown in Scheme 1. A representative figure is shown in Fig. 4a. The protons are assigned (Table 2) on the basis of spin-spin interaction and on comparing with the free ligand data [16]. The significant observation is the appearance of triplet Os-H signal at <-9 ppm (J = 20-22 Hz) for  $[Os(H)(CO)(PPh_3)_2(L)]^n$ (for  $L = Pyai^{-}(2a)$ , n = 0; for L = PyaiR(2b - -2d), n = +1). Imidazole protons, 4- and 5-H, appear at 7.2-7.3 and 7.1–7.2 ppm, respectively.In [Os(Cl)(CO)- $(PPh_3)_2(L)^n$  (L = Pyai(**3a**), n = 0; L = PyaiR, n = +1(3b-3d)) these signals are shifted to higher  $\delta$  by 0.1– 0.2 ppm which may be due to loss of  $\sigma$ -donation on going from Os-H to Os-Cl. The singlet nature of imidazole protons may be due to rapid proton exchange at NMR time scale. A singlet resonance appears at 8.5-8.6 ppm which may be assigned to 7-H of Pyai<sup>-</sup>/PyaiR of  $[Os(H/Cl)(CO)(PPh_3)_2(Pyai/PyaiR)]^{0/+}$ . 1-Me appears as a singlet at 4.1 ppm; 1-CH<sub>2</sub>-CH<sub>3</sub> gives a quartet



PyaiR (1)  $[Os(X)(CO)(PPh_3)_2(PyaiR]^{0/+} [Os(C1)(CO)(PPh_3)_2(PyaiR^-]^{0/+} 2 \text{ or } 3$ R = H (PyaiH, 1a), Me (PyaiMe, 1b), CH<sub>2</sub>CH<sub>3</sub> (PyaiEt, 1c), CH<sub>2</sub>Ph (PyaiCH<sub>2</sub>Ph, 1d);





Scheme 1.

(4.4 ppm, (J = 9.0 Hz)) and a triplet (1.5 ppm (J = 8.0 Hz)), respectively; 1-CH<sub>2</sub>-(Ph) gives a singlet at 5.7 ppm PPh<sub>3</sub> shows multiplets at 7.3–7.4 ppm. Because of insufficient concentration of the complexes in CDCl<sub>3</sub> we could not perform <sup>13</sup>C NMR spectral measurements.

#### 2.3. Electrochemistry

The redox data are summarised in Table 1. Initial scan (+ve to Ag/AgCl) 0.0–1.8 V shows two successive responses (Fig. 5) at 0.6–0.8 and 1.2–1.3 V. The voltammogram does not give well defined peak upon scan reversal and is defined as quasireversible in nature from their peak-to-peak separation data ( $\Delta E_p > 140 \text{ mV}$ ). The voltammogram does not change with scan rate (50–250 mV S<sup>-1</sup>). Os(II) in the complexes can sequentially exhibit Os(III)/Os(II) and Os(IV)/Os(III) redox processes. Thus, two anodic responses are ascribed to Os(III)/Os(II) (0.6–0.8 V) and Os(IV)/Os(III) (1.2–1.3 V) couples. The complexes **3** show higher metal oxidation potential than **2** which may be due to higher electronegativity of Cl in Os–Cl (**3**) than Os–H (**2**).

On scanning to negative direction (0 to -1.8 V) two redox responses are observed (Fig. 5). First response is quasireversible ( $\Delta E_p \ge 100 \text{ mV}$ ) and the second one appears at <-1.3 V which is irreversible in nature. The chelated ligand belongs to  $\pi$ -acidic azo-heterocycle and can accommodate two electrons centred at azo group (-N=N-). On comparing with literature report [11,12,16] we may assign that these responses are due to azo reduction: [-N=N]/[-N-N-]<sup>-</sup> and [-N-N]<sup>-</sup>/[-N-N-]<sup>2-</sup>.

### 2.4. Reaction of $[Os(H)(CO)(PPh_3)_2(Pyai|PyaiR)]^{0/+}$ with NaBH<sub>4</sub> and structural characterisation of product

Imidazole ring is remarkably resistant to hydrogenation [18]. The complexes 2, inherently contain reducing equivalent (Os–H) in the molecule, may reduce -N=N- in the chelated (CO)(PPh<sub>3</sub>)<sub>2</sub>(H-Os)-(-N=N-C=N-) motif to (CO)(PPh<sub>3</sub>)<sub>2</sub>Os-(N-N-C=N)<sup>-</sup>. Radical anion is stabilized by  $\pi$ -acidity of CO and PPh<sub>3</sub> in the molecule. Upon addition of hydridic agent to  $[Os(Cl)(CO)(PPh_3)_2(L)]^+$ substituted Os-Cl to Os-H and produces has  $[Os(H)(CO)(PPh_3)_2(L)]^+$ . The reaction of  $NaBH_4$  with  $[Os(H)(PPh_3)_3(L)]^{\mp}$  (L = bpy) in protic medium has recommended the synthesis of  $[Os(\eta^2-H_2)(PPh_3)_3(L)]^{2+}$  which has labile  $\eta^2$ -H<sub>2</sub> and undergoes immediate substitution reaction [13,14]. Besides,  $[Os(H)(PPh_3)_3(L)]^+$  exhibits interesting insertion reaction of unsaturated molecules  $(RC \equiv CH, CO_2, CS_2, ArN_2^+)$  to the Os-H bond. The reactivity of  $[Os(H)(CO)(PPh_3)_2(Pyai/PyaiR)]^{0/+}$  has been studied in presence of additional external reducing agent;  $NaBH_4$  in ethanol medium for a period of 20 h under stirring condition at room temperature. Red colour of initial solution has changed to orange red. It was then evaporated to dryness washed with water and extracted with chloroform and chromatographed. An orange red band was eluted by benzene–MeCN (6:1 v/v) followed by a tail of deep red band. Slow evaporation of orange red solution has separated good quality crystals. The structural detail is given below. The compound obtained from deep red band is characterised spectroscopically as unreacted  $[Os(H)(CO)(PPh_3)_2(Pyai/PyaiR)]^{0/+}$  complex.

A molecular view of the product obtained from the reaction  $[Os(H)(CO)(PPh_3)_2(Pyai)] + NaBH_4$  is shown in Fig. 3; selected bond parameters are listed in Table 3. Molecule consists of a central Os atom surrounded by six coordination centers and the arrangement is distorted octahedral. The atomic arrangement involves two *trans*phosphine, *N*,*N'*-chelated ligand, hydrido (H<sup>-</sup>) and a CO within the OsP<sub>2</sub>N<sub>2</sub>CH coordination sphere. Interestingly the structure shows reduction of imidazole unit of Pyai<sup>-</sup> to imidazolidinate ion (this is also verified by <sup>1</sup>H NMR



Fig. 3. Molecular structure of [Os(H)(CO)(PPh<sub>3</sub>)<sub>2</sub>(PyaiH<sub>2</sub>)].

Table 3 Selected bond distances and angles of  $[Os(H)(CO)(PPh_3)_2(PyaiH_2)]$  (5a) along with their esd in parentheses

Distances (Å)		Angles (°)	
Os(1)–C(14)	1.858(4)	N(1)–Os(1)–N(7)	73.57(11)
Os (1)– N(1)	2.101(3)	N(1)-Os(1)-C(14)	175.29(13)
Os (1)– N(7)	2.158(4)	N(7)–Os (1)– C(14)	103.06(13)
Os (1)– P(1)	2.3574(15)	P(1)-Os(1)-P(2)	168.12(4)
Os(1)–P(2)	2.3480(15)	P(1)-Os(1)-C(14)	88.56(11)
N(6) - N(7)	1.311(5)	P(2)–Os (1)– C(14)	89.18(12)
N(7)–C(8)	1.435(5)	P(1) - Os(1) - N(1)	94.99(8)
N(6) - C(5)	1.363(6)	P(1)–Os (1)–N(7)	95.39(11)
C(14)–O(14)	1.158(5)	P(2)–Os (1)–N(1)	87.96(8)
Os(1)–H(1)	1.449(2)	P(2)-Os(1)-N(7)	96.48(12)
C(2) - C(3)	1.452(5)	C(14)-Os(1)-H(1)	92.4(16)
C(2) - N(1)	1.307(4)	N(1)-Os(1)-H(1)	91.1(16)
C(3)–N(4)	1.365(5)	P(1)-Os(1)-H(1)	82.9(18)
		P(2)-Os(1)-H(1)	85.6(18)
		N(7)-Os(1)-H(1)	164.5(16)

spectral data). The H<sup>-</sup> is located at *trans* to azo-N coordination. The atomic group Os, N(1), C(5), N(6), N(7) constitute a chelate plane (mean deviation  $\leq 0.04$  Å). N(1), N(7), H(1), C(14) form the square plane. The 3'-pyridyl ring is inclined at an angle 38.76(17)°with the chelate ring. Trans phosphine angle, P(1)–Ru–P(2), is 168.12 (4)° and lies in the lower range of reported data [19]. This large deviation from trans-angle value may be due to steric crowding. The chelate bite angle N(1)–Os–N(7) is 73.57(11)°. Other angles about Os defines distorted octahedral geometry.

The Os–N(7) [(N7) is azo-N] is 2.158 (4) Å is slightly longer than Os–N(1) (N(1) is imidazole) (2.101(3) Å). This is unusual to the structural chemistry of Os-azoheterocycles [20]. In general Os-N(azo) bond distance is significantly shorter than Os-N(imidazole) bond length which is mainly due to involvement of  $\pi$ -acceptance of  $d\pi$  electrons. The C–C distance (C(2)-C(3), 1.452(5) Å) in imidazolidinate unit supports single bond data. The N=N distance is 1.311(5) Å and is elongated by 0.043 Å (free ligand N=N distance in 2-(3'-pyridylazo)imidazole (PyaiH) is 1.268(2) Å [21]). The presence of trans Os-H bond enhances the charge transfer to N=N center and may cause elongation of azo bond. The observed Os-P distances are 2.3480(15), and 2.3574 (15) Å. The Os-C (1.858(4) Å) length is closer to reported Os(II)-carbonyl system. The Os-H distance is 1.449(2) Å. The C-O is 1.158(4) Å and is also slightly elongated than that of reported osmium-carbonyl data [11-14].

The <sup>1</sup>H NMR spectra support (Fig. 4) reduction of imidazole to imidazolidinate. A significant spectral difference for these complexes, **5**, compared to precursor **2** is observed at 3.5–4.5 ppm. Two triplets may be assigned to  $-C(4)H_{2}$ - and  $-C(5)H_{2}$ - protons (Scheme 1). Other protons of pyridine or phenyl group are hardly affected by this reduction (Table 2). 1-R (Me, Et, CH<sub>2</sub>Ph) proton signals are slightly shifted to lower  $\delta$  (by 0.1–0.2 ppm) compared to precursor complexes (**2**). The Os–H signal appears as triplet at <–11.2 ppm (J = 20–22 Hz) for **5** and is shifted to lower  $\delta$  by >2 ppm. It may be due to significant electron donation to metal centre from coordinated azoimidazolidinate compared to azoimidazole chelate.

Cyclic voltammetry of **5** shows two quasi-reversible anodic responses (Fig. 5) corresponding to Os(III)/Os(II) and Os(IV)/Os(III) and azo reductions (Table 1). Redox couples at negative potential are referred to azo reductions. Data in Table 1 show that redox couples appear at less potential for **5** than that of precursor **2**. This supports better electron donation from azo-imidazolidinate in the complexes **5** than **2**.

#### 3. Experimental

#### 3.1. Materials and methods

2-(3'-Pyridylazo)imidazole (PyaiH) and 1-alkyl-2-(3'-pyridylazo)imidazole (PyaiR) were synthesized following



Fig. 4. (a) <sup>1</sup>H NMR spectrum of  $[Os(H)(CO)(PPh_3)_2(PyaiMe)](PF_6)$  and (b)  $-CH_2-CH_2-$  in imidazolidinate part of  $[Os(H)(CO)(PPh_3)_2(PyaiH_2)]$  in CDCl<sub>3</sub>.



Fig. 5. Cyclic voltammogram of  $[Os(H)(CO)(PPh_3)_2(PyaiMe)](PF_6)$  (**2b**) (-----);  $[Os(H)(CO)(PPh_3)_2(PyaiH_2)]PF_6$  (**5b**) (--) in acetonitrile and  $[Os(CI)(CO)(PPh_3)_2(PyaiMe)]$  (**4b**) in dichloromethane using Pt-working electrode, Ag/AgCl reference electrode.

previously published procedure [21].  $[Os(H)(Cl)(CO)-(PPh_3)_3]$  was also prepared by reported method [22]. Imidazole, 3-aminopyridine and all other organic chemicals and inorganic salts were available from Sisco Research Lab, Mumbai, India. The purification of acetoni-trile and preparation of *n*-tetra-butylammonium perchlorate  $[nBu_4N]$ [ClO<sub>4</sub>] for electrochemical work were done as before [9]. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All other chemicals and solvents were of reagent grade and were used without further purification. Commercially available SRL silica gel (60-120 mesh) was used for column chromatography.

Microanalytical data (C, H, N) were collected on Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV-Vis spectra from Perkin-Elmer Lambda 25; FT-IR spectra (KBr disk,  $4000-450 \text{ cm}^{-1}$ ), Perkin-Elmer RX1; <sup>1</sup>H NMR spectra, Bruker (AC) 300 MHz FT-NMR spectrometer. Luminescence property was measured using Perkin Elmer LS 55 fluorescence spectrophotometer at room temperature (298 K). The fluorescence quantum yield of the complexes was determined using Coumarin-120 laser dye as a reference with a known  $\phi_{\rm R}$  of 0.63 in MeCN. The complexes and the reference were excited at 380 nm, maintaining nearly equal absorbance ( $\sim 0.1$ ), and the emission spectra were recorded from 390 to 700 nm. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

$$\phi_{\mathrm{S}}/\phi_{\mathrm{R}} = [A_{\mathrm{S}}/A_{\mathrm{R}}] \times [(\mathrm{Abs})_{\mathrm{R}}/(\mathrm{Abs})_{\mathrm{S}}] \times [\eta_{\mathrm{S}}^2/\eta_{\mathrm{R}}^2].$$

Here,  $\phi_{\rm S}$  and  $\phi_{\rm R}$  are the fluorescence quantum yield of the sample and reference, respectively.  $A_{\rm S}$  and  $A_{\rm R}$  are the area under the fluorescence spectra of the sample and the reference respectively, (Abs)<sub>S</sub> and (Abs)<sub>R</sub> are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and  $\eta_{\rm S}$  and  $\eta_{\rm R}$  are the values of refractive index for the respective solvent used for the sample and reference.

Molar conductances were measured in a Systronics conductivity meter 304 model using ca.  $10^{-3}$  M solutions in MeCN. Electrochemical measurements were performed using computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disk electrodes. All measurements were carried out under nitrogen environment at 298 K with reference to Ag/AgCl, Cl<sup>-</sup> in acetonitrile (for complexes **2**, **3** and **5**) or dichloromethane (for **4**) using [*n*Bu<sub>4</sub>N][ClO<sub>4</sub>] as supporting electrolyte. The reported potentials are uncorrected for junction potential. Magnetic properties were measured using a PAR-155 vibrating sample magnetometer fitted with a Walker scientific magnet. EPR spectra were recorded on a Varian E-109C spectrometer.

#### 3.2. Synthesis of $[Os(H)(CO)(PPh_3)_2(Pyai)]$ (2a)

To a suspension of  $[Os(H)(Cl)(CO)(PPh_3)_3]$  (170 mg, 0.2 mmol) in dry THF (20 ml) 2-(3'-Pyridylazo)imidazole (PyaiH) (52 mg, 0.3 mmol) was added in the same solvent.

The solution was stirred and refluxed for 15 h under dinitrogen. The orange red solution was turned to deep red. It was then cooled and filtered. Dark precipitate appeared on slow evaporation of the solution; it was filtered, washed with cold methanol. Dried in CaCl<sub>2</sub> desiccator in vacuuo. Purification was carried out by column chromatography over alumina column prepared in benzene. Desired red band was eluted by acetonitrile. It was then evaporated and dried over CaCl<sub>2</sub> in vacuuo. The yield was 63%.

The complexes of PyaiR were also prepared under identical reaction condition along with addition of  $NH_4PF_6$  to precipitate  $[Os(H)(CO)(PPh_3)_2(PyaiR)](PF_6)$  (**2b–2d**).

Microanalytical data: Calc. (found) For  $C_{45}H_{37}N_5O-P_2Os$  (**2a**): C, 59.00 (59.13); H, 4.04 (3.88); N, 7.65 (7.82). For  $C_{46}H_{40}N_5OF_6P_3Os$  (**2b**): C, 51.34 (51.50); H, 3.72 (3.78); N, 6.51 (6.44). For  $C_{47}H_{42}N_5OF_6P_3Os$  (**2c**): C, 51.78 (51.89); H, 3.86 (3.80); N, 6.43 (6.50). For  $C_{52}H_{44}N_5OF_6P_3Os$  (**2d**): C, 54.20 (54.33); H, 3.82 (3.78); N, 6.08 (6.04).

#### 3.3. Synthesis of [Os(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub>(PyaiR)](PF<sub>6</sub><sup>-</sup>) (4b-4d)

Procedure for the preparation of [Os(Cl)(CO)(PPh<sub>3</sub>)<sub>2</sub>- $(PyaiMe)](PF_6^{-})$  is given in detail as follows. To an excess of 1-methyl-2-(3'-Pyridylazo)imidazole (PyaiMe) (37.4 mg, 0.2 mmol) dissolved in dry n-heptane (25 ml) was added  $[Os(H)(Cl)(CO)(PPh_3)_3]$  (85 mg, 0.1 mmol), and the mixture was refluxed for 6 h under dry dinitrogen environment. Initial orange-red colour gradually changed to dark green. The mixture was then distilled off and extracted with benzene and evaporated under reduced pressure. A red mass was left insoluble. The green mass collected after evaporation was redissolved in benzene and hexane was layered over it for diffusion. Green crystalline product was isolated but poorly diffracting under X-ray irradiation. Yield, 55%. Microanalytical data are as follows: Anal. Calc. (found) for C<sub>46</sub>H<sub>39</sub>N<sub>5</sub>OClP<sub>2</sub>Os (**4b**): C, 57.22 (57.28); H, 4.04 (4.11); N, 7.26 (7.34). For C<sub>47</sub>H<sub>41</sub>N<sub>5</sub>OClP<sub>2</sub>Os (4c): C, 57.63 (57.72); H, 4.19 (4.14); N, 7.15 (7.26). For C<sub>52</sub>H<sub>43</sub>N<sub>5</sub>OClP<sub>2</sub>Os (4d): C, 59.96 (60.03); H, 4.13 (4.22); N, 6.73 (6.80).

The reaction has been carried out also in *n*-hexane and toluene fixing other conditions same. We have isolated green product **4b** in <5% yield in *n*-hexane and 15% in toluene. Because of insolubility of **4a** we did not proceed to analyse this sample.

# 3.4. Reaction of $[Os(H)(CO)(PPh_3)_2(PyaiR)]^{0/+}$ (2) and $[Os(Cl)(CO)(PPh_3)_2(PyaiR^-)]$ (4) with $Cl_2$ in MeCN

To MeCN solution of  $[Os(H)(CO)(PPh_3)_2(Pyai/PyaiR)]^{0/+}$  few drops of Cl<sub>2</sub> saturated MeCN is added and stirred. Solution colour has changed immediately from red (2) to red-violet or deep green (4) to red-violet. The volume is reduced by slow evaporation and addition of NH<sub>4</sub>PF<sub>6</sub> has separated crystalline compounds. A red-violet band was separated by chromatography. The eluent evaporated to dryness. Then dark mass was water washed and dried over CaCl<sub>2</sub>. Microanalytical data of the complexes supports the composition  $[Os(Cl)(CO)(PPh_3)_2(PyaiR)]$ -(PF<sub>6</sub>) (**3**) and conductivity ( $\Lambda_M = 95-110 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ ) suggests 1:1 electrolyte.

$$\begin{split} & [Os(H)(CO)(PPh_3)_2(PyaiR)]^+ \\ & \xrightarrow{Cl_2 \text{ in } MeCN,} [Os(Cl)(CO)(PPh_3)_2(PyaiR)]^+ \\ & [Os(Cl)(CO)(PPh_3)_2(PyaiR^{-})] \\ & \xrightarrow{Cl_2 \text{ in } MeCN,} [Os(Cl)(CO)(PPh_3)_2(PyaiR)]^+ \end{split}$$

Microanalytical data: Calc. (found) For  $C_{46}H_{42}N_4OClF_6-P_3Os$  (**3a**): C, 56.86 (56.79); H, 3.79 (3.70); N, 7.37 (7.44). For  $C_{46}H_{39}N_5OClP_3F_6Os$  (**3b**): C, 49.77 (49.68); H, 3.52 (3.46); N, 6.31 (6.38). For  $C_{47}H_{41}N_5OClF_6P_3Os$  (**3c**): C, 50.19 (50.28); H, 3.65 (3.71); N, 6.23 (6.30). For  $C_{52}H_{43}N_5OClF_6P_3Os$  (**3d**): C, 52.63 (52.77); H, 3.63 (3.54); N, 5.90 (5.86).

## 3.5. Reaction of $[Os(H)(CO)(PPh_3)_2(Pyai|PyaiR)]^{0/+}$ with NaBH<sub>4</sub>

A representative reaction is given below for the reaction of [Os(H)(CO)(PPh<sub>3</sub>)<sub>2</sub>(Pyai)], 2awith NaBH<sub>4</sub>.In a 100 ml two-necked round-bottomed flask 230 mg (0.25 mmol) of [Os(H)(CO)(PPh<sub>3</sub>)<sub>2</sub>(Pyai)] was suspended in 25 ml of ethanol. NaBH<sub>4</sub> (227 mg, 6 mmol) was added pinch wise to the solution and the reaction mixture was stirred for 20 h. Red colour of suspension has changed to orange red. The solvent was removed under reduced pressure to give an orange-red solid from which reaction product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and chromatographed. An orange red band was eluted by benzene–MeCN (6:1 v/v). Slow evaporation of orange red solution has separated good quality crystals. Reaction with  $[Os(H)(CO)(PPh_3)_2(PyaiR)]^+$  (**2b–2d**). The reaction procedure were similar as 2a, but an orange-red gummy mass were obtained instead of orange-red solid after extraction with CH<sub>2</sub>Cl<sub>2</sub> and removing the solvent. Gummy product was treated with ethanol (5 ml). The addition of an excess of NH<sub>4</sub>PF<sub>6</sub> in water, orange-red precipitate (5b-5d) were separated. The precipitate was filtered, washed with water, ether and hexane. Dried in CaCl<sub>2</sub> desiccator and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol.

The yield of **5** were varied from 45% to 50%. Microanalytical data: Calc. (found) for  $C_{45}H_{39}N_5OP_2Os$  (**5a**): C, 58.87 (58.72); H, 4.25 (4.18); N, 7.63 (7.57). For  $C_{46}H_{42}N_5OF_6P_3Os$  (**5b**): C, 51.24 (51.15); H, 3.90 (3.88); N, 6.50 (6.46). For  $C_{47}H_{44}N_5OF_6P_3Os$  (**5c**): C, 51.69 (51.72); H, 4.03 (4.08); N, 6.41 (6.48). For  $C_{52}H_{46}N_5OF_6-P_3Os$  (**5d**): C, 54.11 (53.87); H, 3.99 (3.82); N, 6.07 (5.96).

#### 3.6. X-ray crystal structure determination

Prismatic orange yellow crystals of  $[Os(H)(CO)(PPh_3)_2$ (PyaiH<sub>2</sub>)] (**5a**) (dimension:  $0.15 \times 0.15 \times 0.15$  mm) were Table 4

Summarised crystallography data for [Os(H)(CO)(PPH<sup>3</sup>)<sub>2</sub> (PyaiH<sub>2</sub>)] (5a)

Crystal parameters	
Empirical formula	C45H39N5OP2Os
Formula weight	917.95
Crystal system	Monoclinic
Space group	Cc
<i>a</i> (Å)	12.197(2)
b (Å)	19.270(3)
c (Å)	16.569(3)
β (°)	104.153(4)
Size (mm)	$0.15 \times 0.15 \times 0.15$
$V(\text{\AA}^3)$	3776.3(11)
$\lambda$ (Å)	0.71073
$\rho_{\text{calcd}} \ (\text{mg m}^{-3})$	1.615
Ζ	4
$T(\mathbf{K})$	93(2)
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	3.505
20 (°)	$4.92 \leqslant 2\theta \leqslant 50.7$
hkl	$-13 \leqslant h \leqslant 14$ ,
	$-15 \leqslant k \leqslant 22,$
	$-15 \leqslant l \leqslant 19$
Reflection collected	11045
Independent reflections	5543 [ $R_{\rm int} = 0.0325$ ]
Parameters	486
$R_1^{\rm a} I > 2\sigma(I)$	0.0205
$wR_2^{b}$	0.0562
GOF <sup>c</sup>	0.961
Largest difference peak and hole (e $Å^{-3}$ )	0.813 and -1.130
$1/[7/(\pi^2) + (0.0000)/(0.0000)] = 1$	$D (T^2 + 2T^2)/2$

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.0000P]$ , where  $P = (F_o^2 + 2F_o^2)/3$ . <sup>b</sup>  $wR_2 = [\sum \{w(F_o^2 - F_o^2)^2\} / \sum \{w(F_o^2)\}]^{1/2}$ .

<sup>c</sup> GOF (goodness-of-fit) is defined as  $[w(F_o - F_c)/(n_0 - n_v)]^{1/2}$ , where  $n_0$  and  $n_v$  denote the number of data and variables, respectively.

grown by slow diffusion of CH<sub>2</sub>Cl<sub>2</sub> solution of the complex into hexane. Crystal parameters and refinement results are summarized in Table 4. Data were collected from Bruker SMART CCD diffractometer using fine-focus sealed tube graphite monochromatised Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 93(2) K. Data collections were performed in the  $\theta$  range 2.46-25.35° of  $-13 \leq h \leq 14$ ;  $-15 \leq k$  $\leq 22$ ;  $-15 \leq l \leq 19$ . Absorption corrections were carried out by multiscan process of dtprofit.ref. Out of total reflections 11045 unique data were 5543 used for structure determination. Data reduction and refinement were carried out by Crystalclear of Rigaku Corporation using the programme of shelexl-97. The structure was solved by direct method and refined by full-matrix least-squares refinement based on  $F_0^2$ . All non-hydrogen atoms were refined anisotropically.

#### 4. Conclusion

2-(3'-Pyridylazo)imidazole (PyaiH) or 1-alkyl-2-(3'-pyridylazo)imidazole has been reacted with  $[Os(H)(Cl)-(CO)(PPh_3)_3]$  in THF to synthesize red  $[Os(H)(CO)-(PPh_3)_2(Pyai/PyaiR)]^{0/+}$  (2). Reaction under dry condition in *n*-heptane following above stoichiometry has separated green azo-anion radical  $[Os(Cl)(CO)(PPh_3)_2(3'-PyaiR^{-1})]$  (4) which have been established by EPR and solid state magnetic data. Upon addition of Cl<sub>2</sub> in MeCN to CH<sub>2</sub>Cl<sub>2</sub>

solution of **2** or **4** the solution colour has changed sharply to red-violet and has isolated  $[Os(Cl)(CO)(PPh_3)_2$ - $(Pyai/PyaiR)]^{0/+}$  (**3**). The reaction of **2**or**4** in ethanol with NaBH<sub>4</sub> suspension under dinitrogen has separated azo-imidazolidine compound  $[Os(H)(CO)(PPh_3)_2(PyaiRH_2)]^{+/0}$ (**5**). One of the structures of azo-imidazolidinate-hydridoosmium-carbonyl has been determined by single crystal X-ray diffraction measurements. Redox property of **2** and **3** show Os(III)/Os(II) and Os(IV)/Os(III) couples at positive potential to Ag/AgCl, Cl<sup>-</sup> reference electrode along with azo reduction at negative side.

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