Available online at www.sciencedirect.com

ScienceDirect

Polyhedron 26 (2007) 600–606

POLYHEDRON

www.elsevier.com/locate/poly

Osmium-carbonyl complexes of naphthylazoimidazoles. Single crystal X-ray structure of $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)$ $\{\alpha\text{-NaiEt} = \text{1-ethyl-2-(naphthyl-}\alpha\text{-azo)imidazole}\}$

T.K. Mondal [a], Joydev Dinda [a], Alexandra M.Z. Slawin [b],
J. Derek Woollins [b], C. Sinha [a,*]

[a] *Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032, West Bengal, India*
[b] *Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK*

Received 18 August 2006; accepted 21 August 2006
Available online 7 September 2006

Abstract

1-Alkyl-2-(naphthyl-α/β-azo)imidazole (α-NaiR **1**; β-NaiR, **2**) react with $[Os(H)(Cl)(CO)(PPh_3)_3]$ in THF and synthesise $[Os(H)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})](PF_6)$ (**3**, **4**). The X-ray structure of $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)$ (**3c**) shows a distorted octahedral geometry. Other spectroscopic studies (IR, UV–Vis, NMR) support the stereochemistry of the complexes. Addition of Cl_2 in MeCN to **3** or **4** gives $[Os(Cl)(CO)(\alpha/\beta\text{-NaiR})(PPh_3)_2](PF_6)$ (**5**, **6**), which were characterized by spectroscopic studies. The redox properties of the complexes show Os(III)/Os(II), Os(IV)/Os(III) and azo reductions.

Keywords: Naphthylazoimidazoles; Hydrido-osmium-carbonyl; X-ray structure; Electrochemistry

---

1. Introduction

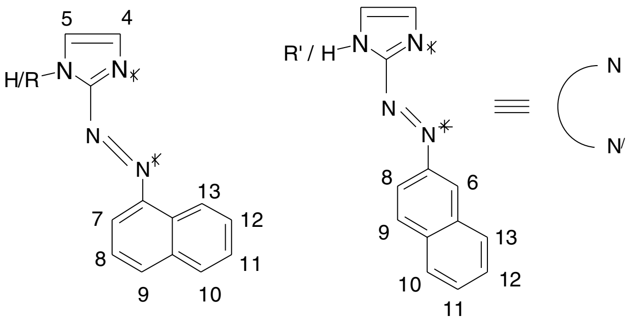
Polypyridyl complexes of ruthenium and osmium are an active area of current research [1–7]. There are a number of M–polypyridine complexes which bear M–H bonds (M = Ru, Os) [8]. The functional group is the diimine, –N=C–C=N–, and the key feature of these heterocycles is their π-acidity. Recent years have witnessed a great deal of interest in the synthesis of new ligands in the framework of the diimine function (–N=C–C=N–) or the functional modification to design an isoelectronic chelating motif. We have been engaged for the last few years in the design of the azoimine function (–N=C–C=N–) which is a functional modification of the diimine unit. We have synthesized the azoimidazole in the azoimine family [9,10]. Imidazole and its derivatives are chosen because of their chemical and biological ubiquity [11], whilst the azo group enhances the π-acidity and is responsible for photochromism [12], pH—responsive and redox activity of the molecules [3]. It is important to stabilize M–H bonds in the presence of a π-acidic chelating framework in the complexes [13–15].

In this work we have used 1-alkyl-2-(naphthyl-α/β-azo)-imidazoles (α/β-NaiR) as a chelating azoimine function [10,16]. We have synthesized $[Os(H)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})]^+$, an osmium-hydrido-carbonyl compound, and the structure has been established by single crystal X-ray diffraction study in one case. The complexes have been reacted with chlorine in acetonitrile. The products, $[Os(Cl)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})](ClO_4)$, were characterised by spectroscopic and electrochemical techniques.

---

[*] Corresponding author. Fax: +91 033 2413 7121.
E-mail address: c_r_sinha@yahoo.com (C. Sinha).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.08.028



α-NaiR(**1**) β-NaiR(**2**)

H (**a**), Me (**b**), CH_2CH_3 (**c**), CH_2Ph (**d**)

2. Results and discussion

2.1. Synthesis and formulation

The reaction of $[Os(H)(Cl)(CO)(PPh_3)_3]$ and 1-alkyl-2-(naphthyl-α/β-azo)imidazoles (α-NaiR (**1**), β-NaiR (**2**) where R = H (a), Me (b), CH_2CH_3 (c), CH_2Ph (d)) in dry THF under dinitrogen yielded a dark red coloured solution. On evaporation of the solvent to half of its original volume and addition of NH_4PF_6, a dark precipitate appeared after cooling in a deep freezer for overnight. The formulation of the complex, $[Os(H)(CO)(PPh_3)_2$-(α/β-NaiR)](PF_6) (**3** for α-NaiR; **4** for β-NaiR) is supported by microanalytical data (see Section 3). Although two geometrical isomers (**3** and **3′** or **4** and **4′**) are possible [CO *trans* to N(azo) or N(imidazole)] we have isolated only one isomer, CO *trans* to N(imidazole) (**3** and **4**). The complexes, **3** and **4**, are diamagnetic and show 1:1 conductivity in acetonitrile solution ($\Lambda_M = 90$–$105\ \Omega^{-1}\ mol^{-1}\ cm^2$). The reaction of α/β-NaiH and $[Os(H)(Cl)(CO)(PPh_3)_3]$ also gave dark coloured crystalline compounds in the presence of NH_4PF_6, but their solubility was too low to carry out any spectral measurements, thus they were not studied further. Reaction of $[Os(H)(CO)(PPh_3)_2$(α/β-NaiR)](PF_6) with Cl_2 in MeCN gave red coloured $[Os(Cl)(CO)(PPh_3)_2$(α/β-NaiR)](PF_6) (**5**, **6**) in high yield (>70%). The hydrido complexes (**3**, **4**) can be regenerated from the chloro complexes (**5**, **6**) by refluxing with $NaBH_4$ in EtOH for 2 h. The formation of hydrido complexes from **5**/**6** has been confirmed by elemental and spectral analysis.

2.2. Molecular structure

The X-ray structure of $[Os(H)(CO)(PPh_3)_2$(α-NaiEt)]-(PF_6) (**3c**) is shown in Fig. 1; selected bond parameters are listed in Table 1. The 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, a chelated 1-ethyl-2-(naphthyl-α-azo)imidazole (α-NaiEt), hydrido (H^-) and a CO within the OsP_2N_2CH coordination sphere. The H^- is located *trans* to the azo-N coordination. The α-naphthyl ring is inclined at an angle of 46.07(11)° with respect to the chelate ring (Os, N(1), C(2), N(2), N(8)). The *trans*-phosphine angle, P(1)–Ru–P(2) of 167.29 (2)° lies in the range of reported data [17,18]. The steric crowding of phenyl and naphthyl groups may provide this large deviation from the perfect *trans*-angle value. The chelate angle N(1)–Os–N(8) is 74.49(8)°. Other angles about Os define the distorted octahedral geometry.

There is no statistically significant difference in the two Os–N bonds; Os(1)–N(8), [(N8) is azo-N] is 2.1117(19) Å and Os(1)–N(1) (N(1) is imidazole) is 2.109(2) Å. The –N=N– bond length is 1.306(3) Å and is longer than the free ligand azo distance (1.267(3) Å) [16] which is in support of dπ(Os) → π^*(azo) charge transmission. The

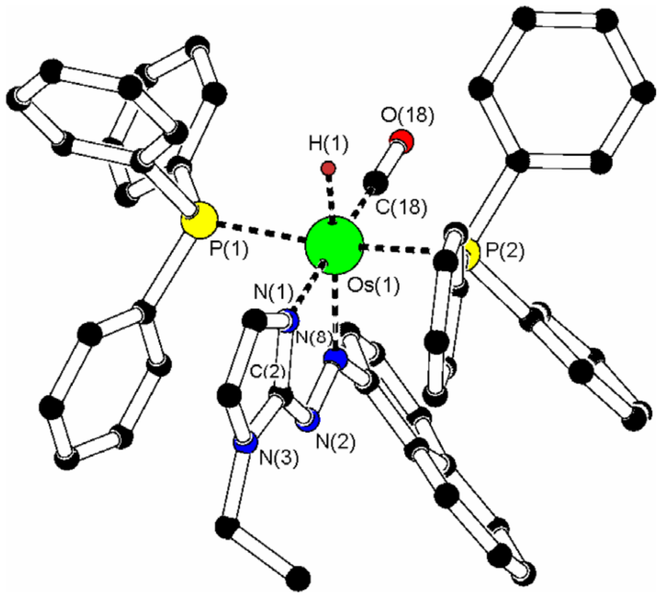


Fig. 1. Single crystal X-ray structure of $[Os(H)(CO)(PPh_3)_2$(α-NaiEt)$]^+$.

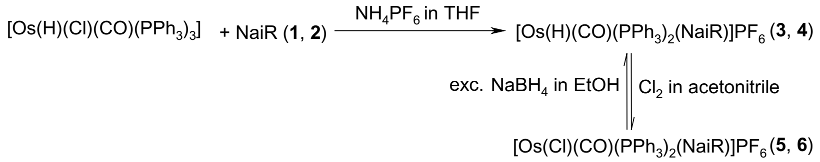


Table 1
Selected bond distances and angles of [Os(H)(CO)$(PPh_3)_2$(α-NaiEt)](PF_6) (**3b**) along with their esd in parentheses

Distances (Å)		Angles (°)	
Os(1)–C (18)	1.855(3)	N(1)–Os(1)–N(8)	74.49(8)
Os (1)–N(1)	2.109(2)	N(1)–Os(1)–C(18)	177.46(9)
Os (1)–N(8)	2.1117(19)	N(8)–Os (1)–C(18)	103.08(9)
Os (1)–P(1)	2.3916(7)	P(1)–Os(1)–P(2)	167.29(2)
Os(1)–P(2)	2.3670(7)	P(1)–Os(1)–C(18)	95.03(8)
N(2)–N (8)	1.306(3)	P(2)–Os (1)–C(18)	89.17(8)
N(8)–C(8)	1.438(3)	P(1)–Os(1)–N(1)	84.50(6)
N(2)–C(2)	1.362(3)	P(1)–Os (1)–N(8)	94.43(5)
C(18)–O(18)	1.160(3)	P(2)–Os (1)–N(1)	91.82(6)
Os(1)–H(1)	1.600	P(2)–Os(1)–N(8)	96.30(5)
		C(18)–Os(1)–H(1)	88.4(10)
		N(1)–Os(1)–H(1)	94.1(10)
		P(1)–Os(1)–H(1)	85.8(9)
		P(2)–Os(1)–H(1)	82.3(9)
		N(8)–Os(1)–H(1)	168.5(10)

Os–H is *trans* to the Os–N=N-(azo) group. The *trans effect* of the Os–H bond may cause elongation of the –N=N– bond. The *trans* Os–H bond enhances the charge transfer to the N=N function and causes the increase in the N=N distance. The Os–C and C–O bond lengths are 1.855(3) and 1.160(3) Å, respectively. The observed Os–P distances, 2.3916(7), 2.3670 (7) Å, are short in the series of $Os(PPh_3)$ chemistry [17,18].

The intramolecular hydrogen bonding interaction generates a supramolecule. A hydrogen bonded dimer serves as a motif (Fig. 2). An F atom in PF_6^- acts as a bridging agent between two complex units. A bifurcated hydrogen bond [(naph)C(14)–H(14)–F(6)(PF_5)–H(27)–C(27)(PPh_3): C(14)–H(14a), 0.95; H(14a)–F(6), 2.520(2); C(14)–F(6), 3.231(3) Å; ∠C–H–F, 132.0° and C(27)–H(27a), 0.95; H(27a)–F(6), 2.400(1); C(27)–F(6), 3.319(3) Å and ∠C–H–F 163.0°] bridges two molecules and forms a supracyclic dimer. PPh_3 protons form several hydrogen bonding interactions with F–P(F_5) and form a 3-D arrangement.

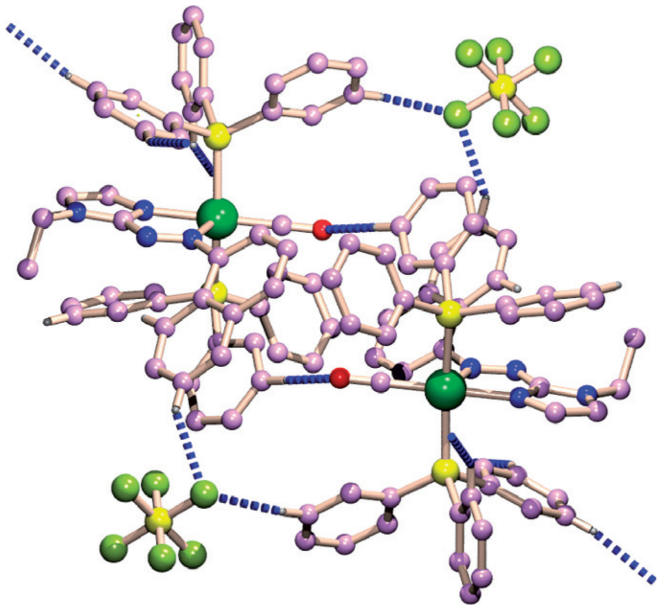


Fig. 2. H-Bonded dimer showing the C–H- - -F- - -H–C unit.

2.3. Spectra and bonding

The complexes [Os(H)(CO)$(PPh_3)_2$(α/β-NaiR)](PF_6) (**3**,**4**) show a sharp stretch at 1920–1940 cm^{-1}, which corresponds to ν(CO). The ν(Os–H) band is observed at ca. 2080–2100 cm^{-1}. Other significant vibrations are ν(N=N) and ν(C=N) at 1350–1380 and 1560–1580 cm^{-1}, respectively. The azo stretching is significantly shifted to the lower frequency region compared to the free ligand value (1400–1410 cm^{-1}) [16] and is in support of back donation, dπOs(II) → π*(azo). The single crystal structure determination in one of the complexes also supports a retro-bonding process (vide supra). For the chlorinated complexes (**5**/**6**) ν(CO) is shifted to 1960–1970 cm^{-1} which is higher than the precursor complexes (**3**/**4**). This is corroborated with the absence of σ-donation of Os–H to the Os–CO motif.

The electronic spectra of the complexes **3** and **4** in MeCN show two high intensity transitions at 310–350 and 410–440 nm and these are assigned to ligand-centred charge transfer transitions. An intense broad band at 490–505 nm (Table 2) (Fig. 3), absent in the free ligand, is obviously assigned to a dπ(Os) → π*(azoimine) transition [10]. The solution spectra of **5** and **6** show blue shifting by 10–30 nm compared to the hydrido analogues, **3** and **4** respectively.

The ^1H NMR spectra of the complexes are taken in $CDCl_3$ (the proton numbering pattern is shown in Scheme 1) and have been assigned (Table 3) on the basis of spin-spin interactions and on comparison with the free ligand values [10,16]. The X-ray structure determination aids the unambiguous assignment of the protons. The most significant observation is the appearance of a triplet Os–H signal at −9.55 to −9.65 ppm ($^2J_{P–H} = 22–25$ Hz) for [Os(H)(CO)$(PPh_3)_2$(α/β-NaiR)](PF_6). Imidazole protons 4- and 5-H appear as a broad singlet at 7.2–7.3 and 7.0–7.1 ppm, respectively. The singlet nature of the imidazole protons may be due to rapid proton exchange on the NMR time scale. 1-R signals of (α/β)-NaiR in [Os(H/Cl)(CO)$(PPh_3)_2$(α/β-NaiR)$]^+$ appear at their usual position [16]; 1-Me appears as a singlet at 4.10–4.15 ppm; 1-CH_2–CH_3 gives a quartet at 4.45–4.50 ppm, ($J = 8.0$ Hz) and a triplet at 1.5 ppm ($J = 8.0$ Hz) for –CH_2– and –CH_3, respectively; 1-CH_2–(Ph) gives a singlet at 5.65–5.75 ppm. PPh_3 shows multiplets at 7.2–7.4 ppm.

2.4. Electrochemistry

The redox data are summarised in Table 2. [Os(H)(CO)$(PPh_3)_2$(α/β-NaiR)](PF_6) (**3**, **4**) and [Os(Cl)(CO)$(PPh_3)_2$(α/β-NaiR)](PF_6) (**5**, **6**) show two successive redox responses (Fig. 4) in MeCN solution with a Pt-working electrode (+ve to Ag/AgCl) between 0.0 and 1.8 V. The voltammogram is quasireversible in nature as is evident from the peak-to-peak separation data (for a reversible

Table 2
UV–Vis spectral[a] and cyclic voltammetric data[a]

Complex	UV–Vis spectra λ_{max} (nm) ($10^{-3} \in M^{-1}\,cm^{-1}$)	Cyclic voltammetry		
		E^1_M	E^2_M	Ligand reductions
3b	334(8.46), 410(12.88), 495(5.34)	0.68(160)	1.18(190)	−0.82(160), −1.24[b]
3c	350(5.42), 415(5.98), 500(5.47)	0.58(160)	1.20(170)	−0.88(180), −1.22[b]
3d	332(4.76), 442(5.64), 504(3.94)	0.70(140)	1.32(170)	−0.78(160), −1.32[b]
4b	352(6.25), 421(7.29), 492(8.20)	0.68(130)	1.35(180)	−0.87(160), −1.35[b]
4c	350(3.88), 428(6.19), 496(2.94)	0.60(160)	1.22(170)	−0.85(180), −1.30[b]
4d	328(4.82), 438(6.34), 498(3.26)	0.70(160)	1.22(170)	−0.82(160), −1.35[b]
5b	337(5.48), 458(7.09), 506(5.38)	0.77(130)	1.30(160)	−0.80(150), −1.25[b]
5c	358(5.48), 430(5.94), 534(5.38)	0.68(120)	1.27(170)	−0.74(150), −1.23[b]
5d	336(5.24), 454(4.78), 520(3.86)	0.81(130)	1.40(160)	−0.72(160), −1.20[b]
6b	338(8.22), 425(9.26), 510(6.36)	0.75(130)	1.30(180)	−0.90(180), −1.40[b]
6c	356(3.68), 468(5.07), 512(6.19)	0.78(120)	1.36(180)	−0.77(170), −1.32[b]
6d	336(4.94), 356(5.44), 505(3.44)	0.80(130)	1.36(170)	−0.78(160), −1.37[b]

[a] Solvent MeCN, Pt-disk working electrode, Ag/AgCl reference electrode, Pt wire auxiliary electrode, [n-Bu$_4$N][ClO$_4$] supporting electrolyte. $E^1_M = 0.5\,(E_{pa} + E_{pc})$, V for Os(III)/Os(II) couple, E^2_M for Os(IV)/Os(III) couple in unit of V, $\Delta E_p = |E_{pa} - E_{pc}|$, mV; E_{pc} (cathodic-peak-potential), E_{pa} (anodic-peak-potential).

[b] E_{pc} (cathodic-peak-potential).

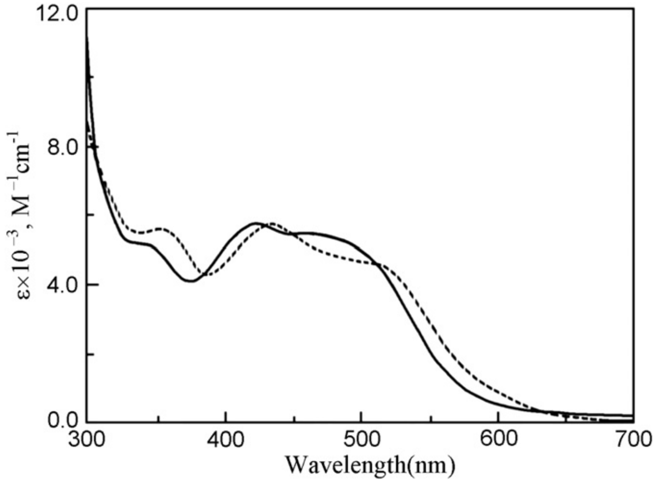


Fig. 3. Absorption spectra of [Os(H)(CO)(PPh$_3$)$_2$(α-NaiEt)](PF$_6$)] (**3c**) (—) [Os(Cl)(CO)(PPh$_3$)$_2$(α-NaiEt)](PF$_6$)] (**5c**) (- - -) (in acetonitrile).

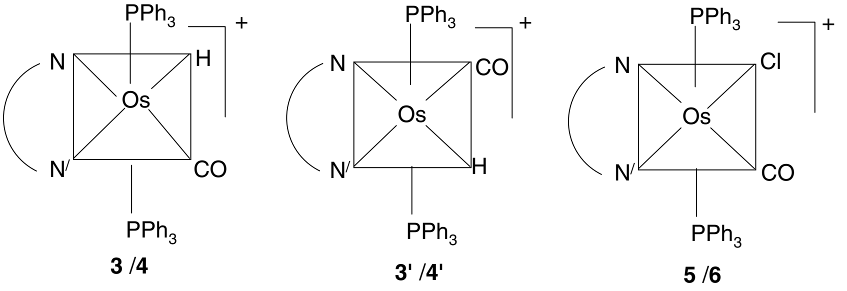
cyclic voltammogram ΔE_p is 60 mV and in the present complexes $\Delta E_p > 120$ mV and is quasi-reversible). The nature of the voltammogram does not change with scan rate (50–250 mV S^{-1}). Os(II) can sequentially exhibit Os(III)/Os(II) and Os(IV)/Os(III) redox processes at positive to Ag/AgCl reference electrode. Thus, two redox couples are referred to metal centred oxidations: Os(III)/Os(II) and Os(IV)/Os(III). Redox couples of [Os(H)(CO)(PPh$_3$)$_2$(α/β-NaiR)](PF$_6$) (**3**, **4**) at 0.6–0.70 and 1.1–1.3 V are shifted to 0.7–0.8 and 1.2–1.4 V, respectively, in [Os(Cl)(CO)(PPh$_3$)$_2$(α/β-NaiR)](PF$_6$) (**5**, **6**). The effect of the electron withdrawing Cl in the latter complexes may be the reason for this redox shifting.

On scanning to the negative direction (0 to −1.8 V), two redox responses are observed (Fig. 4). First response is quasireversible ($\Delta E_p \geqslant 120$ mV) and the second one appears at <−1.2 V which is irreversible in nature. Ligand reduction of azoimidazole complexes appears at negative potential [16b]. The chelated ligand belongs to the azoimine family and can accommodate two electrons centred at the azo group (–N=N–). On comparing with the literature [13,16,19], the reductive responses may be due to accommodation of electrons in the azo dominated function [–N=N]/[–N$\overset{...}{=}$N–]$^-$ and [–N$\overset{...}{=}$N]$^-$/[–N–N–]$^{2-}$.

3. Experimental

3.1. Materials

The 1-alkyl-2-(naphthyl-α/β-azo)imidazoles were synthesized following a previously published procedure [16]. [Os(H)(Cl)(CO)(PPh$_3$)$_3$] was also prepared by a reported method [20]. Imidazole and all other organic chemicals and inorganic salts were available from Sisco Research Lab,



Scheme 1.

Table 3
^1H NMR spectral data of the compounds in $CDCl_3$ at 298 K

Complex	4-H[a]	5-H[a]	6-H[a]	7-H[a]	8-H	9-12-H[d]	13-H[b]	N(1)–R	Os–H[c,g]	PPh_3
3b	7.18	7.05		7.68	7.68[c](7.0)	7.55	7.86(7.5)	4.14[f]	−9.63(23.4)	7.25–7.35
3c	7.15	7.06		7.66	7.66[c](7.0)	7.46	7.84(7.0)	4.46(9.0), 1.50(7.5)[e]	−9.59(22.8)	7.20–7.35
3d	7.18	7.09		7.73	7.73[c](7.0)	7.61	7.90(7.0)	5.78[f]	−9.55(24.0)	7.30–7.40
4b	7.16	7.04	7.93		7.59[b](7.5)	7.50	7.80(7.0)	4.09[f]	−9.67(22.0)	7.25–7.35
4c	7.14	7.00	7.89		7.55[b](7.5)	7.43	7.76(7.0)	4.51(9.0), 1.52(7.0)[e]	−9.60(23.6)	7.20–7.30
4d	7.21	7.11	7.98		7.67[b](7.5)	7.56	7.87(7.0)	5.68[f]	−9.56(22.0)	7.25–7.35
5b	7.36	7.21		7.86	7.86[c](7.0)	7.74	7.94(7.0)	4.23[f]		7.30–7.45
5c	7.38	7.23		7.88	7.88[c](7.0)	7.61	7.98(7.0)	4.57(8.5), 1.58(7.5)[e]		7.30–7.40
5d	7.34	7.25		7.90	7.87[c](7.0)	7.82	7.90(7.0)	5.87[f]		7.40–7.52
6b	7.34	7.18	8.05		7.76[b](7.5)	7.62	7.96(7.0)	4.19[f]		7.35–7.45
6c	7.22	7.16	8.02		7.68[b](7.5)	7.57	7.88(7.5)	4.62(9.0), 1.64(8.0)[e]		7.35–7.45
6d	7.41	7.27	8.10		7.84[b](7.5)	7.72	7.97(7.0)	5.76[f]		7.35–7.45

[a] Broad singlet.
[b] Doublet.
[c] Triplet.
[d] Multiplet.
[e] $\delta(-CH_2-CH_3)$ quartet for $-CH_2-$ and triplet for $-CH_3$.
[f] Singlet.
[g] Coupling constant ^2J refers to $^{31}P-^1H$ coupling.

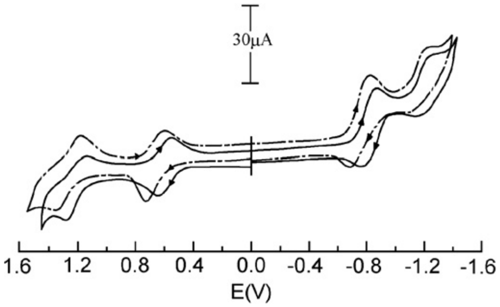


Fig. 4. Cyclic voltammogram of $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)$ (**3c**) (—); $[Os(Cl)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)]$ (**5c**) (–·–) in acetonitrile using a Pt-working electrode and a Ag/AgCl reference electrode.

Mumbai, India. The purification of acetonitrile and preparation of *n*-tetra-butylammonium perchlorate $[n\text{-}Bu_4N][ClO_4]$ for the electrochemical work were done as reported 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.

3.2. Physical measurements

Microanalytical data (C, H, N) were collected on a Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis spectra, Perkin–Elmer; model Lambda 25. IR spectra (KBr disk, 4000–450 cm^{-1}), Perkin–Elmer; model RX-1. ^1H NMR spectra, Bruker (AC) 300 MHz FTNMR spectrometer. Molar conductances were measured using a Systronics conductivity meter 304 model using ca. 10^{-3} M solutions in acetonitrile. Electrochemical measurements were performed using computer-controlled PAR model 250 VersaStat electrochemical instruments with Pt-disk electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to Ag/AgCl in acetonitrile using $[n\text{-}Bu_4N][ClO_4]$ as the supporting electrolyte. The reported potentials are uncorrected for junction potentials. 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.

3.3. Synthesis of $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiMe})](PF_6)$ (**3b**)

To a suspension of $[Os(H)(Cl)(CO)(PPh_3)_3]$ (0.250 g, 0.230 mmol) in dry THF (20 ml) 1-methyl-2-(naphthyl-α-azo)imidazole (α-NaiMe) (0.065 g, 0.28 mmol) was added in the same solvent (10 ml). The solution was stirred and refluxed for 15 h under dinitrogen. The orange red solution turned deep red. It was then cooled and filtered. The filtrate was then evaporated slowly in air to half of its original volume. A THF solution (5 ml) of NH_4PF_6 (0.2 g) was added into this solution and the resulting solution was kept in a deep freezer overnight. A dark precipitate appeared which was filtered, washed with cold THF and then dried in a $CaCl_2$ desiccator in vacuo. Purification was carried out by column chromatography over a silica gel column prepared in benzene. The desired red band was eluted by acetonitrile. It was then evaporated and dried over $CaCl_2$ in vacuo. The yield was 0.16 g (63%).

The other complexes were prepared following an identical procedure. The yield varied between 55% and 65%. Microanalytical data: Calc. (found) for $C_{51}H_{43}N_4OF_6P_3Os$ (**3b**): C, 54.44 (54.35); H, 3.82 (3.76); N, 4.98 (5.11%). For $C_{52}H_{45}N_4OF_6P_3Os$ (**3c**): C, 54.82 (54.95); H, 3.95 (3.88); N, 4.92 (5.01%). For $C_{57}H_{47}N_4OF_6P_3Os$ (**3d**): C, 56.99 (56.89); H, 3.92 (3.86); N, 4.67 (4.63%). For $C_{51}H_{43}N_4OF_6P_3Os$ (**4b**): C, 54.44 (54.39); H, 3.82 (3.78); N, 4.98 (4.94%).

For $C_{52}H_{45}N_4OF_6P_3Os$ (**4c**): C, 54.82 (54.78); H, 3.95 (3.98); N, 4.92 (4.94%). For $C_{57}H_{47}N_4OF_6P_3Os$ (**4d**): C, 56.99 (57.05); H, 3.92 (3.94); N, 4.67 (4.71%).

3.4. Reaction of [Os(H)(CO)(PPh$_3$)$_2$(α/β-NaiR)](PF$_6$) (3, 4) with Cl$_2$ in MeCN

To a MeCN solution of $[Os(H)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})](PF_6)$, a few drops of Cl_2 saturated MeCN was added and the resulting solution was stirred. The solution colour changed immediately from red to red-violet. The volume was reduced by slow evaporation and addition of NH_4PF_6 separated out crystalline compounds. A red-violet band was separated by chromatography. The eluent was evaporated to dryness, then the dark mass was water washed and dried over $CaCl_2$. Microanalytical data of the complexes support the composition $[Os(Cl)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})](PF_6)$ and conductivity data ($\Lambda_M = 100\text{–}110\ \Omega^{-1}\ cm^2\ mol^{-1}$) suggests a 1:1 electrolyte.

$$[Os(H)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})]^+ \xrightarrow{Cl_2\ \text{in}\ MeCN} [Os(Cl)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})]^+$$

Microanalytical data: Calc. (found) for $C_{51}H_{42}N_4OClF_6P_3Os$ (**7b**): C, 52.83 (52.79); H, 3.62 (3.59); N, 4.83 (4.80%). For $C_{52}H_{44}N_4OClF_6P_3Os$ (**7c**): C, 53.22 (53.24); H, 3.75 (3.76); N, 4.77 (4.78%). For $C_{57}H_{46}N_4OClF_6P_3Os$ (**7d**): C, 55.41 (55.38); H, 3.73 (3.71); N, 4.54 (4.52%). For $C_{51}H_{42}N_4OClF_6P_3Os$ (**8b**): C, 52.83 (52.87%); H, 3.62 (3.64%); N, 4.83 (4.86%). For $C_{52}H_{44}N_4OClF_6P_3Os$ (**8c**): C, 53.22 (53.19); H, 3.75 (3.73); N, 4.77 (4.79). For $C_{57}H_{46}N_4OClF_6P_3Os$ (**8d**): C, 55.41 (55.36); H, 3.73 (3.69); N, 4.54 (4.52%).

3.5. X-ray crystal structure determination

Crystals of $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)$ (**3c**) were grown by slow diffusion of a CH_2Cl_2 solution of the complex into hexane. The prismatic red crystal was of dimensions 0.20 × 0.10 × 0.10 mm. Data were collected using a CCD area detector rotating anode radiation source and a confocal optics monochromator of Mo-Kα radiation ($\lambda = 0.71073$ Å) at 93(2) K. Data collections were performed in the 2θ range 3.1–52.74° Absorption corrections were carried out by the multiscan process. Out of a total of 30,568 reflections, 9226 unique data (8451 of $I > 2\sigma(I)$) were used for the structure determination. Data reduction were carried out using Crystalclear 1.3.6 (Rigaku Corporation). The structure solution and refinement were carried out using the programs SHELXS-97 [21] and SHELXL-97 [22]. The structure was solved by direct method and refined by full-matrix least-squares refinement based on F^2. All non-hydrogen atoms were refined anisotropically. The hydridic H atom was fixed at a distance of 1.60 Å from the metal [23]. Crystal parameters and refinement results are summarized in Table 4.

Table 4
Summarised crystallographic data for $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)$

Empirical formula	$C_{52}H_{45}F_6N_4OP_3Os$
Formula weight	1139.03
Crystal system	monoclinic
Space group	*P*2(1)/*n*
a (Å)	12.0841(14)
b (Å)	25.549(3)
c (Å)	15.7643(18)
β (°)	103.684(3)
Size (mm^3)	0.20 × 0.10 × 0.10
V (Å^3)	4728.8(9)
λ (Å)	0.71073
$\rho_{calc.}$ (Mg m^{-3})	1.600
Z	4
T (K)	93(2)
μ Mo-Kα (mm^{-1})	2.865
Total reflection collected	30568
Unique reflections (R_{int})	9226(0.0287)
Refined parameters	609
Largest differences in peak and hole (e Å^{-3})	2.151 and −0.763
R^a ($I > 2\sigma(I)$)	0.0235
wR^b	0.0500
Goodness-of-fit^c	1.043

[a] $R = \sum|F_o - F_c|/\sum F_o$.

[b] $wR = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$ where $w = 1/[\sigma_2(F_o^2) + (0.0183P)^2 + 4.1609P]$, where $P = (F_o^2 + 2F_c^2)/3$.

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

4. Conclusion

1-Alkyl-2-(naphthyl-α/β-azo)imidazole (α/β-NaiR, **1** and **2**) has been reacted with $[Os(H)(Cl)(CO)(PPh_3)_3]$ in THF to synthesise $[Os(H)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})](PF_6)$ (**3**, **4**). The structure of the complexes has been determined by spectroscopic data (FTIR, UV–Vis, ^{1}H NMR) and redox activity was examined by cyclic voltammetry. Single crystal X-ray diffraction measurement in the case of $[Os(H)(CO)(PPh_3)_2(\alpha\text{-NaiEt})](PF_6)$ confirmed the structure. Cl_2 (in MeCN) addition to the hydrido-Os compounds (**3**, **4**) has synthesized $[Os(Cl)(CO)(PPh_3)_2(\alpha/\beta\text{-NaiR})](PF_6)$ (**5**, **6**).

Acknowledgements

Financial support from the Department of Science and Technology, New Delhi and Jadavpur University Potential for Excellence unit are gratefully acknowledged. One of us (T.K.M.) thanks UGC, New Delhi for a fellowship. We thank Dr. G. Mostafa, Department of Physics, Jadavpur University, Kolkata for his help in the structure solution.

Appendix A. Supplementary material

CCDC 288383 contains the supplementary crystallographic data for **3c**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)

1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly. 2006.08.028.

References

[1] (a) E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, Elsevier, Amsterdam, 1984;
(b) J. Reedijk, in: G. Wilkinson, J.A. Mcclerverty (Eds.), Comprehensive Coordination Chemistry, Pergamon, Oxford, UK, 1987.

[2] (a) K. Kalyansundaram, Coord. Chem. Rev. 46 (1982) 159;
(b) S. Serroni, S. Campagna, F. Puntoriero, C.D. Pietro, N.D. Mcclenaghan, F. Loisean, Chem. Soc. Rev. 30 (2001) 367.

[3] (a) B.K. Ghosh, A. Chakravorty, Coord. Chem. Rev. 95 (1989) 239;
(b) N. Bag, A. Pramanik, G.K. Lahiri, A. Chakravorty, Inorg. Chem. 31 (1992) 40.

[4] A.C.G. Hotze, H. Kooijman, A.L. Spek, J.G. Haasnoot, J. Reedijk, New J. Chem. 28 (2004) 565.

[5] R.E. Shepherd, Coord. Chem. Rev. 247 (2002) 147.

[6] (a) C. Das, A. Saha, C.-H. Hung, G.-H. Lee, S.-M. Peng, S. Goswami, Inorg. Chem. 42 (2003) 198;
(b) K.N. Mitra, S. Goswami, Proc. Indian Acad. Sci. (Chem. Sci.) 111 (1999) 461.

[7] (a) B.K. Santra, G.K. Lahiri, J. Chem .Soc., Dalton Trans. (1998) 1613;
(b) G.K. Lahiri, S. Bhattacharya, S. Goswami, A. Chakravorty, J. Chem. Soc., Dalton Trans. (1990) 561.

[8] J.G. Hassnoot, W. Hinrichs, O. Weir, J.G. Vos, Inorg. Chem. 25 (1986) 4140.

[9] (a) T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672;
(b) P. Byabartta, S.k. Jasimuddin, B.K. Ghosh, C. Sinha, A.M.Z. Slawin, J.D. Woollins, New J. Chem. 26 (2002) 1415;
(c) P. Byabartta, J. Dhinda, P.K. Santra, C. Sinha, K. Panneerselvam, F.-L. Liao, T.-H. Lu, J. Chem. Soc., Dalton Trans. (2001) 2825;
(d) S. Pal, T.K. Misra, C. Sinha, A.M.Z. Slawin, J.D. Woollinns, Polyhedron 19 (2000) 1925;
(e) S.K. Jasimuddin, P. Byabartta, G. Mostafa, T.-H. Lu, C. Sinha, Polyhedron 23 (2004) 727;
(f) S.k. Jasimuddin, T. Mathur, G. Mostafa, C. Sinha, Inorg. Chim. Acta 358 (2005) 3601.

[10] (a) J. Dinda, S. Pal, B.K. Ghosh, J. Cheng, F.-L. Liao, T.-H. Lu, C. Sinha, J. Coord. Chem. 55 (2002) 1271;
(b) P. Byabartta, S. Pal, T.K. Misra, C. Sinha, F.-L. Liao, K. Panneerselvam, T.-H. Lu, J. Coord. Chem. 55 (2002) 479.

[11] H. Sigel (Ed.), Metal Ions in Biological System, vol. 13, Marcel Dekker, New York, 1981.

[12] J. Otsuki, K. Suwa, K. Narutaki, C. Sinha, I. Yoshikawa, K. Araki, J. Phys. Chem. A 109 (2005) 8064.

[13] (a) M. Shivakumar, K. Pramanik, P. Ghosh, A. Chakravorty, Chem. Commun. (1998) 2103;
(b) M. Shivakumar, A. Chakravorty, Indian J. Chem. Sect. A 39A (2000) 477;
(c) K. Pramanik, M. Shivakumar, P. Ghosh, A. Chakravorty, Inorg. Chem. 39 (2000) 195.

[14] (a) W. Kaim, Coord. Chem. Rev. 219 (2001) 463;
(b) M. Schwach, H.-D. Hausen, W. Kaim, Inorg. Chem. 38 (1999) 2242;
(c) N. Doslik, T. Sixt, W. Kaim, Angew. Chem., Int. Ed. 37 (1998) 2403.

[15] (a) A. Sanyal, P. Banerjee, G.-H. Lee, S.-M. Peng, C.-H. Hung, S. Goswami, Inorg. Chem. 43 (2004) 7456;
(b) B.A. Goodman, J.B. Raynor, Adv. Inorg. Chem. Radiochem. 13 (1970) 135;
(c) A.L. Balch, R.H. Holm, J. Am. Chem. Soc. 88 (1966) 5201.

[16] (a) J. Dinda, Ph.D. Thesis, The University of Burdwan, Burdwan, India, 2003;
(b) J. Dinda, K. Bag, C. Sinha, G. Mostafa, T.-H. Lu, Polyhedron 22 (2003) 1367;
(c) P. Byabartta, P.K. Santra, T.K. Misra, C. Sinha, C.H.L. Kennard, Polyhedron 20 (2001) 905;
(d) S. Pal, D. Das, P. Chattopadhyay, C. Sinha, K. Panneerselvam, T.-H. Lu, Polyhedron 19 (2000) 1263;
(e) J. Dinda, P.K. Santra, C. Sinha, L.R. Falvello, J. Organomet. Chem. 629 (2001) 28;
(f) J. Dinda, U.S. Ray, G. Mostafa, T.-H. Lu, A. Usman, I. Abdul Razak, S. Chantrapromma, H.-K. Fun, C. Sinha, Polyhedron 22 (2003) 247.

[17] P.K. Santra, C. Sinha, W.J. Sheen, F.-L. Liao, T.-H. Lu, Polyhedron 20 (2001) 599.

[18] K.R. Flower, G.L. Leal, R.G. Pritchard, Inorg. Chem. Commun. 7 (2004) 729.

[19] (a) C.K. Pal, S. Chattopadhyay, C. Sinha, A. Chakravorty, Inorg. Chem. 33 (1994) 6140;
(b) C.K. Pal, S. Chattopadhyay, C. Sinha, A. Chakravorty, Inorg. Chem. 35 (1996) 2442;
(c) C.J. Jonson, R. Chang, J. Chem. Phys. 43 (1965) 3183.

[20] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1975) 45.

[21] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1997.

[22] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany, 1997.

[23] M.A. Green, J.C. Huffmann, K.G. Caulton, J. Organomet. Chem. C78 (1983) 243.