#### Journal of Molecular Structure 996 (2011) 24-30

Contents lists available at ScienceDirect

# Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



# Rhenium tricarbonyl chloro of di-2-pyridylketone 4-aminobenzoyl hydrazone (dpk4abh), *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl]: Synthesis, spectroscopic and electrochemical properties

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#### ARTICLE INFO

Article history: Received 24 January 2011 Received in revised form 4 March 2011 Accepted 5 March 2011 Available online 23 March 2011

Keywords: Rhenium Di-2-pyridyl ketone 4-amino benzoyl hydrazone Synthesis Spectroscopy Electrochemistry

## ABSTRACT

The reaction between di-2-pyridyl ketone 4-aminobenzoylhydrazone hydrate (dpk4abh.H<sub>2</sub>O) and [Re(CO)<sub>5</sub>Cl] in refluxing toluene gave fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl]. Hydrolysis of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] to form fac-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,N-dpkO,OH)] occurs in wet solvents. The identity of fac- $[\text{Re}(\text{CO})_3(\kappa^2-N,\text{N-dpk4abh})\text{Cl}]$  was established from the results of its elemental analysis, spectroscopic measurements, and electrochemical properties. The infrared spectra of  $fac-[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$ show the facial coordination of the carbonyl (C=O) groups, the coordination of dpkabh and none coordination of the carbonyl (C=O) group. <sup>1</sup>H-NMR measurements on fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in  $d_6$ -dmso and  $d_7$ -dmf confirmed the coordination of dpkabh, and demonstrate sensitivity of fac- $[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$  to its surroundings as manifested by the chemical shift variations observed in different solvents. Variable temperature <sup>1</sup>H-NMR studies showed stronger interaction between d<sub>7</sub>-dmf and fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] compared to d<sub>6</sub>-dmso and the amine protons of coordinated dpk4abh undergo faster exchanges with solvated water protons compared to the amide proton. The electronic absorption spectra of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] showed significant solvent dependence. In CH<sub>3</sub>CN, a single intra-ligand charge transfer (ILCT) transition appeared at 332 nm and assigned to  $\pi \rightarrow \pi^*$ of dpk followed by dpk  $\rightarrow$  hydrazone charge transfer. In a protophilic solvent, such as dmf, two intraligand charge transfer (ILCT) transitions assigned to fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh-H)Cl] and fac- $[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$  appeared at 464 and 350 nm, respectively. Reversible interconversion between fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh-H)Cl] was established in protophilic solvents by using a base to shift the equilibrium to the conjugate base and an acid to shift the equilibrium or conjugate base to the neutral form. Acid-base titrations of  $fac-[Re(CO)_3(\kappa^2-N,N-dpk4abh-H)Cl]$  or  $fac-[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$  show acids or bases in concentrations as low as  $1 \times 10^{-6}$  M can be detected and determined using protophilic solutions of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl]. Electrochemical measurements on fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> showed sequential irreversible redox processes consistent with the electrochemical reduction or oxidation of the hydrazone backbone.

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## 1. Introduction

The diverse reactivity patterns and rich physical properties of di-2-pyridyl ketone derivatives (see Scheme 1) and their metal compounds continue to attract research interest because of their potential applications in several areas that include medicine, catalysis, environment, pharmaceuticals, materials science, etc. [1–37]. Di-2-pyridyl ketone derivatives possess a variety of potential binding sites, hence may coordinate to metal moieties in a monoden-

tate, or multidentate fashion to form novel mononuclear and polynuclear compounds [1–12,29]. The biological activity of several di-2-pyridyl ketone derivatives and their metal compounds were investigated and revealed anti-mycobacterium tuberculosis activity, cytotoxicity, and potent and selective antitumor activity [14–19]. Although extensive efforts were devoted to exploring the use of di-2-pyridyl ketone hydrazones as sensitive analytical reagents for the detection and determination of trace amounts of a variety of substrates in biological and industrial samples, the coordination chemistry of di-2-pyridyl ketone hydrazones (dpk4abh) is scarce [20–27]. To our knowledge, only one Fe(II) compound of the conjugate base of dpk4abh (dpk4abh-H), [Fe(dp-k4abh-H)<sub>2</sub>], isolated from the interaction between FeSO<sub>4</sub>·7H<sub>2</sub>O,

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Scheme 1. Selected di-2-pyridyl ketone derivatives.

dpk4abhH2O and triethylamine in aqueous media, was reported [17]. In [Fe(dpk4abh-H)<sub>2</sub>], dpkabh-H coordinates to Fe through a nitrogen atom of a pyridine ring, a nitrogen atom of the hydrazone backbone, and the oxygen atom of the carbonyl group. Tin compounds of the closely related ligand, di-2-pyridyl ketone 2-aminobenzoyl hydrazone (dpk2abh), of formula [Sn(C<sub>6</sub>H<sub>5</sub>)(dpk2abh-H)Cl<sub>2</sub>], [Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(dpk2abh)Cl<sub>2</sub>], [Sn(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)(dpk<sub>2</sub>abh-H)Cl<sub>2</sub>] and  $[Sn(C_6H_5)_3Cl(H_2O) \cdot dpk2abh)]$  were reported [19,28]. In the case of [Sn(C<sub>6</sub>H<sub>5</sub>)(dpk2abh-H)Cl<sub>2</sub>] and [Sn(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(dpk2abh)Cl<sub>2</sub>], and  $[Sn(C_6H_5CH_2)(dpk_2abh-H)Cl_2]$  the ligand (dpk2abh) or its conjugate base (dpk2abh-H) bind to tin through one nitrogen atom of a pyridine ring, a nitrogen atom of the hydrazone backbone, and the oxygen atom of the carbonyl group [28]. In the case of  $[Sn(C_6H_5)_3Cl(H_2O) \cdot dpk2abh)]$ , the ligand does not coordinate to tin [19]. The in vitro studies of the reported tin compounds revealed strong antimicrobial activity of  $[Sn(C_6H_5)_2(dpk2abh)Cl_2]$ and  $[Sn(C_6H_5)_3Cl(H_2O) dpk2abh]$ . None of the tin compounds of dpk2abh or alk2abh-H showed genotoxicity in Bacillus subtilis rec-assay and in the Salmonella-microsone test [19]. We have been interested in the chemistry of di-2-pyridyl ketone derivatives and reported on the synthesis, characterization and structures of several transition metal compounds containing N,N-bidentate and N,O,N- or N,N,O-tridentate di-2-pyridyl ketone derivatives [29-36]. In our efforts to explore how slight variations in the backbone of di-pyridyl ketone derivatives affect their coordination chemistry and physical properties, in this report we describe the synthesis and physical properties of the first rhenium compound of dpk4abh and compare the results with those reported for related compounds. In a recent report, we described the molecular sensing behavior of dpk4abh·H<sub>2</sub>O in non-aqueous media and revealed the presence of two intra-ligand charge transfer transitions (ILCT) associated with dpk4abh·H<sub>2</sub>O and its conjugate base. Spectroscopic and thermodynamic measurements done on non-aqueous solutions of dpk4abh·H<sub>2</sub>O revealed reversible interconversion between dpk4abh and its conjugate base dpk4abh-H and showed group 12 metal ions in concentrations as low as  $1.0 \times 10^{-6}$  M can be detected using protophilic solutions of dpk4abh H<sub>2</sub>O [34].

#### 2. Experimental

#### 2.1. Reagents and reaction procedures

The ligand di-2-pyridyl ketone *p*-aminobezoyl hydrazone hydrate (dpk4abh·H<sub>2</sub>O) was prepared from the reaction between dpk, *p*-aminobenzoylhydrazine, ethanol and three drops of concentrated HCl under reflux. Found C, 64.37; H, 5.08; N, 20.71. C<sub>18</sub>H<sub>17</sub>N<sub>5</sub>O<sub>2</sub> requires C, 64.47; H, 5.11; N, 20.77. IR (KBr disk): v(NH) 3220, v(OH) 3394 and v(C=O) 1642 cm<sup>-1</sup> [34]. All other reagents were obtained from commercial sources and used without further purification.

#### 2.2. Preparation of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl]

A mixture of Re(CO)<sub>5</sub>Cl (200 mg, 0.55 mmol), dpk4abh·H<sub>2</sub>O (250 mg, 0.74 mmol) and toluene (50 mLs) was refluxed for 10 h. The resulting reaction mixture was allowed to cool to room temperature and reduced in volume to ~25 mL. An off-yellow solid was filtered off, washed with hexane, diethyl ether, and dried; yield 250 mg (73%) (Found: C, 41.18; H, 2.37; Cl, 8.99. C<sub>21</sub>H<sub>14</sub>Cl N<sub>4</sub>O<sub>4</sub>Re requires C, 41.48; H, 2.32; Cl, 9.22 %). Infrared data (KBr disk, cm<sup>-1</sup>): v(C≡O) 2026, 1924, 1918; v(C=O) 1684, and v(N−H) 3484, 3466, and 3333 and v(C-H) 3278, 3242, 3183, 3088 and 2925. <sup>1</sup>H-NMR ( $\delta$  ppm): in dmso-d<sub>6</sub> at 303 K: 11.67 (s, 0.7 H, NH), 9.03 (d, 1H, H14-dpk), 8.90 (d, 1H, H14'-dpk), 8.25 (t, 1H, H13-dpk), 8.22 (t, 1H, H13'-dpk), 8.03 (d, 1H, H11-dpk), 7.99 (d, 1H, H11'-dpk), 7.72 (t, 2H, H12 and H12'-dpk), 7.58 (d, 2H,H32 and H36-phen), 6.60 (d, 2H, H33 and H35-phen), 5.89 (broad, 1.0 H, NH2) and 3.30 (water); in dmf-d<sub>7</sub> at 303 K 11.90 (s, 0.9 H, NH), 9.17 (d, 1H, H14-dpk), 9.04 (d, 1H, H14'-dpk), 8.36 (t, 1H, H13-dpk), 8.31 (t, 1H, H13'-dpk), 8.25 (d, 1H H11-dpk), 8.12 (d, 1H, H11'-dpk), 7.82 (t, 1H, H12-dpk), 7.80 (t, 1H, H12'-dpk), 7.76 (d, 2H, H32andH36-phen), 6.70 (d, 2H, H33 and H35-phen), 5.98 (broad, 1.5 H, NH2) and 3.45 (water). UV–vis { $\lambda \pm 2/nm$ , ( $\varepsilon \pm 200/$ cm<sup>-1</sup> M<sup>-1</sup>)} CH<sub>2</sub>Cl<sub>2</sub>: 342 (13,794); CH<sub>3</sub>CN: 346 (13,414); dmf: 476 (27,260), 362 (15,000).

#### 2.3. Hydrolysis of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkabh)Cl]

When a sample of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkabh)Cl] was refluxed in CH<sub>3</sub>CN containing a few drops of H<sub>2</sub>O, yellow *fac*-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,N-dpkO,OH)] was isolated. Yellow crystals of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,O,N-dpkO,OH)] were obtained when *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N, N-dpkabh)Cl] was allowed to stand in CH<sub>3</sub>CN or dmf for a few days in air. The spectroscopic and electrochemical properties of the isolated *fac*-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,N-dpkO,OH)] were similar to those of the previously reported *fac*-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,N-dpkO,OH)]. Singlecrystal X-ray studies on several crystals isolated confirmed the identity of the hydrolysis product as *fac*-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,NdpkO,OH)].

#### 2.4. Physical measurements

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. Solution <sup>1</sup>H-NMR spectra were recorded on a Bruker ACE 500-MHz Fourier-transform spectrometer and referenced to the residual protons in the incompletely deuteriated solvent. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer Spectrum 1000 FT-IR Spectrometer. Electrochemical measurements were performed with the use of a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat and Model 276 interface in conjunction with a 286 PC. Data were acquired with the EG&G PARC Headstart program and manipulated using Microsoft Excel. Measurements were performed in solutions that were 0.1 M in [N(n-Bu)<sub>4</sub>](PF<sub>6</sub>). The  $E_{p,a}$ ,  $E_{p,c}$  and  $E_p = (E_{p,a} + E_{p,c})/2$  values were referenced to the potassium chloride saturated calomel electrode, SCE, at room temperature and were uncorrected for junction potentials. The number of electrons on the redox waves was determined using the oxidative peak current of the reversible one-electron couple of FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> couple as an internal standard. Electrochemical cells were of conventional design based on scintillation vials or H-cells. A glassy-carbon disc was used as the working electrode and a Pt-wire was used as the counter electrode.

#### 2.5. Analytical procedures

Elemental microanalyses were performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, United Kingdom.

#### 3. Results and discussion

Following a procedure similar to those reported for the synthesis of rhenium tricarbonyl compounds of  $\alpha$ -diimine ligands of the type fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -L-L)Cl] where L-L is N,N -bidentate  $\alpha$ -dimine ligand, yellow  $fac-[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$  (see Scheme 2) was isolated in good yield when dpk4abh H<sub>2</sub>O was allowed to react with [Re(CO)<sub>5</sub>Cl] in refluxing toluene [29,31,36]. When the reaction was carried out in refluxing CH<sub>3</sub>CN containing a few drops of water, or when  $fac-[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$ was allowed to stand in CH<sub>3</sub>CN in air for an extended period, fac-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,N-dpkO,OH)] was isolated [29]. The hydrolysis product, fac-[Re(CO)<sub>3</sub>( $\kappa^3$ -N,O,N-dpkO,OH)], exhibits physical properties similar to those of the previously reported fac- $[Re(CO)_3(\kappa^3-N,O,N-dpkO,OH)]$  isolated from the reaction between [Re(CO)<sub>5</sub>Cl] and dpk in refluxing CH<sub>3</sub>CN containing a few drops of water [29]. Attempts to grow crystals of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N, N-dpk4abh)Cl] from CH<sub>3</sub>CN or dmf solutions of fac-[Re(CO)<sub>3</sub>- $(\kappa^2-N,N-dpk4abh)Cl]$  were futile and crystals of fac-[Re(CO)<sub>3</sub>- $(\kappa^3-N,O,N-dpkO,OH)$ ] were obtained and characterized using single-crystal X-ray crystallography.

The identity of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] was established from the results of its elemental analysis, and a number of spectroscopic measurements, and a comparison of the spectroscopic results with those reported for other rhenium compounds of the type fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -L–L)Cl] [29–31]. The IR spectra of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] display peaks consistent with the coordination of dpk4abh (see experimental section) and facial coordination of the carbonyl groups. In the carbonyl  $\nu$ (C==O) stretching region, three strong bands appeared similar to those ob-



Scheme 2. fac-[Re(CO)<sub>3</sub>(dpk4abh)Cl].

served in a variety of rhenium compounds of the type fac-[Re  $(CO)_3(L-L)CI$ , where L-L = bidentate nitrogen ligand, thus confirm the fac-geometry of coordinated carbonyl groups [29-31]. The v(C=0) stretching vibration of coordinated dpk4abh shifts to higher wave number compared to free dpk4abh pointing to the non-coordination of the acyl group and delocalization of the electron dentistry about the hydrazone moiety upon coordination of dpk4abh to rhenium moiety [34]. The combined v(C=C) and v(C=N) of the pyridine vibrations of  $fac-[Re(CO)_3(\kappa^2-N,N$ dpk4abh)Cl] appeared at 1624 and 1604 cm<sup>-1</sup>. In the spectrum of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkphh)Cl] where dpkphh is di-2-pyridyl ketone phenyl hydrazone, the combined C=N and C=C stretching appeared at 1606 and 1561 cm<sup>-1</sup> [34]. In the free ligand, these bands appeared at 1606 cm<sup>-1</sup>. The shift of the combined v(C=C) and v(C=N) in fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] to a higher wavelength, compared to the free ligand, hints to a decrease in electron density of the pyridine rings upon coordination, and binding through the nitrogen atoms of the pyridine rings. In the v(NH)stretching region of the amine group between 3500–3300 cm<sup>-1</sup>, two sharp bands appeared at 3469 and  $3350 \text{ cm}^{-1}$ , confirming the presence of free amine group. The amide v(N-H) and the aromatic v(C-H) of the dpk moiety show weak absorption bands between 3200–2800 cm<sup>-1</sup>. In the spectrum of free dpk4abh H<sub>2</sub>O, the amine v(NH) vibrations appeared at 3460 and 3406 cm<sup>-1</sup>, amide v(N-H) vibration appeared at 3244 and v(C-H) stretches appeared between 3100–2800 cm<sup>-1</sup>. In the v(C=N), v(C-C), v(C-N), v(N-N),  $\delta$ (NH) region in the spectrum of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl], bands appeared similar to those observed in the free ligand, fac- $[Re(CO)_3(\kappa^2-N,N-dpkphh)Cl]$  and other rhenium compounds containing di-2-pyridyl ketone derivatives [36].

The <sup>1</sup>H-nmr spectra of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in d<sub>6</sub>dmso and d<sub>7</sub>-dmf at 303 K are shown in Fig. 1, and the chemical shifts are listed in the experimental section. These spectra, along with the chemical shifts, show significant variation in the chemical shifts of the protons of coordinated dpk4abh, pointing to strong solvent-complex interaction and the sensitivity of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] to its surroundings. In d<sub>7</sub>-dmf, all protons of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] were observed downfield compared to d<sub>6</sub>-dmso, and suggest a stronger



Fig. 1. <sup>1</sup>H-NMR spectrum of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in d<sub>6</sub>-dmso and d<sub>7</sub>-dmf.

solvent–complex interaction in d<sub>7</sub>-dmf compared to d<sub>6</sub>-dmso. Four doublets, one proton each, and four triplets, one proton each, were observed and assigned to the coordinated pyridine rings and suggest that the pyridine rings are not equivalent. The phenyl protons of the benzoyl hydrazone moiety were observed as two doublets, two protons each, up-field compared to dpk protons. These spectra show that in d<sub>6</sub>-dmso at 303 K, the amide proton (N–H) and the amine protons (NH<sub>2</sub>) undergo faster exchange with the solvated water protons compared d<sub>7</sub>-dmf (see experimental section). Chemical shift separations of 0.06 ppm and 0.13 ppm were observed between H11 and H11' in d<sub>6</sub>-dmso and d<sub>7</sub>-dmf, respectively and points to significant structural changes of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] when dissolved in protophilic solvents. In d<sub>6</sub>-dmso and d<sub>7</sub>-dmf a slight change in the chemical shifts of H12 and H12' was noticed.

Variable temperature <sup>1</sup>H-NMR studies done on fac-[Re(CO)<sub>2</sub>( $\kappa^2$ -N.N-dpk4abh)Cll dissolved in d<sub>7</sub>-dmf and d<sub>6</sub>-dmso show temperature dependent and temperature independent protons of coordinated dpkabh. Fig. 2 shows the <sup>1</sup>H-NMR spectra of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in d<sub>6</sub>-dmso at different temperature. These spectra show the amide (NH), amine (NH<sub>2</sub>) and hydrate (H<sub>2</sub>O) protons to exhibit higher sensitivity to temperature variations, compared to the aromatic protons. Upon a gradual increase in temperature, the amide, amine and solvated water protons shift up-field, and the intensity of the amine protons diminished. The decrease in intensity of the amine proton upon increase in temperature points to exchange of the amine protons with water protons. In d<sub>7</sub>-dmf, similar behavior as in d<sub>6</sub>-dmso was observed, and a slow exchange of the amine protons with the solvated water protons was noticed. Solvent-exposed protons are temperature independent and solvent shielded protons show temperature dependence. A plot of the chemical shift of the amide, amine, and water protons vs.  $1/T \times 10^3$ , K<sup>-1</sup> gave straight lines with slopes as shown in Table 1. The higher the slope of the line, the more sensitive the proton is to temperature variations, hinting at the shielding of the proton from its surroundings, and participation in hydrogen bonding. The results obtained in this study point to stronger interaction between fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] and d<sub>7</sub>-dmf compared to  $d_6$ -dmso.

The electronic absorption spectra of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in dmf, dmso, and CH<sub>3</sub>CN are shown in Fig. 3, and the extinction coefficients are given in the experimental section. In CH<sub>3</sub>CN, a single electronic transition appeared at 332 nm and in protophilic solvent (dmf or dmso), two electronic transitions appeared at 464 and 350 nm (see experimental section). The ob-



Fig. 2. Variable temperature <sup>1</sup>H-NMR spectra of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in d<sub>6</sub>-dmso.

#### Table 1

Slopes of  $\delta$  vs.  $1/T \times 10^3$ ,  $K^{-1}$  of *fac*-[Re(CO)<sub>3</sub>(dpk4abh)Cl] in d<sub>6</sub>-dmso and d<sub>7</sub>-dmf.

Solvent	(NH)	(NH <sub>2</sub> )	Hydrate
d <sub>6</sub> -dmso	0.44	0.56	0.51
d <sub>7</sub> -dmf	0.60	0.62	0.69



Fig. 3. Electronic absorption of  $2.00\times 10^{-5}$  M fac-[Re(CO)\_3( $\kappa^2$ -N,N-dpk4abh)Cl] in dmf, dmso, and CH\_3CN.

served electronic transitions are similar to those reported for free dpk4abh and are due to  $\pi \rightarrow \pi^*$  of dpk followed by dpk  $\rightarrow$  aminobenzovl charge transfer. In the free ligand, dpk4abh, two electronic transitions appeared at 426 and 346 nm in protophilic solvents (dmf and dmso) and in CH<sub>2</sub>Cl<sub>2</sub> a single electronic transition appeared at 338 nm [34]. In protophilic solvents, the low energy electronic transitions are assigned to fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,Ndpk4abh-H)Cl], the conjugate base of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,Ndpk4abh)Cl], resulted from deprotonation of amide proton, and the high energy electronic transition is assigned to fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl]. The ratio of the intensity of the low energy electronic transition observed at 464 nm to the intensity of the high energy electronic transition observed at 350 nm increases as the concentration of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] dissolved in dmso decreases. These results show sensitivity of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] to its surroundings and confirm the solvent-complex interaction observed in the <sup>1</sup>H-NMR spectra. When a dmf solution of NaBH<sub>4</sub> was allowed to interact with fac- $[Re(CO)_3(\kappa^2-N,N-dpk4abh)Cl]$  dissolved in dmf, the intensity of the low energy electronic transition increased and the intensity of the high energy electronic transition decreased (see Fig. 4). The reverse was observed when excess NaBF<sub>4</sub> was added to a dmf solution of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl]. These results hint to acid-base interconversion between fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N, N-dpk4abh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,Ndpk4abh-H)Cl] in dmf (see Scheme 3). The acid-base interconversion between fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh-H)Cl] was further confirmed when stoichiometric amounts of benzoic acid dissolved in dmso were added to a mixture of a dmso solution of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] that contain excess NaOH (see Fig. 5). These results showed benzoic acid in concentrations as low as  $1.00\times 10^{-6}\,\text{M}$  can be detected and determined using a protophilic solution of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] and allowed for



**Fig. 4.** Electronic absorption spectra of  $2.00\times10^{-5}$  M fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] (1) in dmf in the presence of excess ( $1.00\times10^{-3}$  M) NaBH<sub>4</sub> (2) and excess ( $1.00\times10^{-3}$  M) NaBF<sub>4</sub> (3).

calculation of the extinction coefficients of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N, N-dpk4abh)Cl] observed at 350 nm and its conjugate base, fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh-H)Cl], observed at 464 nm (see experimental section). The electronic transitions of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] and its conjugate base, fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N, N-dpk4abh)Cl] in protophilic solvents shift to lower energy, compared to the electronic transitions of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkbh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkbh+H)Cl] where dpkbh = di-2-pyridyl ketone benzoyl hydrazone [31]. This is consistent with the electronic transitions appeared at 318 and 440 nm due to to fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkbh-H)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkbh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpkbh-H)Cl], respectively.

The electrochemical properties of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] measured in non-aquesous solvents were investigated using voltammetric techniques. Cyclic voltammograms of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 6. These voltammograms show close similarities, although subtle variations were noticed. On a reductively initiated scan in CH<sub>3</sub>CN (Fig. 6a), an irreversible one electron reduction wave appeared at  $E_{p,c} = -1.40$  V, followed by electrochemically generated product waves at  $E_{p,a} = -0.64$ , +0.54, a quasi-reversible one electron oxidation at  $E_{1/2} = +1.42$  V ( $E_{p,a} = +1.38$  and  $E_{p,c} = +1.46$  V), and an irreversible multi-electron oxidation at  $E_{p,a} = +1.80$  V. In



**Fig. 5.** Electronic absorption spectra of a mixture of  $2.00 \times 10^{-5}$  M *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)CI] and  $1.75 \times 10^{-4}$  M NaOH in dmso (1) in the presence  $1.00 \times 10^{-6}$  (2),  $1.00 \times 10^{-5}$  (3),  $2.00 \times 10^{-5}$  (4),  $3.00 \times 10^{-5}$  (5),  $4.00 \times 10^{-5}$  (6),  $5.00 \times 10^{-5}$  (7),  $6.00 \times 10^{-5}$  (8),  $7.00 \times 10^{-5}$  (9) *M* benzoic acid.

CH<sub>2</sub>Cl<sub>2</sub> (see Fig. 6d), an irreversible reduction appeared at  $E_{p,c} = -1.42$  V followed by an electrochemically generated product wave at  $E_{p,a}$  = + 0.58 V, a reversible oxidation at  $E_{1/2}$  = +1.35 V and an irreversible oxidation at  $E_{p,a}$  = +1.76 V. Scan rate studies on the first reduction waves show no sign of reversibility in CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub>. On oxidatively initiated scan in CH<sub>3</sub>CN (Fig. 6b), voltammetric behavior similar to the reductively initiated scan was observed except new oxidatively generated product waves appeared at  $E_{p,c} = -0.92$  and -1.17 V and the reductively generated product wave observed at  $E_{p,a}$  = +0.58 V on a reductively initiated scan disappeared. On oxidatively initiated scan in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 6e), a reversible oxidation wave appeared at  $E_{1/2}$  = +1.35 V followed by an oxidatively generated product wave at  $E_{p,c} = -1.04 \text{ V}$ and an irreversible reduction at  $E_{p,c} = -1.70$  V. The first reduction wave observed in reductively generated scans in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> is assigned to the to Re<sup>I/0</sup> couple, the quasi-reversible/reversible oxidation waves observed at  $E_{1/2}$  = + 1.42 V in CH<sub>3</sub>CN and  $E_{1/2}$  = + 1.35 V are assigned to the Re<sup>I/II</sup> oxidation, and the multi-electron irreversible oxidation wave that appeared at +1.80 V in CH<sub>3</sub>CN could be assigned to the oxidation of hydrazone backbone. The assigned Re<sup>I/0</sup> and Re<sup>I/II</sup> couples fall in the potential region as



Scheme 3. Acid-base interconversion between fac-[Re(CO)<sub>3</sub>(dpkabh)Cl] and its conjugate base fac-[Re(CO)<sub>3</sub>(dpkabh-H)Cl] in the presence of NaBH<sub>4</sub> and NaBF<sub>4</sub>.



**Fig. 6.** Cyclic voltammograms of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in CH<sub>3</sub>CN (a and b) and dpkabh·H<sub>2</sub>O in CH<sub>3</sub>CN (c) and *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] in CH<sub>2</sub>Cl<sub>2</sub> (d and e) in the presence of 0.1 *M* in [N(n-Bu)<sub>4</sub>](PF<sub>6</sub>) at a glassy carbon working electrode at a scan rate of 400 mV s<sup>-1</sup> vs. SCE.

observed for these couples in a variety of rhenium carbonyl compounds of polypyridyl-like ligands of the type *fac*-[Re(CO)<sub>3</sub>(L–L)Cl] where L–L = dpk, dpk.oxime, dpknph and others [29,31,36]. The oxidatively generated product waves in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> fall in the same vicinity as those observed in cyclic voltammorams of coordinated dpk in rhenium tricarbonyl compounds measured in non-aqueous solvents. Cyclic voltammogram of *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] measured in CH<sub>3</sub>CN between  $-1.00 \rightarrow -3.00$  V shows sequential irreversible reductions at  $E_{p,c} = -1.35$ , -1.98and -2.74 V and an irreversible oxidation appeared at  $E_{\rm p,a} = -1.80 \text{ V}$ . In a reversible scan between  $+1.00 \rightarrow +3.00 \text{ V}$ sequential irreversible oxidations appeared at  $E_{p,a} = +1.33, +1.83$ , +2.32 and +2.58 V. A comparison of the peak currents of the reductions and oxidation waves hint that the reduction wave at -2.74 V and second oxidative waves at +1.83 V are multi-electron in nature at least two electrons compared to the first electronic reductive or oxidative waves. The irreversibility of the reduction and oxidation waves in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> and appearance of electrochemically generated product waves hint to electrochemical decomposition of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] following its reduction or oxidation. Although detailed analysis of the electrochemical behavior of fac-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] remains to be explored, plausible mechanisms for the electrochemical reduction and oxidation of  $fac-[Re(CO)_3(\kappa^2-N.N-dpk4abh)Cl]$  is shown in Scheme 4. The proposed mechanisms are analogous to those reported for the oxidation and reduction of coordinated dpkoxime in fac- $[Re(CO)_3(\kappa^2-N,N-dpkoxime)Cl]$  in non-aqueous media and are consistent with the sequential electronic transfer observed.<sup>37</sup> In CH<sub>3</sub>CN, cyclic voltammogram of free dpkabh is show in Fig. 6c, and shows an irreversible reduction at  $E_{p,a} = -1.85$  V followed by a reductively generated product waves at  $E_{p,a} = -0.60$  and +0.28 V and oxidative waves at  $E_{p,a}$  = +1.34 and +1.60 V. Due to their convenient synthesis, rich physico-chemical prop-

Due to their convenient synthesis, rich physico-chemical properties, and molecular sensing capabilities, work is in progress in our laboratory to isolate a variety of metal compounds of polypyridyl-like ligands, to explore their electro-optical properties, solid state structures, and conformations.

#### 4. Conclusion

The first rhenium complex of dpk4abh has been isolated. Spectroscopic measurements on *fac*-[Re(CO)<sub>3</sub>( $\kappa^2$ -N,N-dpk4abh)Cl] revealed sensitivity to its surroundings and electrochemical studies



Scheme 4. Plausible mechanisms for the reduction and oxidation of fac-[Re(CO)<sub>3</sub>(dpkabh)Cl].

showed sequential irreversible electronic transfers consistent with the reduction and oxidation of the hydrazone moiety. [16] F.R. Pavan, P.I.d.S. Maia, S.R.A. Leite, V.M. Deflon, A.A. Batista, D.A. Sato, S.G. Franzblau, C.Q.F. Leite, Eur. J. Med. Chem. 45 (2010) 1898.
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