Journal of Organometallic Chemistry 694 (2009) 1400–1406

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Syntheses, structural studies and spectroscopic characterisation of pyridyl–phthalimide complexes of *fac*-$(CO)_3Re^I$-diimines

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ARTICLE INFO

Article history:
Received 13 November 2008
Received in revised form 12 December 2008
Accepted 19 December 2008
Available online 16 January 2009

Keywords:
Rhenium
Diimine
Phthalimide
Luminescence

ABSTRACT

The mono-dentate ligands, 3-aminomethyl-*N*-phthalimido-pyridine (L^1) and 3-amino-*N*-phthalimido-pyridine (L^2), were synthesised using a solvent-free melt method. These ligands were then used to access three pairs of functionalised luminescent Re^I complexes of the generic type *fac*-$\{Re(CO)_3(\text{diimine})(L^n)\}(BF_4)$ [where diimine = 4,4′-dimethyl-2,2′-bipyridine (**dmb**); 2,2′-bipyridine (**bpy**); 1,10-phenanthroline (**phen**)]. X-ray crystallography has been used to structurally characterise five of the complexes showing that in the cases of the L^1 species the phthalimide unit is adjacent to and co-planar with the coordinated diimine ligand. Solution state UV–Vis absorption, electrochemistry and IR studies confirm that the proposed formulations and coordination modes exist in solution. The photophysical studies show that the visible emission from each of the six complexes is ^{3}MLCT at room temperature. Within each pair of complexes the precise energy of the emission was subtly dependent upon the axial ligand, L^n with luminescence lifetimes in the range 121–288 ns.

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1. Introduction

Diimine complexes of the ‘*fac*-$\{Re(CO)_3\}$’ core can be exploited as photoactive components within luminescent arrays allowing the design of multimetallic species [1] and responsive chemosensors [2]. More recently they have also been developed and utilised in biological fluorescence imaging applications where stepwise derivitisation allows tuning of the physical properties, exploitation of triplet metal(rhenium)-to-ligand(diimine) charge transfer (^{3}MLCT) emission [3] and elucidation of organelle targeting behaviour including mitochondrial localisation [4]. Such species are photophysically bio-compatible, allowing sensitisation in the visible region thus eradicating problematic endogenous autofluorescent backgrounds. Additional considerations are solubility and charge, to give lipophilic, cationic species allowing cell uptake, intracellular mobility and organelle localisation. In this study we report the syntheses of a series of cationic *fac*-$\{Re(CO)_3(\text{diimine})\text{-}L^n\}^+$ complexes functionalised with a lipophilic, planar phthalimide unit tethered *via* a coordinated pyridine, which we hope will provide a useful basis for biologically applied studies in the future. Phthalimides are known to have potent biological activity [5] and the free ligands L^1 and L^2 utilised in this study have also demonstrated moderate promise in this regard [6] together with other *N*-pyridinyl and *N*-quinolinyl substituted phthalimides which have shown potent cytotoxicity towards several cultured cell lines [7]. Recent reports suggest utilising phthalimide derivatives to allow development of the ‘$Tc^I(CO)_3$’ core with amino acid-based chelating ligands [8] for applications in positron emission tomography.

2. Synthesis

In contrast to the solvent-based reaction conditions previously employed for accessing these ligand systems, L^1 and L^2 were synthesised using a solvent-free melt method. Following recrystallisation from alcohol, yields were typically in excess of 90%. ^{1}H NMR spectra of the products were consistent with the proposed formulations and in agreement with the literature [6].

The neutral diimine precursors were synthesised according to the literature by reacting stoichiometric equivalents of pentacarbonlybromorhenium with either 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine or 1,10-phenanthroline in toluene at 110 °C for 3 h [9]. Conversion to the cationic complexes was achieved by abstracting the axial bromide ligand with $AgBF_4$ in acetonitrile to yield the intermediate species *fac*-$\{Re(CO)_3(MeCN)(\text{bisimine})\}(BF_4)$ [10]. These were subsequently reacted with the pyridyl–phthalimide ligand (L^n) in chloroform at reflux. Typically the reaction was followed by thin layer chromatography (silica, 9:1 dichloromethane:methanol) and complete within 24 h. Column chromatography was not necessary to purify these complexes since the desired complex often precipitated directly from the cooled reaction mixture. Additional recrystallisation from acetonitrile/diethyl ether provided crystalline samples.

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0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2008.12.048

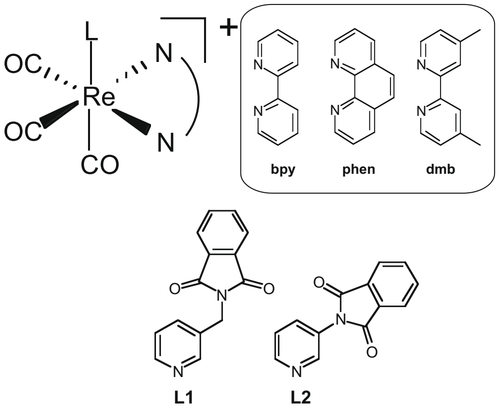
3. Results and discussion

3.1. Characterisation of the complexes

Solution state IR studies (Fig. 3) were conducted in chloroform. For the *fac*-tricarbonyl core the local symmetry can be approximated to *Cs* and as a consequence three absorptions (2A′ + A″) are expected although overlapping bands are common. Within each pair of diimine complexes the highest frequency *v*(CO) band (CO *trans* to L^n) does not vary significantly with axial ligand type.

Electrospray mass spectrometry (positive mode) was utilised and for each complex revealed a cluster of peaks corresponding to the cationic unit, *i.e.* $\{Re(CO)_3(bisimine)(L^n)\}^+$, the isotopic distribution of which confirmed the presence of rhenium (^{185}Re, 37.1%; ^{187}Re 62.9%).

^{1}H NMR spectra were also obtained for each of the six complexes confirming the presence of the bisimine and pyridyl–phthalimide ligands within the Re^I coordination sphere.



Scheme 1. Ligands and general cation of the rhenium complexes used in this study.

3.2. Single crystal X-ray diffraction studies of the complexes

Crystals representing each of the diimine types (*fac*-$\{Re(CO)_3$(**bpy**)$L^1\}(BF_4)$, *fac*-$\{Re(CO)_3$(**bpy**)$L^2\}(BF_4)$, *fac*-$\{Re(CO)_3$(**phen**)$L^1\}(BF_4)$, *fac*-$\{Re(CO)_3$(**phen**)$L^2\}(BF_4)$ and *fac*-$\{Re(CO)_3$(**dmb**)$L^2\}(BF_4)$) were isolated and deemed to be suitable for diffraction studies. In each case this was achieved by vapour diffusion of diethyl ether into a concentrated acetonitrile solution of the complex and crystals were grown over a period of 24 h. The parameters associated with each data collection are shown in Table 1, with associated bond lengths and bond angles in Supplementary material. In each case the structural analyses (Fig. 1) confirmed the proposed coordination geometry for rhenium with a *fac*-tricarbonyl arrangement supplemented with the chelating bisimine and axial *N*-coordinated pyridyl–phthalimide. The two examples incorporating the methyl-linked ligand L^1 show that the phthalimide unit is positioned adjacent to and co-planar with the diimine unit. In contrast, for the L^2 complexes the more rigid architecture positions the phthalimide unit away from the diimine. The bond lengths associated with the coordination sphere are typical of related Re^I complexes of this type [11]. Each of the Re–CO distances lies within the range 1.914–1.933 Å whilst the Re–N distances are typically longer at 2.159–2.225 Å. Generally, the Re–N bond lengths with the axial mono-dentate pyridine are longer (*ca.* 2.22 Å) than those associated with the chelating diimines (*ca.* 2.17 Å). The **bpy** complex with L^1 is more distorted (possibly due to the flexible tethered phthalimide unit and packing forces) from ideal octahedral symmetry (⟨C_{ax}–Re–N_{ax} 175.95(13) vs. 178.89(13) for L^2 complex), which may account for a marginally weakened Re–N_{ax} interaction. In comparison, analysis of the *fac*-$\{Re(CO)_3$-(**phen**)$L^n\}(BF_4)$ structures shows that both are similarly distorted. *fac*-$\{Re(CO)_3$(**bpy**)$L^1\}(BF_4)$ and *fac*-$\{Re(CO)_3$(**phen**)$L^1\}(BF_4)$ show that when the diimine–Re bonding interaction is comparable, the axial Re–N is similarly bonded. Comparison of *fac*-$\{Re(CO)_3$(**bpy**)$L^2\}(BF_4)$ and *fac*-$\{Re\text{-}(CO)_3$(**dmb**)$L^2\}(BF_4)$ revealed that the stronger diimine–Re interaction of the latter results in a weakened Re–N_{ax} bond. Therefore the factors determining the strength of the axial Re–N_{ax}(pyridyl) bond appear to be the donating ability of the diimine co-ligand and the inherent level of distortion within the coordination sphere.

Table 1
Crystal data collection and refinement details for the complexes[a].

	$\{Re(CO)_3(bpy)L^2\}(BF_4)$	$\{Re(CO)_3(bpy)L^1\}(BF_4)$	$\{Re(CO)_3(phen)L^1\}(BF_4)$	$\{Re(CO)_3(phen)L^2\}(BF_4)$	$\{Re(CO)_3(dmb)L^2\}(BF_4)$
Empirical formula	$C_{28}H_{19}BF_4N_5O_5Re$	$C_{29}H_{21}BF_4N_5O_5Re$	$C_{30}H_{20}BCl_2F_4N_4O_5Re$	$C_{30}H_{19}BF_4N_5O_5Re$	$C_{29}H_{24}BF_4N_4O_6Re$
Formula weight	778.49	792.52	860.41	802.51	797.53
T (K)	120(2)	120(2)	100(2)	100(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*Pbca*	P2(1)/*c*	*P*2(1)/*c*	*I*2/*a*
Unit cell dimensions					
a (Å)	12.1221(4)	16.0830(8)	13.184(3)	11.965(3)	21.428(2)
b (Å)	19.0972(5)	13.3736(7)	18.508(5)	18.992(4)	12.3526(13)
c (Å)	12.5934(4)	26.8120(14)	13.851(3)	13.153(3)	22.346(18)
α (°)	90.00	90.00	90.00	90.00°	90.00
β (°)	107.1890(10)	90.00	113.235(5)	106.249(11)	104.637(9)
γ (°)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	2785.13(15)	5766.9(5)	3105.7(13)	2869.7(11)	5722.8(11)
Z	4	8	4	4	8
D_{calc}	1.857	1.826	1.840	1.858	1.851
Absorption coefficient	4.439	4.289	4.156	4.311	4.324
F(000)	1512	3088	1672	1560	3120
Crystal size (mm)	0.53 × 0.16 × 0.09	0.34 × 0.09 × 0.02	0.35 × 0.15 × 0.08	0.37 × 0.12 × 0.07	0.32 × 0.07 × 0.03
Reflections collected	6391	6641	7090	6639	6585
Independent reflections	5793	4690	6271	6028	5712
Goodness-of-fit on *F*	1.029	0.928	1.063	1.046	1.034
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0417$, $wR_2 = 0.1067$	$R_1 = 0.0257$, $wR_2 = 0.0534$	$R_1 = 0.0339$, $wR_2 = 0.0878$	$R_1 = 0.0192$, $wR_2 = 0.0451$	$R_1 = 0.0252$, $wR_2 = 0.0617$
R indices (all data)	$R_1 = 0.0444$, $wR_2 = 0.1083$	$R_1 = 0.0462$, $wR_2 = 0.0576$	$R_1 = 0.0392$, $wR_2 = 0.0909$	$R_1 = 0.0225$, $wR_2 = 0.0466$	$R_1 = 0.0324$, $wR_2 = 0.0656$

[a] The structure was refined on ${F_o}^2$ using all data.

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