

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263476440>

Structural, electrochemical and photophysical investigations of Re(I)-complexes of λ^3 (3)N-tridentate heterocyclic ligands

Article in Dalton Transactions · June 2014

DOI: 10.1039/c4dt01454e · Source: PubMed

CITATIONS

16

READS

102

2 authors:



Amlan Kumar Pal

Indian Institute of Technology Jammu

57 PUBLICATIONS 955 CITATIONS

[SEE PROFILE](#)



Garry S. Hanan

Université de Montréal

242 PUBLICATIONS 5,794 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Covalently modified polyoxometalate with d6 metal photosensitizer [View project](#)



supramolecular 3D architectures on surfaces [View project](#)

Structural, electrochemical and photophysical investigations of Re(I)-complexes of κ^3N -tridentate heterocyclic ligands†Cite this: *Dalton Trans.*, 2014, **43**, 11811Received 18th May 2014,
Accepted 13th June 2014

DOI: 10.1039/c4dt01454e

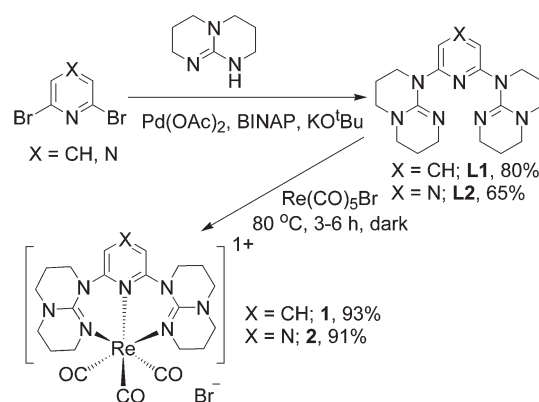
www.rsc.org/dalton

fac, fac-[Re^I(CO)₃]-complexes of new κ^3N -tridentate ligands were synthesized and characterized by various analytical techniques including XRD. The regulation of electronic properties of the complexes upon ligand modification is discussed.

Interest in rhenium(I)-tricarbonyl-polypyridyl complexes has grown considerably in the last decade as they find use as light-harvesting chromophores in solar energy conversion,¹ fluorescent probes in cell-imaging,² sensor development³ and as supramolecular synthons.⁴ While complexes of type *fac, cis*-[Re(CO)₃(bpy)X]⁵ (X = Cl or Br) (bpy = 2,2'-bipyridine), *fac, cis*-[Re(CO)₃(tpy- κ^2N)X]⁶ (tpy = 2,2':6',2''-terpyridine) and *mer, cis*-[Re(tpy- κ^3N)(CO)₂X]⁷ are relatively well known, complexes of type *fac, fac*-[Re(L- κ^3N)(CO)₃]⁺ (where L = 2,6-disubstituted pyridyl-tridentate ligand) are virtually non-existent.⁸ Although a few macrocyclic⁹ or tripodal face-capping¹⁰ ligands around a Re^I(CO)₃-centre have been reported, their properties are not well explored. The effect of the introduction of electron donating or withdrawing substituents on the ligand would allow the electronic properties of this class of complex to be fine-tuned.

Herein we report the syntheses and characterization of two different *fac, fac*-[Re(dgpy/dgpz- κ^3N)(CO)₃]⁺-complexes with dgpy (**L1**) (dgpy = 2,6-diguanyldipyridine) and dgpz (**L2**) (dgpz = 2,6-diguanyldipyrzine), **1** and **2**, respectively.

Ligands **L1** and **L2** were synthesized using Pd-catalyzed C-N bond-forming reactions. Complexes **1** and **2** were prepared by direct mixing of Re(CO)₅Br and ligand in 1 : 1.2 molar ratio in hot toluene (Scheme 1). Although *mer, cis*-[Re(tpy- κ^3N)(CO)₂X] (where X = Cl or Br)⁷ can be synthesized through a *fac*-[Re(CO)₃(tpy- κ^2N)X] intermediate,⁶ the additional thermodynamic stabilization upon κ^3N -coordination by **L1** and **L2** with the formation of sterically relaxed six-membered chelate



Scheme 1 Syntheses of ligands **L1**, **L2** and complexes *fac, fac*-[Re(**L1**- κ^3N)(CO)₃][Br] (**1**) and *fac, fac*-[Re(**L2**- κ^3N)(CO)₃][Br] (**2**).

rings, affords these chemically robust complexes in high yields and with much milder reaction conditions.

The ¹H and ¹³C NMR spectra (Fig. S1–S4 in ESI†) of complexes **1** and **2** display a high degree of symmetry of the aromatic protons and carbon atoms. The six annular methylene units are nonequivalent by both ¹H and ¹³C NMR spectroscopy in contrast to free H-hpp (H-hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-(a)]pyrimidine), in which only three proton resonances are found in its ¹H NMR at 400 MHz due to tautomerism.¹¹ Similar observations were reported by Coles and co-workers^{11d} for a methylene-linked bis(guanidyl) compound, H₂C{hpp}₂. The noticeable downfield shift of ~22 ppm of the alkene C-atom in the aliphatic backbone of **2** compared to that of **1** suggests a strong electron withdrawing effect of the pyrazine (Pz) core through the N_{hpp}-Re-N_{Pz} unit. This fact is also supported by a shorter Re-N_{Pz} distance compared to Re-N_{Py} distance in their respective crystal structures (Fig. 1).

Single crystals were obtained by slow vapour diffusion of diethyl ether into dichloromethane solutions of **1** and **2**. The coordinatively saturated Re(I) ions in **1** and **2** are in a distorted octahedral geometry, where both ligands **L1** and **L2** and the carbonyl groups adopt *fac*-coordination around Re(I). This *fac*-coordination is facilitated due to the flexible aliphatic

Département de Chimie, Université de Montréal, 2900 Édouard-Montpetit, Montréal, Québec H3T-1J4, Canada. E-mail: garry.hanan@umontreal.ca;

Fax: +1 514 343-7586; Tel: +1 514 340-5156

† Electronic supplementary information (ESI) available: Synthetic details of all compounds, other figures, tables, DFT, TD-DFT data as indicated in main text and X-ray structural data of **1** and **2**. CCDC 922649 and 975057. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01454e

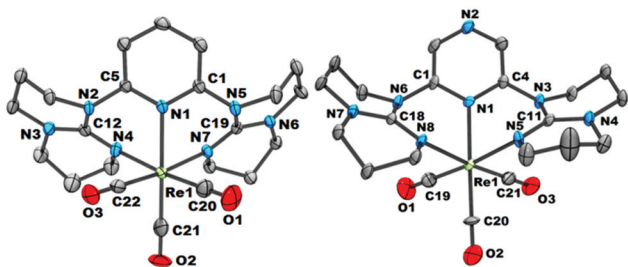


Fig. 1 Perspective views of complexes **1** and **2**, exhibiting the facial coordination of **L1** and **L2**. Hydrogen atoms and anions are not shown for clarity; ellipsoids correspond to 50% probability.

backbone and larger bite angle of the 6-membered chelate rings around the metal ions, while a *mer*-coordination of *tpy* gives rise to comparatively strained 5-membered chelate rings. The alkyl chains adopt a similar conformation with respect to the Re(i) centre as do other coordination complexes incorporating (CH₂)-bridged donor atoms.¹² Complexes **1** and **2** are virtually isostructural and unlike the symmetrical structure in solution, all of the carbonyl groups in these solid state structures are non-symmetrical. The average N–C–N–C dihedral angle of complexes **1** and **2** are ~130° (average of <N1–C1–N5–C19 and <N1–C5–N2–C12) and 129° (average of <N1–C4–N3–C11 and <N1–C1–N6–C18), respectively, suggesting broken π -conjugation between the pyridine or pyrazine unit and the hpp units. The optimized ground state geometries of **1** and **2** are in reasonable agreement with the X-ray structural data (Table S2 in ESI†) and the Re–C and Re–N distances are in the range expected for similar tricarbonyl complexes.^{8,13,14} The axial Re–C distance (*trans* to pyridine) in complex **1** is shorter (1.901(5) Å) than that of complex **2** (1.931(5) Å) due to the lower basicity of the pyrazine ring in **2** compared to that of the pyridine ring in **1**. In both the complexes, the central Re–N_{Py/Pz} bond is shorter than the corresponding distances to the outer rings,^{8,15a} as found for tridentate terpyridine Re(i) and Ru(II) complexes.^{15b,c}

The electronic absorption spectra for **L1**, **L2**, **1** and **2** were recorded in dry, degassed acetonitrile at ambient temperature. Both complexes exhibit two ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions below 300 nm.¹⁶ A third transition at 318 nm for complex **2** is also an LC transition as suggested by TD-DFT calculations (Fig. S5 and Table S3 in ESI†). A singlet metal-to-ligand charge transfer (¹MLCT) transition exhibits a broad, tailing absorption band between 350–500 nm with a molar absorptivity of 5000 M⁻¹ cm⁻¹.⁸ The maxima of the observed lowest energy transitions of **1** and **2** are at 346 nm and 377 nm, respectively, and they also shift bathochromically upon lowering the polarity of the solvent from acetonitrile to dichloromethane. These facts suggest a ¹MLCT nature for these transitions and indeed the TD-DFT calculations of **1** and **2** support this assignment as HOMO–1 to LUMO for both **1** ($\Delta E_{\text{LUMO}-(\text{HOMO}-1)} = 4.44$ eV) and **2** ($\Delta E_{\text{LUMO}-(\text{HOMO}-1)} = 3.96$ eV). The transitions have mixed LC (major) and ¹MLCT (minor) components (see Tables S4–S9 in ESI† for more details).

The non-equivalency of the carbonyl units is also shown by IR frequencies (Fig. S8 in ESI†), where three different C–O

bands are observed. In complex **1**, for example, the strong sharp band at 2003 cm⁻¹ may be attributed to C20–O1 stretching, while the strong, broad band at 1867 cm⁻¹, with a shoulder at ~1885 cm⁻¹ could be assigned to the C21–O2 and C22–O3 stretching modes, respectively, which are in good agreement with its TD-DFT calculation (see Table S10 in ESI†).

The electrochemical behavior of the ligands and complexes was examined by cyclic voltammetry and differential pulse voltammetry (Table S11 and Fig. S9 in ESI†). All of the electron transfer phenomena were found to be monoelectronic. Complexes **1** and **2** exhibit ligand-based reductions centered on the pyridine and pyrazine units, respectively, as suggested by DFT calculations of their LUMOs (Fig. 2 and Fig. S10 in ESI†). The 500 mV anodic shift in reduction potential of complex **2** compared to that of **1** is due to the electron deficiency of pyrazine as compared to pyridine, which is in agreement with the calculated higher energy of the LUMO of **1** (–1.70 eV) than that of **2** (–2.35 eV). This trend has also been reported in structurally similar Ru(II)-polypyridyl complexes.¹⁷ In the anodic region, both complexes exhibit two ligand-based oxidations at ~0.79 V and 1.09 V. These values are also in good agreement with the DFT calculations, as the HOMO and SOMO (SOMO = singly occupied molecular orbital) of mono- and di-oxidized complexes, respectively, reside predominantly on coordinated hpp units (see Tables S4, S6–S8†). The two distinct ligand-based oxidations may suggest a metal-mediated superexchange phenomenon.¹⁸ For both complexes, the third quasi-reversible oxidation at 1.43 V is assigned to metal-based oxidation, which occurs at 320 mV less positive potential than in [Re(bpy)(CO)₃(Py)]⁺,¹⁹ suggesting that ligands **L1** and **L2** are more σ -donating than bpy and Py. Due to broken π -conjugation between the hpp and the saturated heterocyclic moieties, the metal-based oxidation is now fairly invariant to the changes in electronic properties of Py or Pz unit, therefore, the combined σ -donation from two hpp units is the dominating factor in metal-based oxidation. This fact allows the ligand-based reductions to be separately tuned by simple modification of the electronic nature of the central aromatic ring.

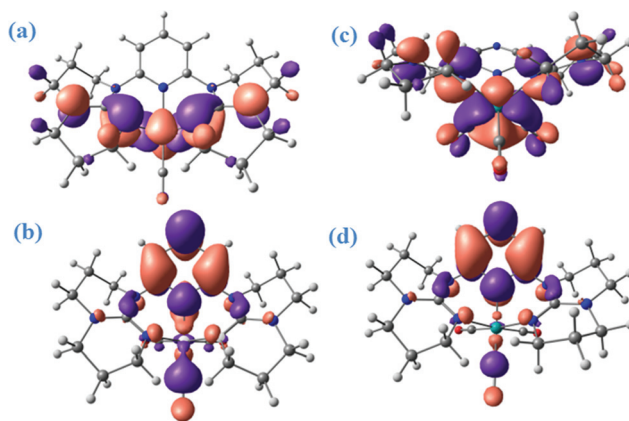


Fig. 2 Kohn–Sham molecular orbital sketches of (a) HOMO and (b) LUMO of **1** and (c) HOMO and (d) LUMO of **2**.

The emission spectra of **L1**, **L2** and the complexes were recorded in dry, degassed acetonitrile at ambient temperature. The ligands emit in the high energy region (~370 nm). A red-shift of 22 nm in the emission maxima from **L1** to **L2** is also observed, which is concomitant with the bathochromic shift of 29 nm in their lowest energy absorptions of **L1** to **L2**. The red-shift is due to the lower π^* level in **L2** compared to that of **L1**, while the HOMOs for **L1** and **L2** remain at similar energies. Complexes **1** and **2** were found to be blue-emitters (luminescence at ~400 nm) at ambient temperature compared to *fac*, *fac*-[Re(bqp- κ^3N)(CO)₃](Cl) (606 nm) (bqp = 2,6-bis(8'-quinolyl)pyridine).⁸ In contrast to complex [Re(Py)₂(CO)₃Cl]²⁰ or complexes of type *mer*,*cis*-[Re(tpy- κ^3N)(CO)₂(L)]⁺ (where L = CH₃CN, PPh₃, Py, PEt₃) which do not exhibit room temperature luminescence, complexes **1** and **2** are luminescent due to strong σ -donation from the hpp units. Owing to this σ -donation the energy of the ³MC (³MC = triplet metal-centered) state increases, consequently enhancing ³MLCT-³MC state energy gap, thus diminishing thermal population of the ³MC state and facilitating emission from the ³MLCT state. The ¹MLCT maximum in **2** (377 nm) is red-shifted by 31 nm as compared to ¹MLCT maxima in **1** (346 nm) with a concomitant red-shift of 37 nm for the ³MLCT maximum of complex **2** (418 nm) as compared to that of complex **1** (381 nm).

Conclusions

In conclusion, the analytical and crystal data provide evidence for facial coordination of **L1** and **L2** around Re(i)-centres. To the best of our knowledge, these are among the very rare examples of tridentate 2,6-disubstituted azaheterocyclic ligands exhibiting κ^3N -facial coordination around Re(i) in presence of three carbonyls. Due to the strong σ -donation from the ligands, these complexes are electrochemically appealing, as complexes **1** and **2** exhibit quasi-reversible rhenium-based oxidation at ~1.02 V (*vs.* Fc⁺/Fc) which is ~320 mV less positive compared to the oxidation of rhenium in [Re(bpy)(CO)₃(Py)][ClO₄]⁺ (+1.34 V).^{19,21} The ¹MLCT and ³MLCT maxima can be fine-tuned by modifications in the electronic properties of the unsaturated aromatic backbone. Due to the structural rigidity as face-capped complexes and exciting redox and photophysical properties, these complexes may be useful as photosensitizers in a range of photochemical reactions and light-emitting devices.

The authors gratefully thank the Natural Sciences and Engineering Research Council of Canada (NSERC), the Centre for Self-Assembled Chemical Structure (CSACS) and the University of Montreal for financial support.

Notes and references

1 T. J. Meyer, Molecular level artificial photosynthetic materials, in *Progress in inorganic chemistry*, John Wiley & Sons, Inc., New York, 1997, vol. 44.

- 2 (a) A. J. Amoroso, M. P. Coogan, J. E. Dunne, V. Fernandez-Moreira, J. B. Hes, A. J. Hayes, D. Lloyd, C. Millet, S. J. A. Pope and C. Williams, *Chem. Commun.*, 2007, 3066; (b) J. G. Vaughan, B. L. Reid, P. J. Wright, S. Ramchandani, B. W. Skelton, P. Raiteri, S. Muzzioli, D. H. Brown, S. Stagni and M. Massi, *Inorg. Chem.*, 2014, **53**, 3629.
- 3 (a) H. L. Bozec and V. Guerschais, Molecular organic materials for optics, in *Topics in Organometallic Chemistry*, Springer, Heidelberg, Dordrecht, New York, 2010, ch. 2, vol. 28; (b) C. A. Bader, R. D. Ng, S. Y. Brooks, A. Sorvina, M. V. Werrett, P. J. Wright, A. G. Anwar, D. A. Brooks, S. Stagni, S. Muzzioli, M. Silberstein, B. W. Skelton, E. M. Goldys, S. E. Plush, T. Shandala and M. Massi, *RSC Adv.*, 2014, **4**, 16345.
- 4 (a) C. A. Berg-Brennan, D. I. Yoon, R. V. Slone, A. P. Kazala and J. T. Hupp, *Inorg. Chem.*, 1996, **35**, 2032; (b) M. V. Werrett, D. Chartrand, J. D. Gale, G. S. Hanan, J. G. MacLellan, M. Massi, S. Muzzioli, P. Raiteri, B. W. Skelton, M. Silberstein and S. Stagni, *Inorg. Chem.*, 2011, **50**, 1229; (c) D. Chartrand, C. A. C. Ruiz and G. S. Hanan, *Inorg. Chem.*, 2012, **51**, 12738; (d) A. Bessette, S. Nag, A. K. Pal, S. Derossi and G. S. Hanan, *Supramol. Chem.*, 2012, **24**, 595.
- 5 (a) E. E. Benson, M. D. Sampson, K. A. Grice, J. M. Smieja, J. D. Froehlich, D. Friebe, J. A. Keith, E. A. Carter, A. Nilsson and C. P. Kubiak, *Angew. Chem., Int. Ed.*, 2013, **52**, 4841; (b) H. Takeda, K. Koike, H. Inoue and O. Ishitani, *J. Am. Chem. Soc.*, 2008, **130**, 2023.
- 6 (a) J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952; (b) A. J. Amoroso, A. Banu, M. P. Coogan, P. G. Dwards, E. G. Hossain and K. M. Abdul Malik, *Dalton Trans.*, 2010, **39**, 6993; (c) D. R. Black and S. E. Hightower, *Inorg. Chem. Commun.*, 2012, **24**, 16.
- 7 A. Juris, S. Campagna, I. Bidd, J.-M. Lehn and R. Ziessel, *Inorg. Chem.*, 1988, **27**, 4007.
- 8 D. J. Losey, B. A. Frenzel, W. M. Smith, S. E. Hightower and C. G. Hamaker, *Inorg. Chem. Commun.*, 2013, **30**, 46.
- 9 M. Casanova, E. Zangrando, F. Munini, E. Iengo and E. Alessio, *Dalton Trans.*, 2006, 5033.
- 10 (a) R. S. Herrick, T. J. Brunner, C. Maus, K. Crandall, A. Cetin and C. J. Ziegler, *Chem. Commun.*, 2006, 4330; (b) D. V. Griffiths, Y.-K. Cheong, P. Duncanson and M. Motevalli, *Dalton Trans.*, 2011, **40**, 10215; (c) K. Wu, D. Mukherjee, A. Ellern, A. D. Sadow and W. E. Geiger, *New J. Chem.*, 2011, **35**, 2169.
- 11 (a) S. Nag, J. G. Ferreira, L. Chenneberg, P. D. Ducharme, G. S. Hanan, G. L. Ganga, S. Serroni and S. Campagna, *Inorg. Chem.*, 2011, **50**, 7; (b) A. K. Pal, S. Nag, J. G. Ferreira, V. Brochery, G. La Ganga, A. Santoro, S. Serroni, S. Campagna and G. S. Hanan, *Inorg. Chem.*, 2014, **53**, 1679; (c) A. K. Pal, P. D. Ducharme and G. S. Hanan, *Chem. Commun.*, 2014, **50**, 3303; (d) S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2004, **43**, 7564; (e) M. P. Coles, *Chem. Commun.*, 2009, 3659; (f) M. S. Khalaf, S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Dalton Trans.*, 2010, **39**, 1635;

- (g) M. P. Coles, P. J. Aragon-Saez, S. H. Oakley, P. B. Hitchcock, M. G. Davidson, Z. B. Maksic, R. Vianello, I. Leito, I. Kaljurand and D. C. Apperley, *J. Am. Chem. Soc.*, 2009, **131**, 16858; (h) A. K. Pal, N. Zaccheroni, S. Campagna and G. S. Hanan, *Chem. Commun.*, 2014, **50**, 6846; (i) A. K. Pal and G. S. Hanan, *Dalton Trans.*, 2014, **43**, 6567; (j) A. K. Pal, B. Laramée-Milette and G. S. Hanan, *Inorg. Chim. Acta*, 2014, **418**, 15; (k) A. K. Pal, B. Laramée-Milette and G. S. Hanan, *RSC Adv.*, 2014, **4**, 21262.
- 12 (a) B. De Groot, G. S. Hanan and S. J. Loeb, *Inorg. Chem.*, 1991, **30**, 4644–4647; (b) G. R. Giesbrecht, G. S. Hanan, J. E. Kickham and S. J. Loeb, *Inorg. Chem.*, 1992, **31**, 3286–3291.
- 13 S. E. Hightower, R. C. Corcoran and B. P. Sullivan, *Inorg. Chem.*, 2005, **44**, 9601.
- 14 A. J. Hallett and S. J. A. Pope, *Inorg. Chem. Commun.*, 2011, **14**, 1606.
- 15 (a) M. Jäger, R. J. Kumar, H. Görls, J. Bergquist and O. Johansson, *Inorg. Chem.*, 2009, **48**, 3228; (b) E. A. Medlycott and G. S. Hanan, *Chem. Soc. Rev.*, 2005, **34**, 133; (c) A. K. Pal and G. S. Hanan, *Chem. Soc. Rev.*, 2014, DOI: 10.1039/C4CS00123K, advanced article.
- 16 D. J. Stufkens and A. Vlček Jr., *Coord. Chem. Rev.*, 1998, **177**, 127.
- 17 (a) K. O. Johansson, J. A. Lotoski, C. C. Tong and G. S. Hanan, *Chem. Commun.*, 2000, 819; (b) M. I. J. Polson, J. A. Lotoski, K. O. Johansson, N. J. Taylor, G. S. Hanan, B. Hasenknopf, R. Thouvenot, F. Loiseau, R. Passalacqua and S. Campagna, *Eur. J. Inorg. Chem.*, 2002, **10**, 2549; (c) Y.-Q. Fang, M. I. J. Polson and G. S. Hanan, *Inorg. Chem.*, 2003, **42**, 5.
- 18 P. H. Dinolfo, M. E. Williams, C. L. Stern and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 12989.
- 19 L. A. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, *Inorg. Chem.*, 1990, **29**, 4335.
- 20 M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998.
- 21 A correction factor of 0.395 V corresponding to the oxidation of ferrocene in acetonitrile at ambient temperature using [*n*-Bu₄N]PF₆ (0.1 M) as an electrolyte has been deducted from the reported oxidation value of 1.74 V vs. SCE in ref. 18.