Electronic Supplementary Material (ESI) for Dalton Transactions

3N-Heterocyclic carbenes as π*-acceptors in luminescent Re(I) triscarbonyl complexes

Lee A. Casson,[a] Sara Muzzioli,[b] Paolo Raiteri,[a] Brian W. Skelton,[c] Stefano Stagni,*[b] Massimiliano Massi*[a] and David H. Brown*[a,d]

[a] *Department of Chemistry, Curtin University, GPO Box U 1987, Perth, Australia 6845. Fax: +618 9266 2300; Tel: +618 9266 1279; E-mail: m.massi@curtin.edu.au, d.h.brown@curtin.edu.au.*

[b] *Department of Physical and Inorganic Chemistry, University of Bologna, viale del Risorgimento 4, 40126 Bologna, Italy. E-mail: stefano.stagni@unibo.it.*

[c] *Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia.*

[d] *School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia.*

Electronic Supplementary Information

Table S1. Selected bond lengths [Å] and angles [°] for *fac*-[Re(CO)$_3$(**N^C**)Br].

Br(1)-Re(1)	2.6436(3)
Re(1)-C(20)	1.915(3)
Re(1)-C(30)	1.938(3)
Re(1)-C(10)	1.969(3)
Re(1)-C(12)	2.114(3)
Re(1)-N(21)	2.198(2)
C(20)-Re(1)-C(30)	90.13(11)
C(20)-Re(1)-C(10)	87.56(11)
C(30)-Re(1)-C(10)	91.17(11)
C(20)-Re(1)-C(12)	100.70(10)
C(30)-Re(1)-C(12)	91.48(10)
C(10)-Re(1)-C(12)	171.31(10)
C(20)-Re(1)-N(21)	172.55(10)
C(30)-Re(1)-N(21)	95.15(9)
C(10)-Re(1)-N(21)	97.55(10)
C(12)-Re(1)-N(21)	73.97(9)
C(20)-Re(1)-Br(1)	87.90(8)
C(30)-Re(1)-Br(1)	175.99(8)
C(10)-Re(1)-Br(1)	92.24(8)
C(12)-Re(1)-Br(1)	85.45(7)
N(21)-Re(1)-Br(1)	86.50(6)

Table S2: Absorption frequencies and intensities calculated with TDDFT for *fac*-[Re(CO)$_3$(**N^C**)Cl]. The levels involved in the transitions and their contributions are also reported.

Wavelength (nm)	Intensity (arb. units)	Transition levels	Contribution
397.65	0.0207	HOMO-1 -> LUMO	2.5%
		HOMO -> LUMO	95.5%
375.72	0.1298	HOMO-1 -> LUMO	94.0%
		HOMO -> LUMO	2.7%
350.41	0.0031	HOMO-2 -> LUMO	95.8%
328.67	0.0819	HOMO -> LUMO+1	95.5%
318.63	0.0197	HOMO-3 -> LUMO	2.0%
		HOMO-1 -> LUMO+1	93.9%
301.79	0.0064	HOMO -> LUMO+2	23.1%
		HOMO -> LUMO+3	68.3%
299.42	0.1515	HOMO-3 -> LUMO	85.8%
		HOMO-1 -> LUMO+3	3.2%
		HOMO -> LUMO+3	2.0%
294.61	0.0278	HOMO-4 -> LUMO	5.0%
		HOMO-3 -> LUMO	4.9%
		HOMO-2 -> LUMO+3	2.3%
		HOMO-1 -> LUMO+2	6.7%
		HOMO-1 -> LUMO+3	37.0%
		HOMO -> LUMO+2	23.5%
		HOMO -> LUMO+3	3.1%
292.96	0.0004	HOMO-2 -> LUMO+1	92.5%
		HOMO-2 -> LUMO+4	2.6%

Table S3: Absorption frequencies and intensities calculated with TDDFT for *fac*-[Re(CO)$_3$(**N^C**)Br]. The levels involved in the transitions and their contributions are also reported.

Wavelength (nm)	Intensity (arb. units)	Transition levels	Contribution
401.38nm	0.0152	HOMO-1 -> LUMO	2.3%
		HOMO -> LUMO	95.8%
382.80nm	0.0951	HOMO-1 -> LUMO	94.9%
		HOMO -> LUMO	2.4%
349.94nm	0.0022	HOMO-2 -> LUMO	95.9%
331.80nm	0.0519	HOMO -> LUMO+1	95.4%
323.01nm	0.0211	HOMO-1 -> LUMO+1	94.4%
310.38nm	0.0677	HOMO-3 -> LUMO	93.5%
304.14nm	0.0089	HOMO -> LUMO+2	26.0%
		HOMO -> LUMO+3	66.2%
298.88nm	0.0854	HOMO-5 -> LUMO	4.3%
		HOMO-4 -> LUMO	48.3%
		HOMO-1 -> LUMO+2	5.0%
		HOMO-1 -> LUMO+3	14.5%
		HOMO -> LUMO+2	13.8%
		HOMO -> LUMO+3	3.8%
		HOMO -> LUMO+4	5.0%
296.42nm	0.1137	HOMO-5 -> LUMO	3.3%
		HOMO-4 -> LUMO	35.4%
		HOMO-1 -> LUMO+2	10.0%
		HOMO-1 -> LUMO+3	34.5%
		HOMO -> LUMO+2	4.7%
		HOMO -> LUMO+4	5.9%

Figure S1: HOMO-4 of *fac*-[Re(CO)$_3$(**N^C**)Cl] (left panel) and *fac*-[Re(CO)$_3$(**N^C**)Br] (right panel).

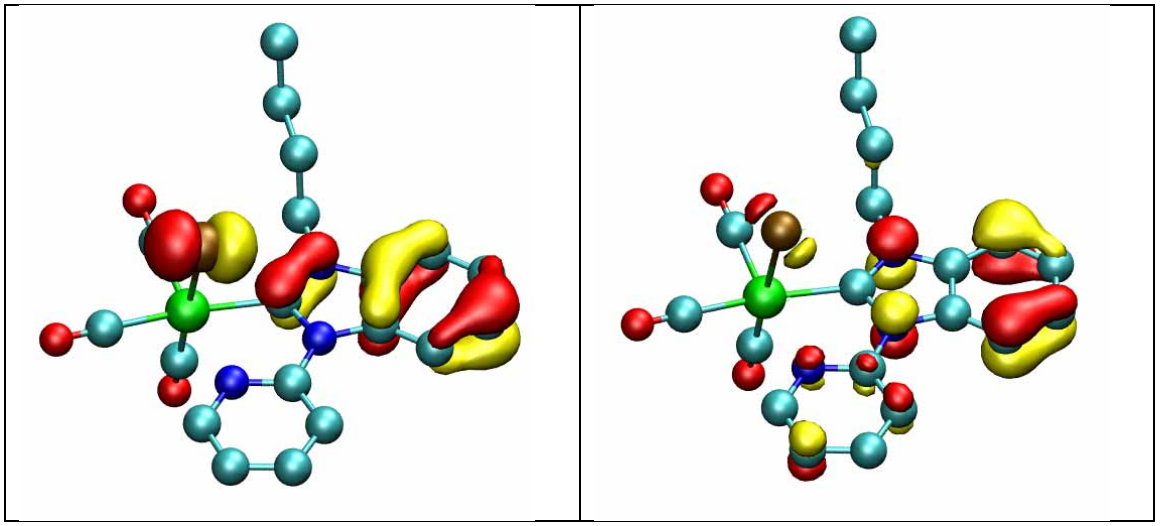

Figure S2: HOMO-3 of *fac*-[Re(CO)$_3$(**N^C**)Cl] (left panel) and *fac*-[Re(CO)$_3$(**N^C**)Br] (right panel).

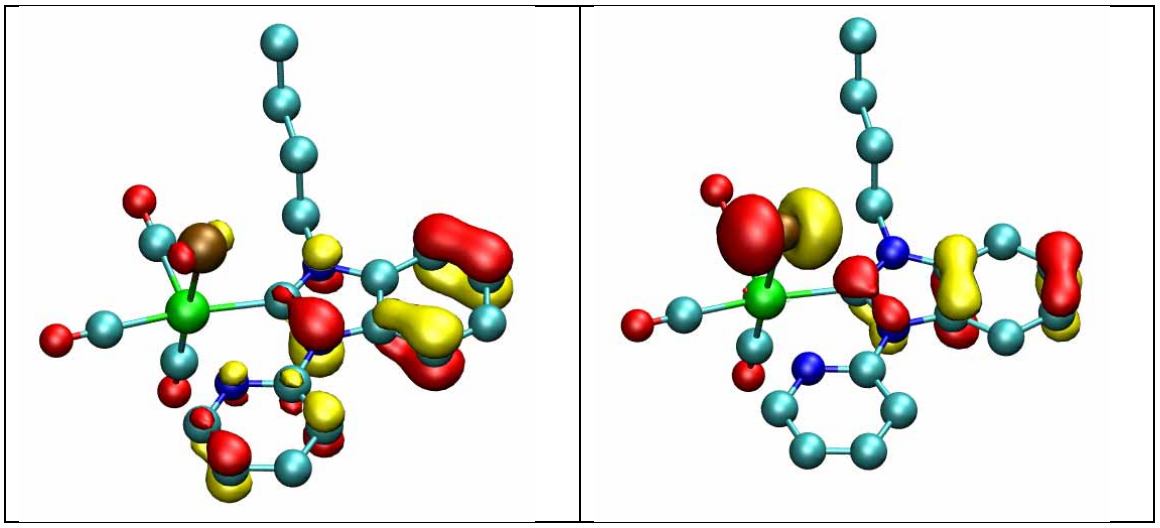

Figure S3: HOMO-2 of *fac*-[Re(CO)$_3$(**N^C**)Cl] (left panel) and *fac*-[Re(CO)$_3$(**N^C**)Br] (right panel).

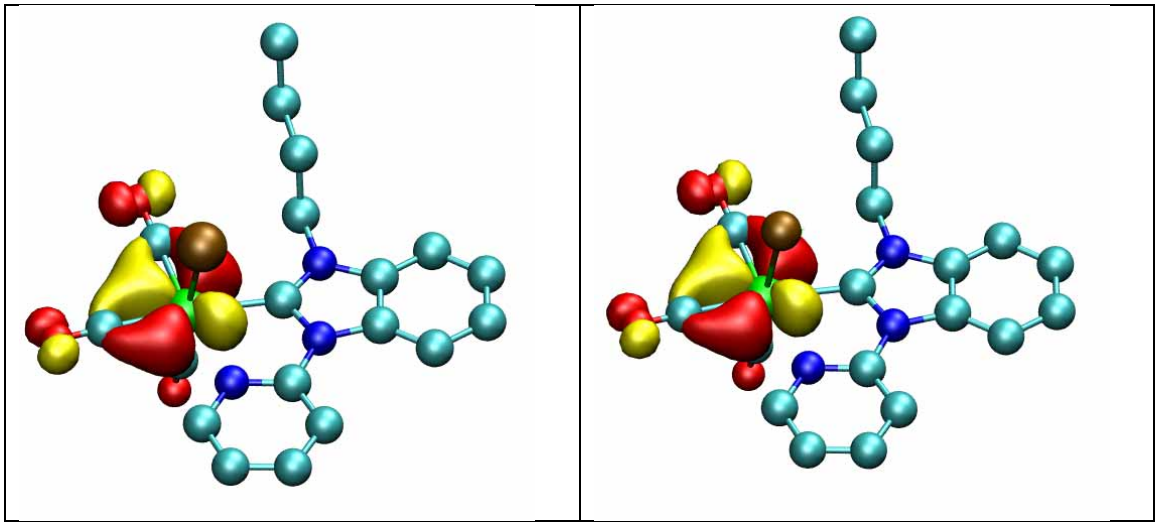

Figure S4: LUMO+1 of *fac*-[Re(CO)$_3$(**N^C**)Cl] (left panel) and *fac*-[Re(CO)$_3$(**N^C**)Br] (right panel).

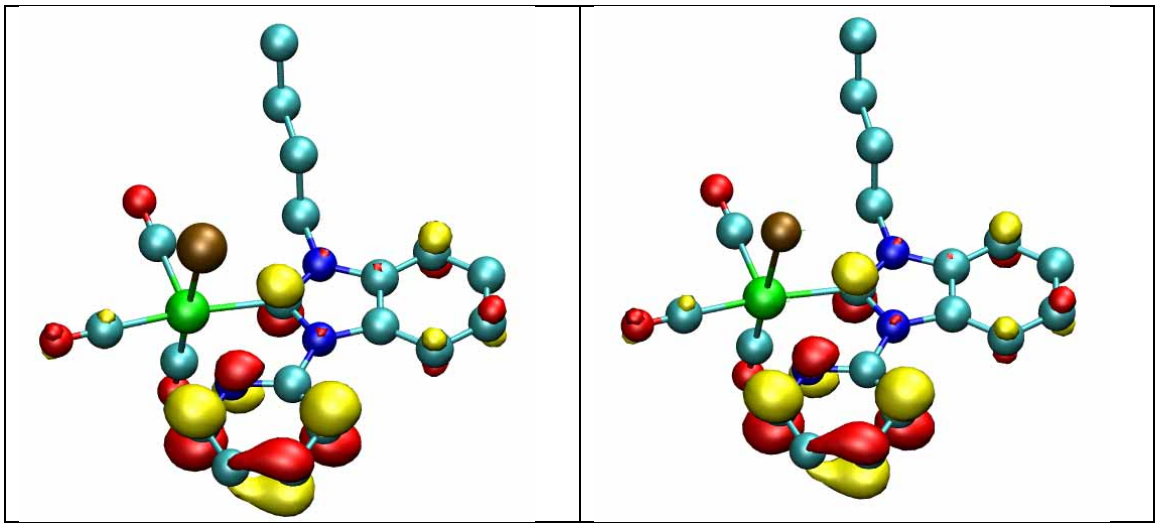

Figure S5: LUMO+2 of *fac*-[Re(CO)$_3$(**N^C**)Cl] (left panel) and *fac*-[Re(CO)$_3$(**N^C**)Br] (right panel).

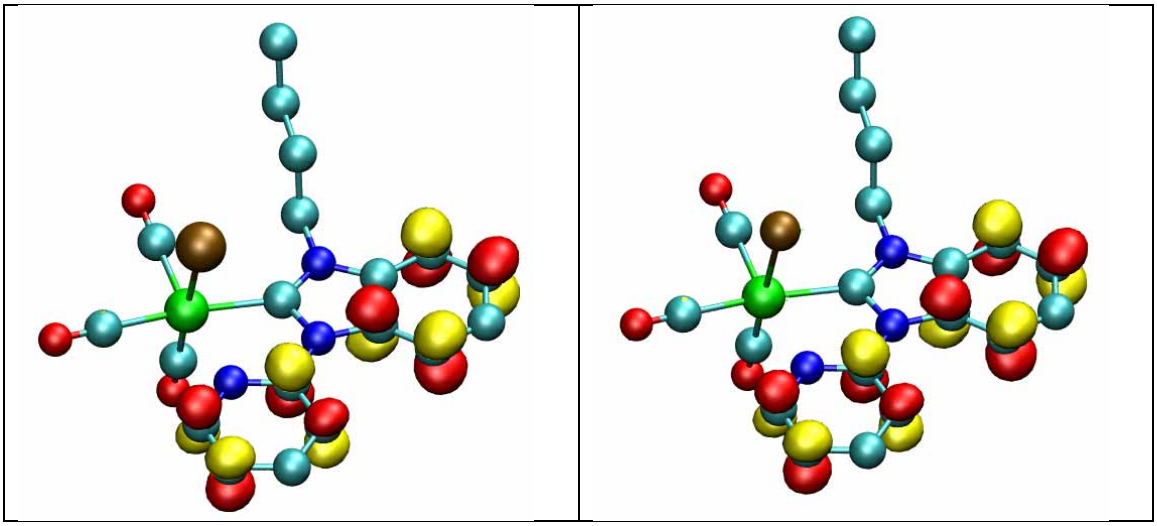

Figure S6: LUMO+3 of *fac*-[Re(CO)$_3$(**N^C**)Cl] (left panel) and *fac*-[Re(CO)$_3$(**N^C**)Br] (right panel).

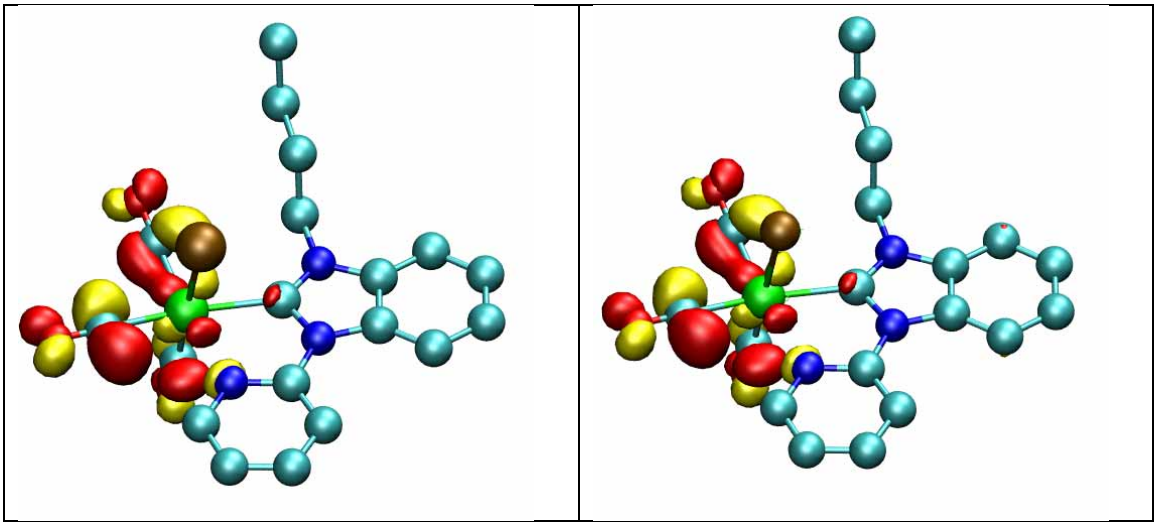

Figure S7. Absorption spectra of *fac*-[Re(CO)$_3$(**N^C**)Br] and *fac*-[Re(CO)$_3$(**N^C**)Cl] calculated with TDDFT obtained by using the intensities reported in Table S3 and S4 and applying a Gaussian broadening with an exponent of 0.002 nm^{-2}.

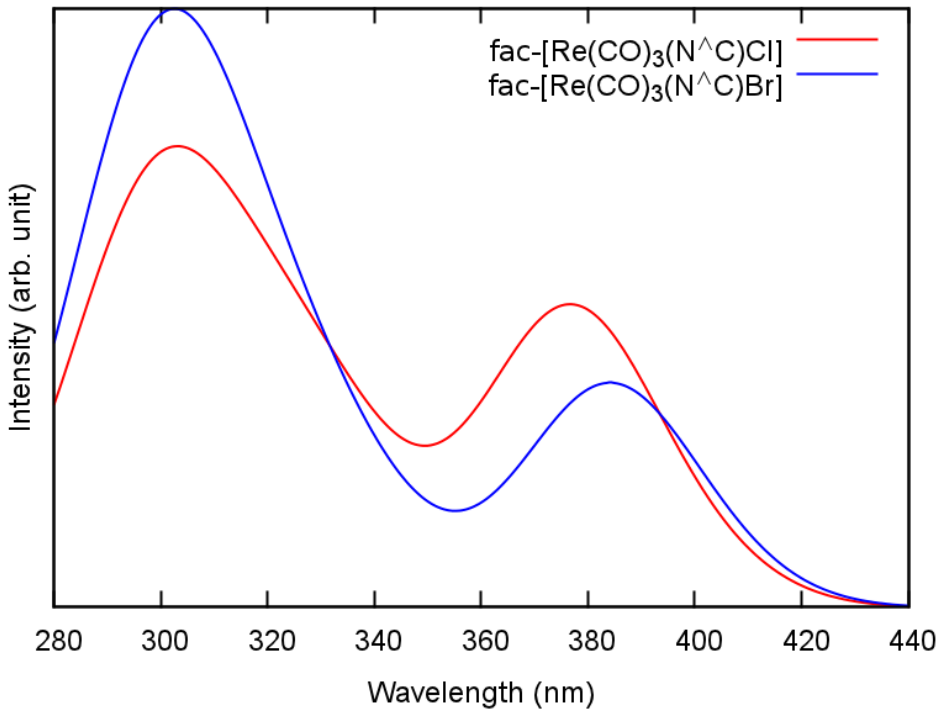

Figure S8. Multiple emission spectra (λ_{exc} = 350 nm) of *fac*-[Re(CO)$_3$(**N^C**)Cl] in a 10^{-6} M in air-equilibrated acetonitrile solution (t_1 = 0 min., t_5 = 60 min.).