Novel Re(I) tricarbonyl coordination compounds based on 2-pyridyl-1,2,3-triazole derivatives bearing a 4-amino-substituted benzenesulfonamide arm: Synthesis, crystal structure, computational studies and inhibitory activity against carbonic anhydrase I, II and IX isoforms.

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**Table S1.** Selected $^1$H, $^{13}$C NMR data in DMSO-$d_6$ (δ in ppm) of the ligands 3a and 3b and their corresponding complexes 4a and 4b

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**Figure S1.** Labelled ORTEP diagram of ligand 3a (top) and 3b (bottom) with thermal ellipsoids shown at 50% probability and hydrogen omitted for clarity

**Figure S2.** Partial view of the crystal packing of 4a and 4b with hydrogen bonds and π-π contacts shown as dashed lines

**Figure S3.** Experimental (top) and electronic transitions calculated with TDDFT/B3LYP method (down) for 4a and 4b
Table S1. Selected $^1$H, $^{13}$C NMR data in DMSO-$d_6$ (δ in ppm) of the ligands 3a and 3b and their corresponding complexes 4a and 4b

| Compound | Phenyl moiety | Triazole ring | Carbonyl groups |
|----------|---------------|---------------|-----------------|
|          | $CH_\alpha$  | $CH_\omega$   | $CH_\alpha$    | $CH_\omega$   | $C≡O$ |
| 3a       | 8.04          | 8.26          | 120.5          | 127.5         | 9.46  | 121.6 |
| 3b       | 7.53          | 7.83          | 126.2          | 128.4         | 8.73  | 123.1 |
| 4a       | 8.14          | 8.25          | 121.4          | 127.8         | 10.08 | 124.6 | 189.4 | 196.5 | 197.4 |
| 4b       | 7.68          | 7.90          | 126.4          | 129.2         | 9.31  | 126.2 | 189.5 | 196.7 | 197.5 |

Table S2. Selected experimental and calculated IR data of the carbonyl groups [$ν$ ($C≡O$) (cm$^{-1}$)/KBr] for 4a and 4b

|          | $ν$ (C≡O) (cm$^{-1}$) |          | $ν$ (C≡O) (cm$^{-1}$) |
|----------|-----------------------|----------|-----------------------|
| 4a       |                       | 2027     | 2101 Δ                 | 2092 Δ       | 65    | 2029     | 2101 Δ                 | 2091 Δ       | 62    |
| 4b       |                       | 1931     | 2032 Δ                 | 1985 Δ       | 54    | 1920     | 2030 Δ                 | 1983 Δ       | 63    |
|          |                       | 1905     | 2002 Δ                 | 1969 Δ       | 64    | 1902     | 2003 Δ                 | 1966 Δ       | 64    |

For both complexes 4a and 4b, the $ν_{C=O}$ stretching bonds in the 2029-1902 cm$^{-1}$ region were lower than the calculated frequencies by 54-65 cm$^{-1}$ in MeOH solvent and 72-110 cm$^{-1}$ in gas phase. It should be noted that we found a similar mean deviation in previous works.$^{(1)}$ The values of the experimental frequencies ($ν_{C=O}$) are in good agreement with the mean of theoretical values. In addition, the calculated frequencies are lower than those in the free ligand (free $ν_{C=O} = 2143$ cm$^{-1}$), which is consistent with the fact that the back-donation to $π^*$ empty molecular orbitals in the carbonyl ligand.$^{(2)}$

(1) M. Wolff, L. Munoz, A. François, C. Carayon, A. Seridi, N. Saffon, C. Picard, B. Machura, E. Benoist, *Dalton Trans.* **2013**, *42*, 7019-7031
(2) P. Cantero-López, L. Le Bras, D. Páez-Hernández, R. Arratia-Pérez, *Dalton Trans.* **2015**, *44*, 20004-20010

Table S3. Selected experimental bond lengths [Å] and angles [°] for 3a and 3b

| Bond Lengths       | 3a       | 3b       |
|--------------------|----------|----------|
| N(2)-N(3)          | 1.314(3) | 1.313(2) |
| N(3)-N(4)          | 1.357(3) | 1.343(2) |
| N(4)-C(7)          | 1.349(4) | 1.343(2) |
| N(2)-C(6)          | 1.366(4) | 1.363(2) |
| C(6)-C(7)          | 1.364(4) | 1.376(2) |
| C(8)-N(4)          | 1.429(4) | 1.467(2) |
| C(6)-C(5)          | 1.469(4) | 1.467(2) |

| Bond Angles        | 3a       | 3b       |
|--------------------|----------|----------|
| C(6)-N(2)-N(3)     | 109.4(2) | 108.7(1) |
| N(2)-N(3)-N(4)     | 106.5(2) | 107.4(1) |
| N(3)-N(4)-C(7)     | 110.9(2) | 111.2(1) |
| N(3)-N(4)-C(8)     | 120.3(2) | 119.6(1) |
| N(2)-C(6)-C(5)     | 122.7(3) | 121.7(1) |
| C(6)-C(5)-N(1)     | 115.4(3) | 116.4(1) |
| C(9)-C(8)-N(4)     | 119.0(3) | 110.7(1) |
| C(4)-C(5)-C(6)     | 121.1(3) | 121.2(1) |
### Tables S4 and S5. X-ray, calculated bond lengths [Å] and the angles [°] of 4a and 4b

#### 4a

| Bond lengths | X-ray | Gas phase | Δ | Methanol | Δ |
|--------------|-------|-----------|---|----------|---|
| Re(1)-Cl(1)  | 2.490(1) | 2.521 | -0.031 | 2.560 | -0.070 |
| Re(1)-C(14)  | 1.920(4) | 1.930 | -0.010 | 1.925 | -0.005 |
| Re(1)-C(15)  | 1.916(4) | 1.927 | -0.011 | 1.927 | -0.011 |
| Re(1)-C(16)  | 1.926(5) | 1.920 | +0.006 | 1.912 | +0.014 |
| Re(1)-N(1)   | 2.202(3) | 2.241 | -0.039 | 2.244 | -0.042 |
| Re(1)-N(2)   | 2.161(3) | 2.176 | -0.015 | 2.176 | -0.015 |
| O(3)-C(14)   | 1.140(5) | 1.158 | -0.018 | 1.161 | -0.021 |
| O(4)-C(15)   | 1.142(5) | 1.160 | -0.018 | 1.162 | -0.020 |
| O(5)-C(16)   | 1.133(6) | 1.165 | -0.032 | 1.165 | -0.032 |

**Bond angles**

| Bond angles | X-ray | Gas phase | Δ | Methanol | Δ |
|-------------|-------|-----------|---|----------|---|
| C(15)-Re(1)-C(14) | 90.3(2) | 90.83 | -0.49 | 90.68 | -0.34 |
| C(14)-Re(1)-C(16) | 87.4(2) | 91.73 | +4.33 | 91.38 | +3.98 |
| C(15)-Re(1)-C(16) | 88.6(2) | 91.83 | +3.23 | 91.32 | +2.72 |
| C(14)-Re(1)-N(2) | 98.8(2) | 97.60 | +1.23 | 97.57 | +1.26 |
| C(15)-Re(1)-N(2) | 170.3(2) | 169.43 | +0.89 | 170.51 | -0.19 |
| C(16)-Re(1)-N(2) | 94.8(2) | 94.26 | +0.54 | 93.12 | +3.68 |
| C(14)-Re(1)-N(1) | 173.1(2) | 170.32 | +2.77 | 170.93 | +2.16 |
| C(15)-Re(1)-N(1) | 96.6(2) | 96.85 | -0.29 | 97.32 | -0.76 |
| C(16)-Re(1)-N(1) | 93.0(2) | 93.91 | -1.93 | 92.67 | +0.36 |
| N(1)-Re(1)-N(2,2) | 74.3(1) | 74.14 | +0.12 | 74.11 | +0.15 |
| C(14)-Re(1)-Cl(1) | 94.0(2) | 91.46 | +2.55 | 91.32 | +2.69 |
| C(15)-Re(1)-Cl(1) | 92.6(2) | 91.12 | +1.47 | 90.98 | +1.61 |
| C(16)-Re(1)-Cl(1) | 178.1(1) | 175.62 | +2.49 | 176.43 | +1.68 |
| N(1)-Re(1)-Cl(1) | 85.4(1) | 82.53 | +2.88 | 84.33 | +1.08 |
| N(2)-Re(1)-Cl(1) | 83.8(1) | 82.34 | +1.42 | 82.40 | -0.44 |
| O(3)-C(14)-Re(1) | 175.6(5) | 178.25 | -2.55 | 178.28 | -2.68 |
| O(4)-C(15)-Re(1) | 177.6(4) | 177.41 | +0.19 | 178.36 | -0.76 |
| O(5)-C(16)-Re(1) | 176.6(4) | 179.35 | -2.75 | 179.83 | -3.23 |

#### 4b

| Bond lengths | X-ray | Gas phase | Δ | Methanol | Δ |
|--------------|-------|-----------|---|----------|---|
| Re(1)-Cl(1)  | 2.485(1) | 2.527 | - | 2.5624 | -0.077 |

The predicted

| Bond angles | X-ray | Gas phase | Δ | Methanol | Δ |
|-------------|-------|-----------|---|----------|---|
| C(15)-Re(1)-C(17) | 89.3(1) | 90.80 | -1.46 | 90.72 | -1.38 |
| C(15)-Re(1)-C(16) | 90.3(1) | 91.60 | -1.32 | 91.36 | -1.08 |
| C(16)-Re(1)-C(17) | 88.8(1) | 91.78 | -2.94 | 91.29 | -2.45 |
| C(15)-Re(1)-N(2) | 96.9(1) | 97.73 | -0.81 | 97.45 | -0.53 |
| C(17)-Re(1)-N(2) | 173.2(1) | 169.13 | +4.03 | 170.58 | +2.58 |
| C(16)-Re(1)-N(2) | 93.9(1) | 94.69 | -0.83 | 93.17 | +0.69 |
| C(15)-Re(1)-N(1) | 170.9(1) | 170.56 | +0.37 | 170.76 | +0.17 |
| C(17)-Re(1)-N(1) | 99.4(1) | 96.85 | +2.57 | 97.45 | +1.97 |
| C(16)-Re(1)-N(1) | 92.2(1) | 93.66 | -1.44 | 92.73 | -0.51 |
| N(1)-Re(1)-N(2) | 74.2(1) | 74.05 | -0.16 | 74.06 | +0.15 |
| C(15)-Re(1)-Cl(1) | 94.9(1) | 91.47 | +3.43 | 91.46 | +3.44 |
| C(17)-Re(1)-Cl(1) | 92.0(1) | 91.40 | +0.60 | 90.81 | +1.19 |
| C(16)-Re(1)-Cl(1) | 174.7(1) | 175.54 | -0.79 | 176.45 | -1.70 |
| N(1)-Re(1)-Cl(1) | 82.5(1) | 82.85 | -0.31 | 84.15 | -1.61 |
| N(2)-Re(1)-Cl(1) | 84.7(1) | 81.71 | +3.04 | 84.34 | +0.41 |
| O(3)-C(15)-Re(1) | 178.4(2) | 178.16 | +0.24 | 178.22 | +0.18 |
| O(5)-C(17)-Re(1) | 179.0(3) | 177.41 | +1.59 | 178.42 | +0.58 |
| O(4)-C(16)-Re(1) | 177.2(2) | 179.38 | -2.18 | 179.80 | -2.60 |
geometrical parameters of 4a and 4b in the gas phase and methanol solvent are found and compared with the experimental X-ray single crystal data. We can see that the calculated values which included the solvent effect did not differ statistically from the gas phase results, where the structures still keep similar geometrical features. Incontestably, P3LYB/LANL2DZ method displays a very good estimation of Re–Cl distances, with some variation ranging from 0.006 to 0.011 Å in vacuum and 0.005 to 0.015 Å in methanol medium for the two Re-compounds. Whereas, the variation of Re–N distance, is 0.015[0.015] and 0.039[0.042] Å in the gas phase [MeOH solvent] for 4a and 0.029[0.028] and 0.039[0.042] Å in the gas phase [MeOH solvent] for 4b, the Re–Cl distances errors for 4a and 4b are 0.031 and 0.0416 Å in the gas phase and 0.070 and 0.077 Å in the methanol solvent, respectively. Turki et al. noted that the larger errors recorded for the Re–Cl elongation are attributed to a drawback of the DFT technique especially with regard to the dynamic correlation effects, which is important in metal-based complexes including a polar M–Cl bond. (3)

In our case, the differences between modeled results and experimental data are within the range of allowed errors considering the environmental factors such as solvent impact and crystal packing. Moreover, the values of calculated bond lengths (Re–C, Re–N and Re–Cl) and bond angles for both transition metal complexes 4a and 4b were similar, which clearly indicates that methylene (–CH2–) spacer linked to a chelate part does not affect the geometry of structures around the rhenium(I) center. In each complex equatorial Re–C distances are larger than the axial Re–C distances evidenced the back-donation from the rhenium center to π-antibonding orbital in the carbonyl trans to the chloride ion.

(3) M. Turki, C. Daniel, S. Záliš, A. Vlček, J. van Slageren, D.J. Stufkens, J. Am. Chem. Soc. 2001, 123, 11431-11440.

Table S6. Hydrogen bonds for 3a, 3b, 4a and 4b [Å and °]

|     | D   | A       | D—H [Å] | H•••A [Å] | D•••A [Å] | D—H•••A [°] |
|-----|-----|---------|---------|-----------|-----------|-------------|
| 3a  | N(10)-H(10A)...N(2)#1 | 0.90(3) | 2.11(3) | 3.009(4)  | 173(3)    |
|     | N(10)-H(10B)...N(1)  | 0.87(4) | 2.11(4) | 2.956(4)  | 167(3)    |
|     | N(5)-H(5B)...N(6)    | 0.82(4) | 2.18(4) | 2.971(4)  | 162(3)    |
|     | N(5)-H(5A)...N(7)#1  | 0.89(4) | 2.15(4) | 3.047(4)  | 178(3)    |
| 3b  | C(4)-H(4)...O(1)#1   | 0.95    | 2.49    | 3.376(2)  | 154.9     |
|     | C(7)-H(7)...O(1)#1   | 0.95    | 2.50    | 3.260(2)  | 137.5     |
|     | C(8)-H(8B)...N(2)#2  | 0.99    | 2.53    | 3.413(2)  | 149.1     |
|     | N(5)-H(5B)...N(1)#3  | 0.89(2) | 2.16(2) | 2.939(2)  | 145.7(18) |
|     | N(5)-H(5A)...O(2)#2  | 0.83(2) | 2.42(2) | 3.196(2)  | 156(2)    |
| 4a  | N(5)-H(5a)...N(3)#1  | 0.88(5) | 2.58(5) | 3.267(6)  | 135(4)    |
|     | N(5)-H(5b)...Cl(1)#2 | 0.78(5) | 2.50(6) | 3.271(5)  | 169(5)    |
| 4b  | N(5)-H(5a)...O(6)#2  | 1.00(4) | 1.90(4) | 2.889(5)  | 170(3)    |
|     | N(5)-H(5b)...Cl(1)#1 | 0.95(5) | 2.64(5) | 3.347(3)  | 132(3)    |
|     | O(6)-H(6a)...Cl(1)   | 0.84    | 2.33    | 3.134(3)  | 161.0     |

Symmetry codes (3a) : #1 x+1, y, z; (3b) : #1 -x+1, -y+1, -z+1; #2 x, -y+3/2, z+1/2; #3 -x+1, y-1/2, -z+3/2; (4a) : #1 -x+2, -y+1, -z; #2 x+1/2, y-1/2, -z+1/2; (4b) : #1 -x+1, -y, -z+1; #2 x+1, y, z.
|       | Cg(I) | Cg(J) | Distance Cg(I)–•••Cg(J) [Å] | Interplanar distance [Å] | β [°] |
|-------|-------|-------|-----------------------------|----------------------------|-------|
| **3a** | Cg(1) | Cg(5) | 3.844(1) | 3.463 | 25.7 |
|       | Cg(2) | Cg(2)#1 | 3.761(1) | 3.376 | 26.3 |
|       | Cg(3) | Cg(5)#2 | 3.775(1) | 3.435 | 24.5 |
|       | Cg(4) | Cg(4)#3 | 3.679(1) | 3.410 | 22.1 |
| **3b** | Cg(1) | Cg(2)#1 | 3.627(1) | 3.419 | 19.5 |
| **4a** | Cg(1) | Cg(1)#1 | 3.752(2) | 3.364 | 26.3 |
|       | Cg(2) | Cg(2)#1 | 3.676(2) | 3.252 | 27.8 |
|       | Cg(2) | Cg(2)#2 | 3.833(2) | 3.275 | 31.3 |
|       | Cg(3) | Cg(3)#1 | 3.606(2) | 3.270 | 24.9 |
|       | Cg(3) | Cg(3)#3 | 3.964(2) | 3.316 | 33.2 |
| **4b** | Cg(1) | Cg(1)#1 | 3.758(2) | 3.586 | 17.4 |

β is the angle between the Cg(I) → Cg(J) vector and the normal to plane I.

Symmetry codes: (3a) #1 –x, -y+1, -z+2 ; #2 x, y+1, z ; #3 -x, -y, -z+1 ; (3b) #1 x, -y+3/2, z+1/2 ; (4a) #1 2-x, y, 1/2-z ; #2 2-x, 2-y, -z ; #3 2-x, 1-y, -z ; (4b) #1 2-x, 1-y, 1-z

Table S7. π-π interactions for 3a, 3b, 4a and 4b

Cg1, Cg2, Cg3, Cg4 and Cg5 are the centroids of the N2-N4/C7/C6, N1/C1-C5, C8-C13, N6/C14-C18 and C21-C26 rings, respectively
The calculated charge values on the Re atom (-0.936 a.u. in 4a and -0.935 a.u. in 4b) are remarkably lower than the formal charge +1, proving a significant charge donation from the ligands. The 5d orbitals (d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}, and d_{z^2}) of the Re atom give population of 1.38671, 1.54572, 1.54371, 1.15433, 1.04702 and 1.57283, 1.37830, 1.53994, 1.02897, 1.15590 for the formed complexes 4a and 4b, respectively (Table S8).

As expected, the carbon atoms of the carbonyl group possess positive charges, while the oxygen atoms are negatively charged. The smallest positive charge is carbon in the trans position to the chlorine atom (0.693 for 4a and 0.692 for 4b). For each CO group of complexes 4a and 4b, one σ and two π natural bond orbitals is characterized for the carbon–oxygen bonds and one orbital for the Rhenium–carbon bonds. The hybridization of NBO analysis shows clearly that Re–C bond orbitals in all cases are polarized towards the carbon atom, and that the detected C–O bond orbitals are strongly polarized towards the oxygen extremity. Each oxygen atom of CO ligand has one lone pair (LP) orbital, and the antibonding occupancies are cited in round brackets.

The calculated atomic charges values are consistent with resonance structure Re\(^+\)–C\(^–\)≡O, exhibiting the best bonding interaction between Re atom and carbonyl ligands in 4a and 4b complexes.
Table S9. The natural populations of the 5d orbitals of the Re center in complexes 4a and 4b

| Occupancy | 4a       | 4b       |
|-----------|----------|----------|
| d_{xy}    | 1.38671  | 1.57283  |
| d_{xz}    | 1.54572  | 1.37830  |
| d_{yz}    | 1.54371  | 1.53994  |
| d_{x^2-y^2}| 1.15433  | 1.02897  |
| d_{z^2}   | 1.04702  | 1.15590  |
Table S10. Selected wavelengths (\(\lambda_{\text{exp}}\) and \(\lambda_{\text{cal}}\)), calculated excitation energies (E), oscillator strengths (f), and dominant excitation character for low-lying singlet of 4a and 4b

| Excitations | \(\lambda_{\text{exp}}[\text{nm}]\) | \(\lambda_{\text{cal}}[\text{nm}]\) | E_{\text{cal}}[\text{eV}] | f_{\text{cal}} | Character |
|-------------|------------------|------------------|------------------|------------------|------------------|
| 4a          |                  |                  |                  |                  |                 |
| H \rightarrow L | 331 | 376.27 | 3.29 | 0.0033 | d(\pi(\text{Cl})\rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) ) [MLCT/LLCT] |
| H-1 \rightarrow L | 359.55 | 3.45 | 0.0737 | d(\pi(\text{Cl})\rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) ) [MLCT/LLCT] |
| H \rightarrow L+1 | 328.87 | 3.77 | 0.0005 | d \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [MLCT] |
| H \rightarrow L+2 | 274 | 273.65 | 4.53 | 0.0746 | \pi(\text{L})/\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+3 | 271.98 | 4.56 | 0.0916 | \pi(\text{L})/\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+4 | 270.67 | 4.58 | 0.0208 | \pi(\text{L})/\pi(\text{Cl}) \rightarrow \pi^*(\text{L}) [ICL/LLCT] |
| H \rightarrow L+5 | 264.44 | 4.69 | 0.0482 | \pi(\text{L}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+6 | 262.37 | 4.72 | 0.0494 | \pi(\text{L}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+7 | 236.15 | 5.25 | 0.2246 | \pi(\text{L})\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+8 | 232.68 | 5.33 | 0.3292 | \pi(\text{L}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+9 | 229.52 | 5.40 | 0.3035 | \pi(\text{L})\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+10 | 222.36 | 5.57 | 0.0946 | \pi(\text{L})\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+11 | 221.99 | 5.58 | 0.1195 | \pi(\text{L})\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+12 | 216.85 | 5.72 | 0.1005 | \pi(\text{L})\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+13 | 215.33 | 5.76 | 0.1750 | \pi(\text{L})\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [ILCT/LLCT] |
| H \rightarrow L+14 | 204 | 213.54 | 5.81 | 0.0016 | d(\pi(\text{Cl})\rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [MLCT/LLCT] |
| H \rightarrow L+15 | 213.05 | 5.82 | 0.0164 | d(\pi(\text{Cl})\rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [MLCT/LLCT] |
| H \rightarrow L+16 | 211.31 | 5.87 | 0.0068 | d(\pi(\text{Cl})\rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [MLCT/LLCT] |
| H \rightarrow L+17 | 206.55 | 5.99 | 0.0096 | d(\pi(\text{Cl})\rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) [MLCT/LLCT] |

For 4a and 4b, the low-energy absorption bands at 333 and 331 nm have mixed metal-to-ligand [MLCT] and ligand-to-ligand [LLCT] charge transfer character. Accordingly, these electronic transitions originate mainly from the mixed orbitals of the rhenium center and chlorine to the \(\pi\)-antibonding orbitals of the chelating ligand and carbonyl group, which can be described as \{d(\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO}) \text{ or } \pi^*(\text{L})\}. The band assignments were presented like those previously reported by other researchers, for related Re(CO)_3-complexes with similar bidentate ligands.¹⁴

For complex 4a, the transitions of HOMO-3→LUMO and HOMO-3→LUMO+1, corresponding to intense band at 290 nm, can be described as \{\pi(L)/\pi(\text{Cl}) \rightarrow \pi^*(\text{L})/\pi^*(\text{CO})\} and \{\pi(L)/\pi(\text{Cl}) \rightarrow \pi^*(\text{L})\}, respectively, with ligand-ligand/intra-ligands [LLCT/ILCT] charge transfer character. Similarly, the transitions of HOMO-3/HOMO-4/HOMO-6/HOMO-7→LUMO and HOMO-3→LUMO+3, corresponding to the second intense band at 274 nm for 4b, possess similar LLCT/ILCT character. It appeared that the experimental absorption to band at 246 and 206 nm for 4a, 274 and 204 nm for 4b have been mostly attributed to ligand-to-ligand charge transfer (LLCT), which are occurring from the chelate ligand and chlorine ion to \(\pi^*(\text{L})\) or \(\pi\)-antibonding orbital of the CO ligands, metal-to-ligand (MLCT) charge transfer and intra-ligands (IL) excitations. The ligand-ligand/intra-ligands CT [LLCT/IL]
transitions have the major contribution to these bands because of larger values of their oscillator strength “f”.

(4) (a) M. Obata, A. Kitamura, A. Mori, C. Kameyama, J.A. Czaplewska, R. Tanaka, I. Kinoshita, T. Kusumoto, H. Hashimoto, M. Harada, Y. Mikata, T. Funabiki, S. Yano, *Dalton Trans.*, 2008, 3292-3300; (b) P.A. Scattergood, A. Sinopoli, P.I.P. Elliott. *Coord. Chem. Rev.*, 2017, 350, 136-154.

**Figure S1.** Labelled ORTEP diagram of ligand 3a (top) and 3b (bottom) with thermal ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity. Only one of the two independent molecules in the asymmetric unit is shown for clarity (3a).
Figure S2. A partial view of the crystal packing of 4a and 4b with hydrogen bonds and π–π contacts shown as dashed lines. The purple spheres represent the centroids of the rings involved in π–π interactions.
Figure S3. Experimental (top) and electronic transitions calculated with TDDFT/B3LYP method (down) for 4a and 4b
