

## Dinuclear Re<sup>I</sup> complex based on 1,2,4,5-tetrakis(diphenylphosphino)pyridine: synthesis and luminescence properties

Maxim Yu. Petyuk, Irina Yu. Bagryanskaya, Oleg I. Artyushin, Valery K. Brel and Alexander V. Artem'ev

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### §1. General remarks

Solvents: MeCN (HPLC grade, Cryochrom), CHCl<sub>3</sub>, CCl<sub>4</sub>, diethyl ether and toluene (chemically pure, Ekos-1) prior to use were purified by common protocols. The starting precursor Re(CO)<sub>5</sub>Br was prepared from commercial Re<sub>2</sub>(CO)<sub>10</sub> and Br<sub>2</sub> (≥99%, Sigma) by the literature procedure<sup>S1</sup>. 2,3,5,6-Tetrakis(diphenylphosphino)pyridine (L) was synthesized using published procedure<sup>S2</sup>.

FT-IR spectrum was recorded on a Bruker Vertex 80 spectrometer at ambient temperature. XRPD analysis was performed on a Shimadzu XRD-7000 diffractometer (Cu-Kα radiation, Ni – filter, 3–35° 2θ range, 0.03° 2θ step, 1s per point). <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded using a Bruker AV-500 spectrometer at 500.13 and 202.46 MHz, respectively, with solvent peaks as reference. The <sup>31</sup>P{<sup>1</sup>H} NMR shifts are expressed with respect to 85% H<sub>3</sub>PO<sub>4</sub>/D<sub>2</sub>O as an external standard. The microanalysis was performed on a MICRO cube analyzer. Thermogravimetric analysis (TGA/c-DTA/DTG) was carried out in a closed Al<sub>2</sub>O<sub>3</sub> pan under helium flow at 10 °/min heating rate using a NETZSCH TG 209 F1. Photoluminescence spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) with a cooled PC177CE-010 photon detection module equipped with an R2658 photomultiplier. The luminescence decays and delayed luminescence spectra were measured on the same instrument. The absolute values of PLQY were recorded using a Fluorolog 3 Quanta-phi device.

### §2. Synthesis and characterization data

<sup>S1</sup> S. P. Schmidt, W. C. Troglor and F. Basolo, *Inorg. Synth.*, 1990, **28**, 154

<sup>S2</sup> O. I. Artyushin, A. V. Vologzhanina and V. K. Brel, *Russ. J. Gen. Chem.*, 2021, **91**, 750.

A solution of  $[\text{Re}(\text{CO})_5]\text{Br}$  (50 mg, 0.12 mmol) and L (50 mg, 0.06 mmol) in toluene (5 mL) was stirred at 110 °C for 3 h under argon atmosphere. The precipitated beige powder was centrifuged, washed with cold toluene ( $1 \times 3$  mL) and dried in vacuum. Yield: 89 mg (95%). Anal. calcd for  $\text{C}_{59}\text{H}_{41}\text{Br}_2\text{NO}_6\text{P}_4\text{Re}_2$ : C, 46.74; H, 2.73; N, 0.92. Found: C, 46.81; H, 2.76; N 0.90.  $^1\text{H}$  NMR (500.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75–6.75 (m, 41H, Ph and  $\text{Py}^4$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CDCl}_3$ ):  $\delta$  29.44 (d,  $^3J_{\text{P-P}} = 16$  Hz, 2,6-P), 16.19 (d,  $^3J_{\text{P-P}} = 16$  Hz, 3,5-P). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3057, 2035, 1967, 1921, 1618, 1587, 1532, 1483, 1435, 1358, 1308, 1188, 1161, 1096, 1028, 999, 745, 694, 627, 575, 538, 463, 422.

### §3. Powder X-ray crystallography

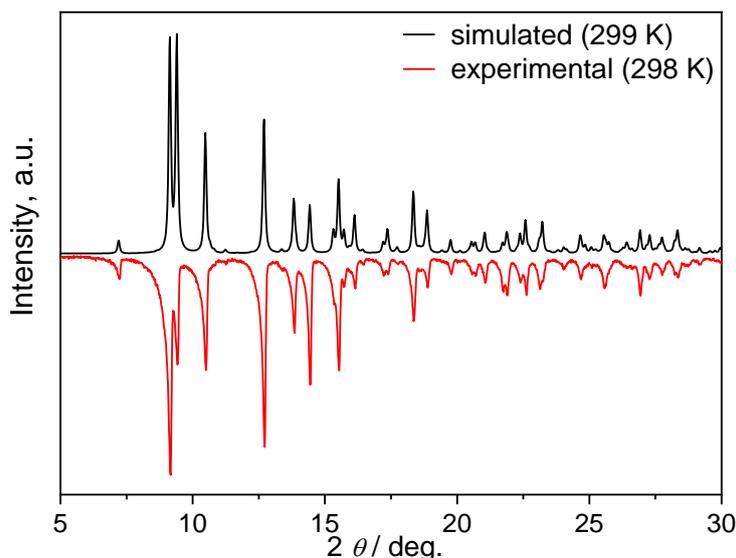


Figure S1. Experimental and simulated PXRD patterns of **1**.

### §4. Thermogravimetric analysis

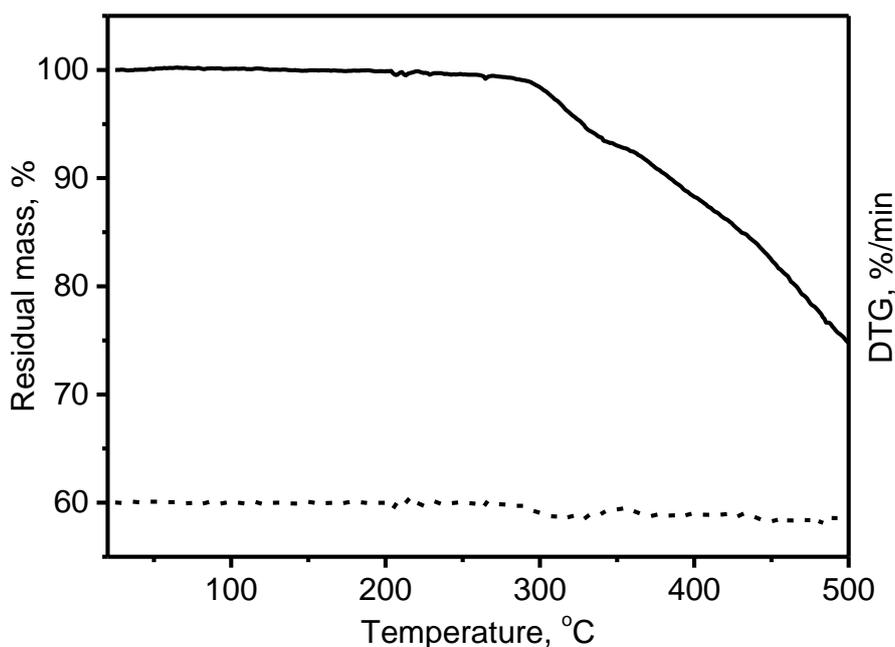
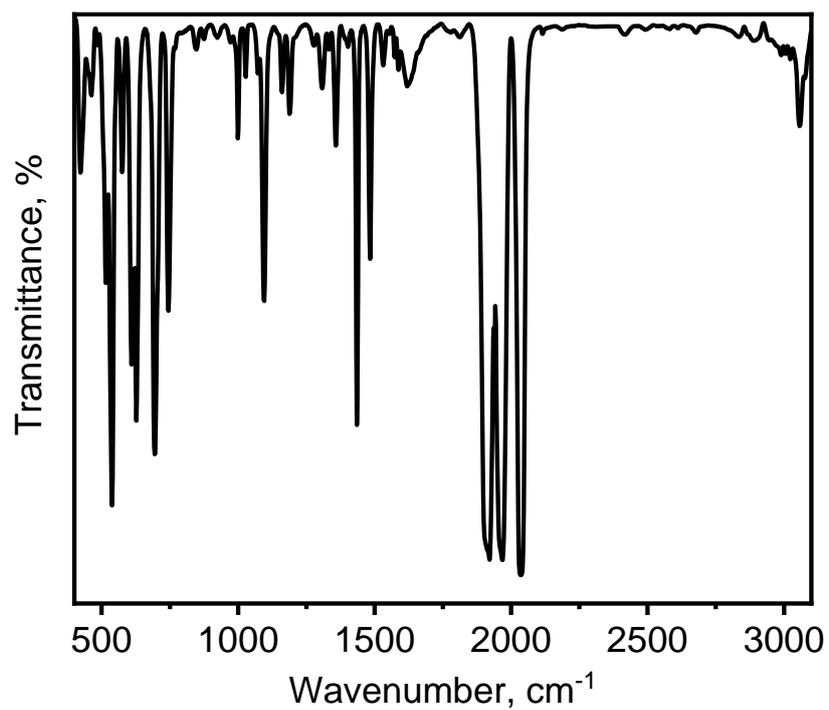
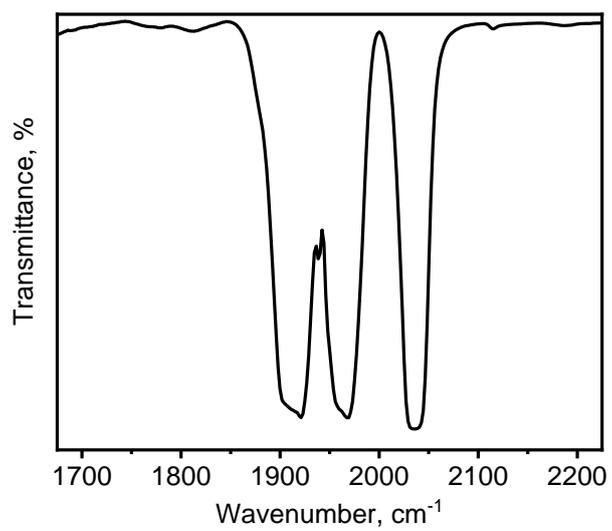


Figure S2. TGA (solid line) and DTG (dashed line) curves for **1**.

## §5. FTIR spectra



**Figure S3.** FTIR spectrum of **1** in the range of 400–3100 cm<sup>-1</sup>.



**Figure S4.** FTIR spectrum of **1** in the carbonyl region.

## §6. $^1\text{H}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra

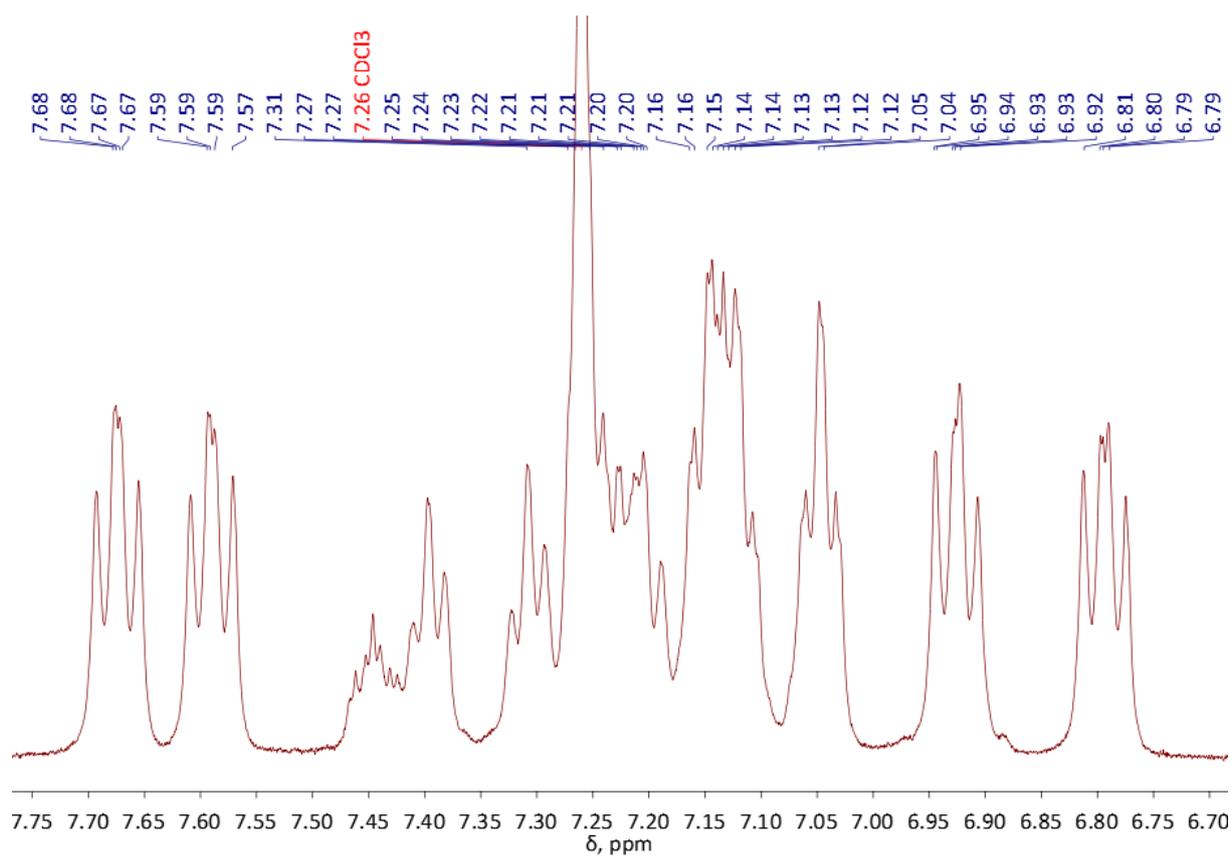


Figure S5.  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  (aromatic region).

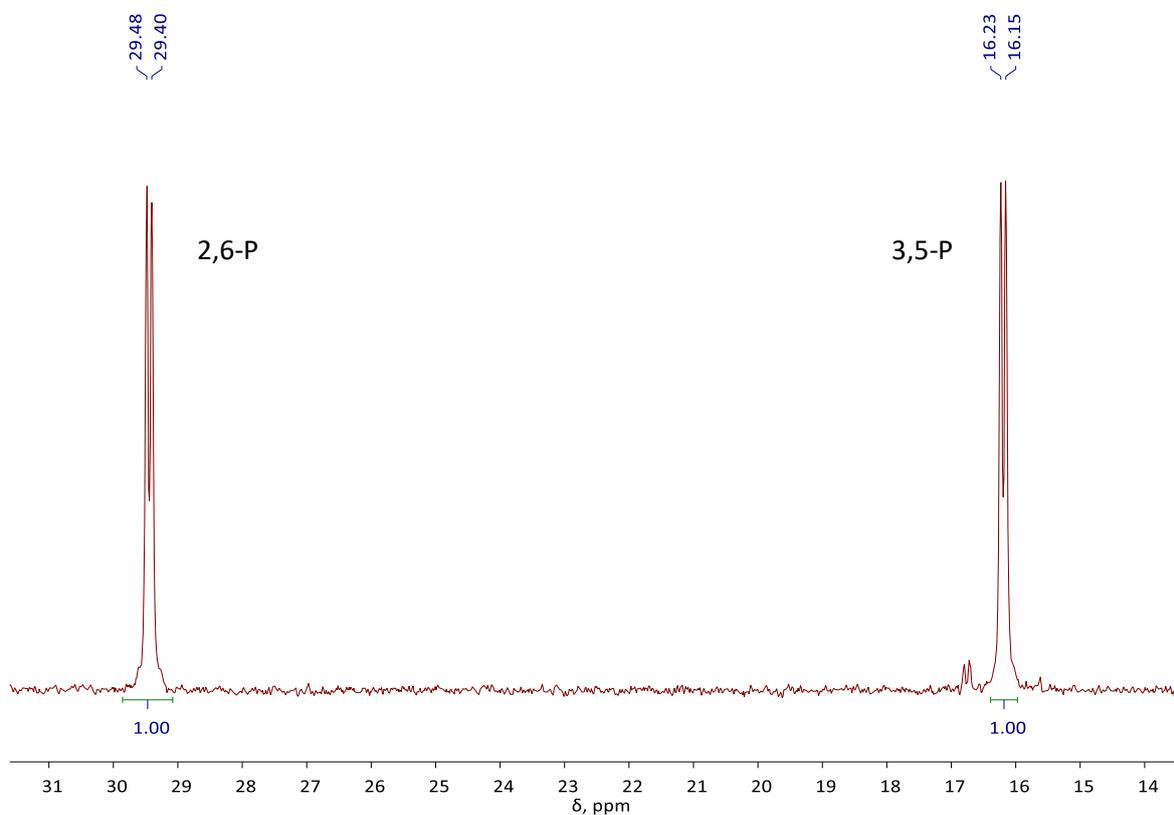


Figure S6.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CDCl}_3$ .