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Dinuclear Re^{I} complex based on 1,2,4,5-tetrakis(diphenylphosphino)-pyridine: synthesis and luminescence properties

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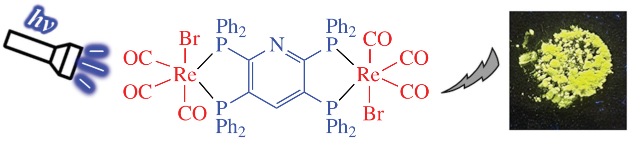
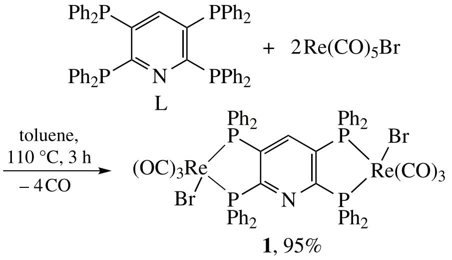
The reaction of 1,2,4,5-tetrakis(diphenylphosphino)pyridine (L) with $Re(CO)_5Br$ (in a molar ratio of 1 : 2) leads to the bis-chelated complex $[Re_2(CO)_6(L)Br_2]$ in 95% yield. At ambient temperature, the solid complex exhibits green phosphorescence (λ_{max} = 535 nm) with a quantum yield of 12% and a lifetime of 90 µs.



Keywords: rhenium(I), halocarbonyl complexes, tetraphosphine ligands, phosphorescence, synthesis.

The Re^{I} halocarbonyl complexes attract considerable attention owing to their enhanced stability coupled with remarkable photophysical properties.[1–5] At room temperature, these compounds, both in solution and in a solid state, exhibit long-lived phosphorescence from green to NIR region.[1] Therefore, these Re^{I} complexes are promising agents for bioimaging applications[6,7] and photodynamic therapy of cancer.[8–10] Moreover, the Re^{I} complexes were highlighted as potential emitters for OLED devices,[11–13] photosensitizers for solar cells,[14,15] and photocatalysts.[16] Among the Re^{I} halocarbonyl complexes are those supported by diverse diamine ligands, the LUMO energy of which largely determines the energy of phosphorescence. Meanwhile, luminescent Re^{I} halocarbonyl complexes based on phosphine ligands are rare and less studied, although they can also exhibit interesting photophysical properties.[17]

To synthesize a new Re^{I} emissive complex based on a phosphine ligand, we implemented the reaction of $Re(CO)_5Br$ with 1,2,4,5-tetrakis(diphenylphosphino)pyridine (L). Note that the coordination chemistry of this ligand is unexplored, although its benzene analog 1,2,4,5-tetrakis(diphenylphosphino)benzene (TDPB) was successfully used for the design of emissive metal complexes.[18–23] One can expect that replacing a central benzene core in TDPB with pyridine would significantly change and/or improve the photophysical properties of the metal complexes derived.



Scheme 1

We anticipated that the treatment of ligand L with 2 equiv. of $Re(CO)_5Br$ results in the replacement of two CO groups at each Re^{I} center and the formation of the bis-chelated complex $[Re_2(CO)_6(L)Br_2]$ **1** and confirmed this suggestion experimentally: the expected complex was formed in about quantitative yield upon the refluxing of reactants in toluene at 110 °C for 3 h (Scheme 1).

Figure 1 shows the X-ray derived structure of complex **1**.† Its molecule contains the ligand L whose P atoms are involved in the formation of two chelating ReP_2C_2 rings with two $Re(CO)_3Br$ units in an envelope conformation with the Re atom out of the average P_2C_2 plane. Because of this, the whole

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† The single crystals of **1** were grown by a slow diffusion of diethyl ether vapor into a chloroform solution of the product. Diffraction data were obtained on a Bruker Kappa Apex II diffractometer equipped with a CCD detector (MoKα, graphite monochromator, ϕ,ω-scans) at 299 K. The structures were solved by direct methods (SHELXL97) and refined by a full matrix least-squares anisotropic-isotropic (for H atoms) procedure using the SHELXL-2014/7 programs set.[24] Absorption corrections were applied using an empirical multiscan method with the SADABS program.[25] The positions of the hydrogen atoms were calculated with the riding model.

Crystallographic data for **1**. Crystals of $C_{59}H_{41}Br_2NO_6P_4Re_2$ (M = 1516.03) are monoclinic, space group $P2_1/c$, at 299 K: a = 26.5181(15), b = 11.2660(6) and c = 20.4061(11) Å, β = 112.279(2)°, V = 5641.3(5) Å^3, Z = 4, d_{calc} = 1.785 g cm^{-3}, μ(MoKα) = 0.71073 cm^{-1}. 104482 reflections were measured and 16565 independent reflections (R_{int} = 0.058) were used in the further refinement. The refinement converged to wR_2 = 0.0777, and GOF = 1.015 for all independent reflections [R_1 = 0.0340, was calculated against F for 12767 observed reflections with $I > 2\sigma(I)$].

CCDC 2087459 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

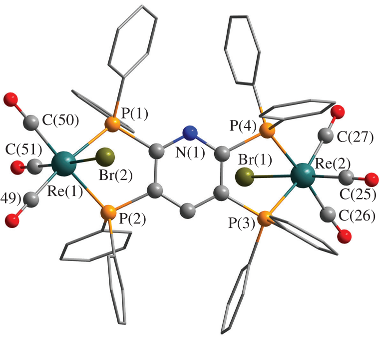

Figure 1 X-ray structure of **1** (H atoms are omitted). Averaged distances (Å) and angles (°): Re–C, 1.940; C–O, 1.126; Re–Br, 2.652; Re–P, 2.449; and P–Re–P, 80.01.

molecular scaffold looks like a chair conformation. An octahedral geometry of each Re atom is completed by the Br atom and three CO ligands. The bond lengths and angles around the metal atoms are consistent with those of other [Re(P^P)$(CO)_3$Br] complexes. In general, the molecule of **1** has a geometry similar to that of a related complex based on TDPB.[22] In the crystal, the molecules of **1** are associated together through weak C–H···O, C–H···Br, and C–H···C contacts to form a supramolecular 3D network.

Physically, compound **1** is an air-stable powder moderately soluble in CH_2Cl_2 or $CHCl_3$ and poorly soluble in MeCN. Its phase purity was confirmed by powder X-ray diffractometry[‡] and microanalysis data. Thermogravimetric analysis (TGA and DTG)[‡] revealed that complex **1** remained unchanged at least to 250 °C. In the FTIR spectrum[‡] of **1**, the stretching vibrations of CO ligands appear as strong bands at 2035, 1967, and 1921 cm^{-1}. Based on published data,[26] the higher energy band can be attributed to axial CO ligands, and the remaining bands can be ascribed to the equatorial CO ligands. The ^{1}H and ^{31}P{^{1}H} NMR spectra[‡] of **1** are in agreement with its X-ray structure.

We compared the photophysical properties of complex **1** and parent ligand L. Upon UV illumination at ambient temperature, both compounds displayed moderate yellowish green and green solid-state luminescence, respectively [Figures 2(*a*)–(*d*)]. The emission spectra of L and **1** showed very similar broad bands at 515 and 535 nm, respectively [Figure 2(*e*)]. Their excitation profiles were very similar, but the excitation edge of **1** was slightly shifted to higher wavelengths. Note that the emission energy is nearly independent of the excitation wavelength. The associated emission lifetimes of 49 and 90 μs for L and **1** at 300 K clearly suggest that the luminescence originated from the exited triplet states. The quantum yields of phosphorescence at λ_{ex} = 380 nm were 26% for L and 12% for **1**. Considering the similarity of the emission and excitation profiles of L and **1**, we can tentatively ascribe the emission of the latter to a metal-perturbed intraligand phosphorescence (^{3}IL). The lower quantum efficiency of **1** was likely associated with higher nonradiative deactivation, *e.g*., due to the vibration of CO groups.

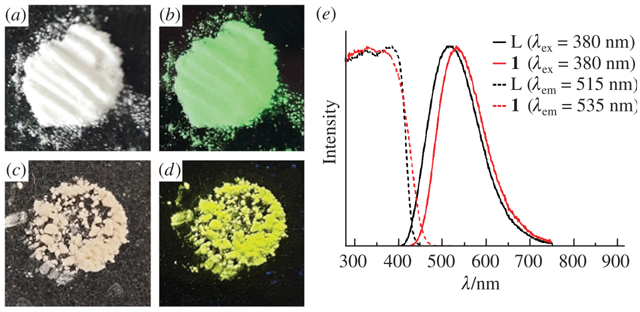

Figure 2 The samples of (*a*, *b*) L and (*c*, *d*) **1** under illumination with (*a*, *c*) daylight and (*b*, *d*) a 365-nm UV lamp. (*e*) The emission and excitation spectra of ligand L and complex **1** at 300 K.

Comparison of the emission properties of **1** with those of the complex $[Re_2(CO)_6(TDPB)Br_2]$[22] revealed that a change of the central ligand core from benzene to pyridine had a negligible effect on the emission energy ($\lambda_{max} \approx$ 530 nm *vs.* 535 nm of **1**), but it resulted in strong enhancement of the quantum yield (from 1 to 12%) and lifetime (from 16 to 90 μs) at 300 K. Therefore, the pyridine-based ligand L has some advantages over TDPB in terms of higher quantum performance for related metal complexes.

In conclusion, the bis-chelated complex $[Re_2(CO)_6(L)Br_2]$, which was synthesized by a reaction of $Re(CO)_5Br$ with 1,2,4,5-tetrakis(diphenylphosphino)pyridine (L), a new promising multidentate ligand. The structure and photophysical properties of the complex were characterized. In a solid state at 300 K, this compound emits moderate yellowish green phosphorescence, likely, due to the intraligand-type excited states (^{3}IL).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.013.

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[‡] See details in Online Supplementary Materials.

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