Electrophosphorescent homo- and heteroleptic copper(I) complexes prepared from various bis-phosphine ligands†

Omar Moudam,[a] Adrien Kaeser,[a] Béatrice Delavaux-Nicot,[a] Carine Duhayon,[a] Michel Holler,[b] Gianluca Accorsi,[c] Nicola Armaroli,*[c] Isabelle Séguy,[d] Jose Navarro,[d] Pierre Destruel*[d] and Jean-François Nierengarten*[a]

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Homo- and heteroleptic copper(I) complexes obtained from various chelating bis-phosphine ligands and $Cu(CH_3CN)_4BF_4$ have been used for the preparation of light emitting devices.

The increasing market demand for low-cost flat-panel displays and efficient lighting sources is a strong driving force for intensive research on organic light-emitting diodes (OLEDs).[1] Fluorescent semi-conducting polymers have been widely used for such applications.[1] However, the internal quantum efficiency of the resulting devices is limited to 25% by the non-emissive triplet excitons produced in OLEDs based on singlet emitters.[1] To overcome this problem, devices employing triplet emitters have been developed in the past few years.[2] Such OLEDs using phosphorescent heavy metal complexes can, in principle, reach a quantitative internal quantum efficiency as both singlet and triplet excitons participate in the emission owing to intersystem crossing of the singlet excited states to the triplet states. To date, most of the electrophosphorescent materials used for OLED applications are complexes of noble metal ions such as Ir^{III}, Pt^{II}, Ru^{II} and Os^{II}.[2] Recent reports have however shown that inexpensive and non-toxic Cu^I coordination compounds are also promising candidates for light emitting devices.[3–6] As part of this research, we became interested in electrophosphorescent heteroleptic Cu^I complexes containing 1,10-phenanthroline (phen) and bis-phosphine (P–P) ligands.[6,7] By changing systematically the nature of the chelating P-ligand, we found that some of them produce stable homoleptic Cu^I complexes rather than the expected Cu^I(Phen)(P–P) derivative. In this paper, we now report on a series of homo- and heteroleptic $Cu^I(P–P)_2$ compounds prepared on the basis of this initial finding. Whereas examples of homoleptic $Cu^I(P–P)_2$ derivatives have been already described,[8] analogous heteroleptic Cu^I complexes combining two different P–P ligands have never been reported to the best of our knowledge. Finally, we also show that some of these compounds are promising materials for OLED applications.

Cu^I(Phen)(P–P) derivatives are usually prepared by reaction of 1,10-phenanthroline with a 1 : 1 mixture of the bis-phosphine ligand and a Cu^I salt such as $Cu(CH_3CN)_4BF_4$. When this standard procedure was applied to 1,2-bis(diphenylphosphino)-benzene (dppb) and bis(diphenylphosphino)methane (dppm), the formation of the expected Cu^I(Phen)(P–P) derivatives was not observed. Actually, the homoleptic complexes $Cu^I(dppb)_2$ (**1**) and $Cu^I(dppm)_2$ (**2**) were thus produced as their tetrafluoroborate salts. The structural assignment of **1** and **2** thus obtained was deduced from their $^{31}P\{H\}$ NMR spectra displaying sharp singlets at δ 8.1 and −7.3 ppm, respectively. The structures of both **1** and **2** were further confirmed by mass spectrometry. The expected molecular ion peaks were observed at *m*/*z* 955.7 for **1** ($[M - BF_4^-]^+$, calcd for $C_{60}H_{48}P_4Cu$: 955.20) and 831.2 for **2** ($[M - BF_4^-]^+$, calcd for $C_{50}H_{44}P_4Cu$: 831.17). Finally, it can be added that compounds **1** and **2** were obtained in good yields by reaction of dppb and dppm (2 equiv.), respectively, with $Cu(CH_3CN)_4BF_4$ (1 equiv.) in CH_2Cl_2. For complex **1**, crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **1**.‡ As shown in Fig. 1, the Cu^I center adopts a highly distorted tetrahedral geometry as a result of the small bite angle of the dppb ligand (84.7°). It can be noted that the Cu atom

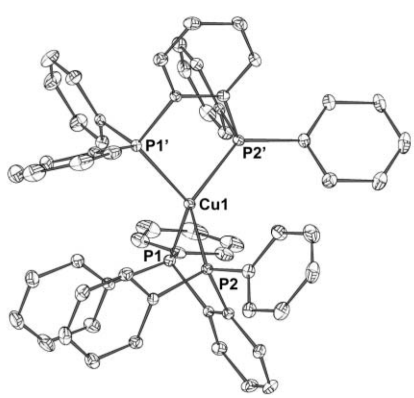

Fig. 1 ORTEP plot of the structure of the cation in **1**. Thermal ellipsoids are drawn at the 30% probability level. The prime (′) characters in the atom labels indicate that these atoms are at equivalent position (3/2 − *x*, *y*, 3/2 − *z*). Selected bond lengths and bond angles: Cu(1)–P(1): 2.3092(8) Å; Cu(1)–P(2): 2.2907(9) Å; P(1)–Cu(1)–P(2): 84.72(3)°; P(1)–Cu(1)–P(1′): 122.59(5)°; P(1)–Cu(1)–P(2′): 120.94(3)°; P(2)–Cu(1)–P(2′): 127.85(5)°.

[a]*Laboratoire de Chimie de Coordination du CNRS (UPR 8241), 205 route de Narbonne, 31077, Toulouse Cedex 4, France. E-mail: jfnierengarten@lcc-toulouse.fr; Fax: +33 (0) 5 61 55 30 03; Tel: +33 (0) 5 61 33 31 51*
[b]*Laboratoire de Physico-Chimie Bioinorganique, ULP-CNRS (UMR 7177), Institut de Chimie, ECPM, 25 rue Becquerel, 67087, Strasbourg Cedex 2, France*
[c]*Istituto per la Sintesi Organica e la Fotoreattività, Molecular Photoscience Group, Consiglio Nazionale delle Ricerche, Via Gobetti 101, 40129, Bologna, Italy. E-mail: armaroli@isof.cnr.it; Fax: +39 051 639 98 44; Tel: +39 051 639 98 20*
[d]*Laboratoire Plasma et Conversion d'Energie (LAPLACE), UPS-CNRS (UMR 5213), 118 route de Narbonne, 31062, Toulouse Cedex 9, France. E-mail: Pierre.destruel@laplace.ups-tlse.fr; Fax: +33 (0) 5 61 55 64 52; Tel: +33 (0) 5 61 55 62 61*

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lies on a two fold axis. The Cu–P distances are in the range expected from other known structures.[8]

The attempted preparation of the Cu^I(Phen)(P–P) derivatives from dppm and dppb revealed a peculiar behavior for these two ligands. Effectively, the reaction of 1,10-phenanthroline (1 equiv.) with a 1 : 1 mixture of other bis-phosphine ligands (bis[2-(diphenylphosphino) phenyl] ether: POP; 1,2-bis(diphenylphosphino)ethane: dppe; 1,3-bis(diphenylphosphino) propane: dppp) and $Cu(CH_3CN)_4BF_4$ in CH_2Cl_2 gave the expected Cu^I(Phen)(P–P) complexes. This difference maybe be explained by the differences in bite angles for the different chelating P-ligands. When this angle is small enough (dppm and dppb), the metal center can easily accommodate two ligands. In contrast, steric factors resulting from the wider P–Cu–P angle for the other bis-phosphines substantially destabilize the $Cu(P–P)_2$ derivative, thus preventing its formation under our experimental conditions.

In principle, by replacing the phen ligand with dppm or dppb in the reaction sequence used to prepare the Cu^I(Phen)(P–P) derivatives, heteroleptic $Cu^I(P–P)_2$ complexes should be obtained. This hypothesis was first tested by adding dppm (1 equiv.) to a 1 : 1 mixture of POP and $Cu(CH_3CN)_4BF_4$ in CH_2Cl_2. Complex [Cu(POP)(dppm)]BF_4 (**3**) was effectively thus obtained in a good yield (80%). The $^{31}P\{H\}$ NMR spectrum of **3** revealed two signals at δ −4.4 and −8.9 ppm in good agreement with the proposed structure. It is worth noting that no detectable changes were observed in the $^{31}P\{H\}$ NMR spectrum of a CD_3CN solution of **3** after one week, thus showing that there is no ligand exchange in solution. X-Ray quality crystals of **3** were obtained by vapor diffusion of Et_2O into a CH_2Cl_2 solution of the complex.§ The asymmetric unit of the crystal structure contains two complexes of **3** in two different conformations along with one unit-occupancy and one 0.5-occupancy CH_2Cl_2 molecules. As shown in Fig. 2, the structure of **3** reveals a highly distorted tetrahedral coordination environment about Cu^I with P–Cu–P bond angles ranging from 73.28(12) to 125.43(13)°. It can be noted that the POP ligand is bound to the metal only through its pair of P donor atoms, the ether O atom being at a nonbonding distance from the Cu(I) center (>3.1 Å).

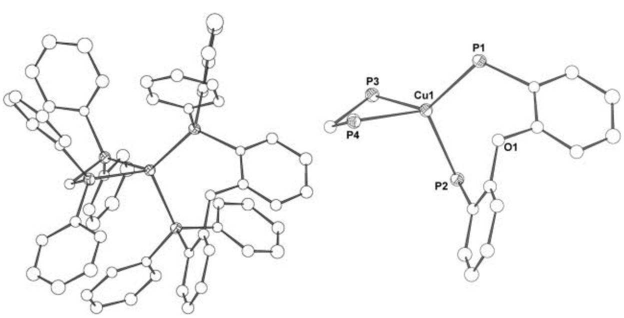
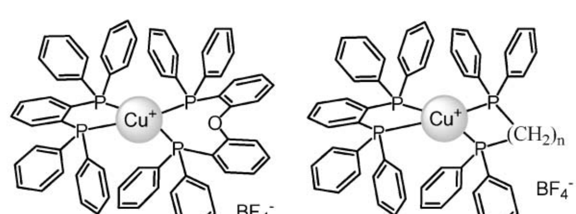


Fig. 2 Left: plot of the structure of the cation in **3** (only one conformer is shown). Right: details of the coordination sphere around the Cu^I cation. Thermal ellipsoids are drawn at the 30% probability level, only the Cu and P atoms were refined anisotropically. Selected bond lengths and bond angles: Cu(1)–P(1): 2.279(4); Cu(1)–P(2): 2.304(3); Cu(1)–P(3): 2.333(3); Cu(1)–P(4): 2.425(4); P(1)–Cu(1)–P(2): 110.51(13)°; P(1)–Cu(1)–P(3): 124.44(13)°; P(1)–Cu(1)–P(4): 125.43(13)°; P(2)–Cu(1)–P(3): 109.77(13)°; P(2)–Cu(1)–P(4): 108.26(13)°; P(3)–Cu(1)–P(4): 73.28(12)°.

Similarly, addition of dppb (1 equiv.) to 1 : 1 mixtures of various bis-phosphine ligands (POP, dppe, dppp) and $Cu(CH_3CN)_4BF_4$ in CH_2Cl_2 gave the heteroleptic complexes **4–6** in good yields (Fig. 3). Their structure was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis.

The dppm containing derivatives **2** and **3** are oxygen sensitive. Indeed, when these compounds were stored without particular precaution, oxidation of the dppm ligand was observed. In contrast, all the dppb-based complexes are stable under normal laboratory conditions. For this reason, only compounds **1** and **4–6** were further investigated. The electrochemical properties of these complexes were determined by cyclic voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV). All the experiments were performed at room temperature in CH_2Cl_2 solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, with a Pt wire as the working electrode and a saturated calomel electrode (SCE) as a reference. Potential data for all of the compounds are collected in Table 1. In the cathodic region, a ligand-centered reduction is observed at *ca.* −2.2 V *vs.* SCE for all the compounds. In the anodic region, all the Cu^I complexes show a first quasi-reversible one-electron process followed by an irreversible oxidation. The first wave is assigned to the oxidation of the Cu^I cation while the second one corresponds to a ligand centered process. The quite high potentials observed for the oxidation of the metal center indicate a good stabilization of these Cu^I complexes. The positive shift seen for the first oxidation of **4** when compared to **1**, **5** and **6** is ascribed, at least in part, to the electron withdrawing effect of the diphenyl ether subunits of the POP ligand. However, it is also believed that complex **4** is less flexible owing to a more entangled structure resulting from the large bite angle of the rigid POP ligand. As a result, distortion towards a square planar coordination geometry upon oxidation of the Cu^I center becomes more difficult in this particular case and the corresponding Cu^{II} complex is thus more destabilized.

The photoluminescence (PL) properties of CH_2Cl_2 solutions of **1**, **4**, **5** and **6** are summarized in Table 2. The emission is tentatively assigned to metal-to-ligand charge transfer (MLCT) excited states[5] and appears to be substantially influenced by conformational changes from a pseudo-tetrahedral coordination geometry to a flattened structure in the excited state that may facilitate the formation of non-emissive penta-coordinated exciplexes as typically observed for Cu^I complexes.[9] Hence, the lifetime of compound **4**, for which this distortion is expected to be more difficult, is the longest and its emission quantum yield the highest. These observations are in agreement with the differences observed in the first oxidation potential of **4** when compared to **1**, **5** and **6** (*vide supra*). Whereas the emission quantum yields in solutions are



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5 (n = 2)
6 (n = 3)

Fig. 3 Heteroleptic Cu^I complexes **4–6**.

Table 1 Electrochemical data of **1**, **4**, **5**, and **6** determined by OSWV on a Pt working electrode in CH_2Cl_2 + 0.1 M $^nBu_4NBF_4$ at room temperature[a]

	E_{ox1}/V	E_{ox2}/V	E_{red1}/V
1	+1.19	+1.66	−2.20
4	+1.50	+1.64	−2.23
5	+1.19	+1.63	−2.18
6	+1.17	+1.30	−2.22

[a] OSWVs were obtained using a sweep width of 20 mV, a frequency of 10 Hz, and a step potential of 5 mV.

Table 2 Luminescence data in CH_2Cl_2 (air free solutions) at 298 K

	λ_{max}/nm[a]	Φ_{em} (%)[b]	τ/ns[c]
1	556	1×10^{-2}	244
4	494	2	2440
5	546	2×10^{-2}	231
6	544	8×10^{-2}	2.5–5.8

[a] Emission maxima from uncorrected spectra, λ_{exc} = 330 nm. [b] Emission quantum yields in air free solutions. [c] Excited state lifetimes.

quite low, compounds **1** and **4** exhibit a bright luminescence in the solid state at room temperature as well as in rigid frozen CH_2Cl_2 solutions at 77 K. Indeed, under these conditions, geometric distortions prompting non-radiative deactivation of the MLCT excited states[10] are prevented. This is further confirmed by the 50 nm blue shift of the emission maxima when going from room temperature to 77 K for both **1** and **4**. A similar trend is observed for **5** and **6**, however the effect is less dramatic. Indeed, the less rigid dppe and dppp ligands may facilitate some excited-state distortion.

Based on the PL data, complexes **1** and **4** were selected for light emitting device fabrication. Poly(vinyl carbazole) (PVK) was chosen as the host material because of its good hole-transport ability, broad band-gap and overlap of the emission spectra with the absorption spectra of **1** and **4**. The light emitting devices were fabricated by spin coating a thin film of a **1**–PVK or a **4**–PVK blend (*ca.* 120 nm) on an ITO substrate. The concentration of **1** and **4** in the PVK matrix was 12.5% in weight. After the film had been dried under vacuum at room temperature for 2 h, the cathode was fabricated by thermal evaporation of an Al layer (100 nm). The electroluminescence (EL) spectra of **1** and **4** in PVK films are displayed in Fig. 4 and S4 respectively.†

In both cases, the EL spectra are red shifted and significantly broader when compared to the PL spectra recorded in CH_2Cl_2 solutions (see ESI†). As a result, almost white light is produced by both devices. The current–voltage–brightness (*I–V–B*) characteristics (Fig. 4 and S4†) of the devices prepared from **1** and **4** indicate both turn-on voltages of 15 V and brightnesses up to 490 (for **1**) and 330 cd m^{-2} (for **4**) at 20 V. The device efficiencies have not been yet optimized, but they should be improved by using appropriate hole blocking and electron transfer layers in the device configuration. Work in this direction is currently under way in our laboratories.

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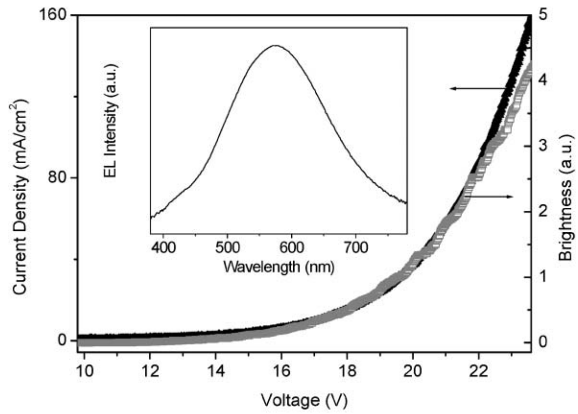

Fig. 4 *I–V–B* characteristics of the device obtained from **1**. Inset: EL spectra of **1** at a concentration of 12.5 wt% in a PVK matrix.

Notes and references

‡ $C_{60}H_{48}P_4CuBF_4$ (M_r = 1043.29), monoclinic space group *P* 2/*n*, Z = 2, *a* = 13.5721(9), *b* = 12.5841(8), *c* = 14.9692(12) Å, α = 90, β = 100.516(6), γ = 90°, *V* = 2513.7(3) Å^3, 308 parameters, 11 658 reflections measured, 5719 unique (R_{int} = 0.04), 3534 reflections used in the calculations [$I > 2.5\sigma$], *R* = 0.0509, w*R* = 0.0579. CCDC 645319. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707398d

§ $C_{61.75}H_{51.50}B_1Cl_{1.50}Cu_1F_4O_1P_4$ (M_r = 1137.01), triclinic space group $P\bar{1}$, *Z* = 4, *a* = 14.6080(14), *b* = 19.213(2), *c* = 21.0316(17) Å, α = 80.126(11), β = 80.686(11), γ = 89.676(12)°, *V* = 5737.2(10) Å^3, 651 parameters, 57 446 reflections measured, 20986 unique (R_{int} = 0.09), 6820 reflections used in the calculations [$I > 2\sigma$], *R* = 0.0714, w*R* = 0.0789. CCDC 645318. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707398d

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