ORGANOMETALLICS

Coordination Complexes of P-Containing Polycyclic Aromatic Hydrocarbons: Optical Properties and Solid-State Supramolecular Assembly

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Supporting Information

ABSTRACT: A series of complexes including σ^3, λ^3 -Pmodified polycyclic aromatic hydrocarbon (PAH) as a ligand have been prepared showing that the ligand possesses a classical "phosphine-like" reactivity. The use of different metals (Pd(II), Cu(I), Re(I), Au(I)) having different coordination number allows tuning the optical properties of the complexes, which is dominated basically by the electronic transitions of the ligand itself. The study of the solid-state properties by mean of X-ray diffraction also shows that the combination of coordination chemistry and π -stacking interactions between the PAH ligand allows obtaining a great diversity of solid-state structures.



INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) attract considerable attention due to their unique electronic properties, making them appealing for applications in molecular electronics such as organic solar cells and field-effect transistors.¹⁻³ Their unique properties stemming from the extended π -conjugation within planar or curved backbones are affected by the geometries (sizes, symmetries, boundaries, and cores) and the electronics. Furthermore, the π -stacking ability of these compounds allows an efficient charge transport between the molecules.⁴ An original approach to tune the properties of the PAHs or to organize them in the solid state is to use them as ligands toward metal complexes and benefit both electronic and structural properties of the transition metals and the large organic π system. In this regard, the first examples used the concepts of π coordination of arene ligands toward transition metals.⁵ For example, the η^6 -coordination of $[\eta^5-C_5Me_5)Fe(II)]$ (A, Figure 1), Cr(CO)₃, Ru(p-cymene), or Rh(I)(ⁱBu₃P)₂ to PAHs of various size up to the hexa-peri-hexabenzocoronene was developed.6 This method allowed introducing new redox properties directly linked to the nature of the metal. This strategy has also been successfully extended to graphene layers and curved PAHs such as corannulene.⁷ The η^2 -coordination of Ag(I) was also found to be an interesting approach to tune the properties of the PAHs.⁸ The crystallographic structure of the triple-decker complex B (Figure 1) revealed both inter- and intramolecular π -stacking interactions between the PAH

ligands.^{8a} This study nicely showed how the presence of the metal ion allows the modification of the solid-state structure of PAHs. All these strategies use the π -surface of the PAH to coordinate to the metal fragment. Another approach consists of grafting the metal fragment to the PAH through a σ -bond. This approach was used to link PAHs to Pt-acetylide (C, Figure 1), ferrocenyl, Ir-carbenes, Au-aryl fragments, or bipyridine rhenium tricarbonyl.9 This strategy allowed obtaining new redox and photophysical properties linked to the presence of the metal such as phosphorescence. These strategies are based on the organometallic chemistry of PAHs. Recently, new synthetic methods allowed preparing heteroatom-containing $PAHs^{10}$ such as N, ¹¹ B, ¹² S, ¹³ O, ¹⁴ or P. ¹⁵ In the case of N- or P-containing PAHs, the heteroatom has a crucial importance because it allows the use of its coordination ability to prepare new coordination complexes. In this field, the first step was made by Draper et al., who prepared Ru(II) (D, Figure 1) and Pd(II) complexes using their unprecedented N-containing heterosuperbenzene as a ligand.¹⁶ The authors showed that the presence of the metal allows new optical transitions (MLCT based) as well as new redox properties compared to the parent

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Figure 1. Examples of organometallic (A, B, C) and coordination complexes (D, E) using PAHs as ligands (counterions have been omitted for clarity).

PAH.^{16b,17} Finally, a last method to prepare metal-containing PAHs relies on the extension of the C-sp² backbone around a metalloporphyrin¹⁸ or a metallophthalocyanine unit.¹⁹ For example, compound E (Figure 1) displays intense visible and near-IR absorption and a very low HOMO–LUMO gap. However, the exceptional electronic properties of the compound come more from the presence of the porphyrinic cycle than the presence of the metal.

We recently synthesized a P-containing PAH (L1 and L2, Scheme 1) that showed a tunable HOMO-LUMO gap using P-modification.¹⁵ For example, the corresponding (thio)oxidized derivative SL1 (Scheme 1) appeared to be an efficient emitter in the active layer of a white-emitting OLED.²⁰ In the present article, we extend our strategy based on the use of Pcontaining ligands as two-electron donors toward transition metals.²¹ We show that the insertion of different metals (Pd(II), Cu(I), Re(I), Au(I)) having different coordination numbers allows tuning the optical properties of the complexes, as has been evidenced by combined experimental and theoretical approaches. The study of the solid-state properties by means of X-ray diffraction also shows that the metal has a huge impact on the supramolecular organization. These results show how the insertion of a P atom into the PAH backbone allows tuning both optical and supramolecular assembly using the coordination ability of the P-ligand.

RESULTS AND DISCUSSION

Synthesis and Characterization. P-containing PAHs L1 and L2 (Scheme 1) were synthesized according to our previously reported synthetic method.^{15,20} An appealing

chemical property of these σ^3 , λ^3 -P-derivatives is their reactivity toward metal ions. Reaction of L1 with one equivalent of AuCl afforded complex AuL1 (³¹P NMR = +26.5 ppm) in good yield (Scheme 1).¹⁵ The reaction of AuL1 with one equivalent of AgOTf, then with another equivalent of σ^3 , λ^3 -P-ligand L1, led to the formation of the complex $Au(L1)_2$ (³¹P NMR = +40.8 ppm), composed of two PAHs assembled around a Au(I) metal center (Scheme 1). The two gold complexes AuL1 and $Au(L1)_2$ were characterized by MS and X-ray diffraction. The coordination chemistry of this novel family of ligands is not limited to Au(I) chemistry. Indeed, we chose to investigate the coordination chemistry of these ligands toward Pd(II), Cu(I), and Re(I) ions since these metal ions exhibit different coordination geometries (square planar, tetrahedral, and octahedral geometries, respectively) and can accommodate different numbers of PAH ligands in the coordination sphere. The reaction of L1 and L2 with Cu(I), Pd(II), or Re(I) precursors led to the formation of cationic complex $Cu(L1)_2$ $(^{31}P \text{ NMR} = -2.9 \text{ ppm})$ and neutral complexes $Pd(L2)_2$ $(^{31}P$ NMR = +28.6 ppm) and **ReL1** (³¹P NMR = +3.4 ppm) (Scheme 1). The formation of the cationic complex $Cu(L1)_2$ and the neutral complex $Pd(L2)_2$ results in the substitution of two acetonitrile ligands of $[Cu(CH_3CN)_4]PF_6$ and [PdCl₂(CH₃CN)₂] precursors by two ligands L, respectively. For the complex $Pd(L2)_2$, the ³¹P NMR spectrum revealed the presence of only one isomer. By comparison with the related bis-phosphole palladium complexes,²² the chemical shift at +28.6 ppm can be attributed to a *cis*-configured complex.²³ In the case of $Cu(L1)_2$, two acetonitrile ligands remain coordinated on the Cu(I) ion, at least in the solid state. The





Table 1. Selected Bond Distances (Å) and Angles (deg) for AuL_1 , ReL_1 , $Au(L_1)_2$, and $Cu(L_1)_2$ and the Reference Compound SL1 with Estimated Standard Deviations in Parentheses

Сехо									
	AuL ₁	ReL ₁	$Au(L1)_2^{b}$	$Cu(L1)_2$	SL1 ^b				
P-C ₂	1.810(9)	1.829(5)	1.805(3)	$1.821(3)/1.828(3)^a$	1.808(4)				
$P-C_5$	1.823(9)	1.832(6)	1.825(3)	1.830(3)/1.816(3)	1.815(4)				
$C_2 - C_3$	1.376(12)	1.365(8)	1.367(4)	1.370(4)/1.355(5)	1.366(6)				
$C_3 - C_4$	1.452(11)	1.447(8))	1.450(4)	1.445(5)/1.447(4)	1.452(6)				
$C_4 - C_5$	1.379(12)	1.359(7)	1.361(4)	1.365(5)/1.359(5)	1.351(6)				
P-C _{exo}	1.829(10)	1.808(6)	1.815(3)	1.838(3)/ 1.828(3)	1.817(5)				
P-M	2.222(2)	2.4999(16)	2.3037(11)	2.2524(11)/ 2.2569(11)					
$C_2 - PC_5$	92.5(4)	91.1(3)	92.62(13)	91.22(15)/90.91(15)	92.2(2)				
C2-P-Cexo	105.1(4)	105.6(2)	107.9(4)	105.50(15)/108.57(14)	103.6(2)				
C5-P-Cexo	103.4(4)	108.5(3)	108.6(3)	107.07(14)/105.47(15)	110.8(2)				

steric hindrance at the metal center probably forbids the additional substitution of another acetonitrile ligand by the bulky PAH L1. The complex **ReL1** was prepared by reacting the ligand L1 with ReCl(CO)₅ in toluene at 80 °C under argon.²⁴ After purification, all these complexes were isolated with moderate yields (55–60%) and were characterized by NMR, MS, and X-ray diffraction.

The aromatic systems and the phosphole ring possess a tremendous variety of complexing modes (σ - and/or η - complexes),^{5-16,25} but here we have shown that σ^3 , λ^3 -P-

containing PAHs L1 and L2 display the classical "phosphinelike" reactivity not only toward (thio)-oxidation and alkylation but also toward different metal centers, allowing the straightforward formation of unprecedented structures.

X-ray Crystal Structure. The chemical structures of complexes ReL1, AuL1, Au(L1)₂, and Cu(L1)₂ were confirmed by X-ray diffraction studies performed on single crystals obtained by slow vapor diffusion of pentane into dichloromethane solutions. The crystal data and the experimental details are given in the Supporting Information.



Figure 2. X-ray crystallographic structure of AuL1 with the view of the discrete dimers observed in the packing,



Figure 3. X-ray crystallographic structure of ReL1 with the view of the discrete dimers observed in the packing.



Figure 4. View of the infinite columns observed in the packing for complexes AuL1, ReL1, Au(L1)₂, and Cu(L1)₂.

Selected bonding parameters and angles of these complexes are summarized in Table 1.

The complexes ReL1 and AuL1, having one ligand L1 in their coordination sphere, present similar metric data for the ligand L1, which remain basically unchanged compared to those observed in the solid-state structure of the purely organic compound.¹⁵ Effectively, the coordinated P-center, lying in the sp²-C plane, has a pyramidal shape with usual valence angles, and the C-P and C-C bond lengths are similar to those reported for P-based PAHs (see Table 1).²⁰ Furthermore, the

PAH fragment (including the P-center) is almost planar. The difference lies in the solid-state organization of these complexes since they do not crystallize in the same space group.

The Au(I) complex AuL1 crystallizes in the C2/c space group of the monoclinic system (Tables 1 and S1). The asymmetric unit contains the neutral complex AuL1 (Figure 2) and is completed by one CH₂Cl₂ solvent molecule that does not show short contact interactions with the complex AuL1. In this derivative, the P-center of the ligand L acts as expected, as a two-electron donor toward the Au(I) metal center (d(P-Au),



Figure 5. X-ray crystallographic structure of Au(L1)₂ with the view of the discrete dimers observed in the packing.



Figure 6. X-ray crystallographic structure of $Cu(L1)_2$ with the view of the discrete dimers observed in the packing.

2.222(2) Å), and the P–Au–Cl fragment is almost linear (P–Au–Cl, 173.07(12)°). The coordinated P-center has a distorted tetrahedral geometry (angles are ca. 92.5° for the endocyclic C–P–C angle), and the PAH fragment (including the P-center) is almost planar (maximum deviation for the mean plane, ca. 0.15 Å).

Derivative **ReL1** crystallizes in the $P\overline{1}$ space group of the triclinic system (Tables 1 and S1). The asymmetric unit contains a neutral complex **ReL1** (Figure 3) and included 1.5 CH₂Cl₂ solvent molecules to complete the asymmetric unit and do not show any short contact interaction with the complex **ReL1**. The coordination sphere of the Re(I) metal center is distorted octahedral with the coordinated chloride and phosphorus atoms in *cis*-positions. The P–Re bond length is classical for a σ^3 -P-center acting as a two-electron donor on a Re(I) ion (d(P-Re), 2.4999(16) Å), and the polyaromatic fragment (including the P-center) presents a slight deviation to the planarity (maximum deviation for the mean plane including the P-center, ca. 0.37 Å) and a dihedral angle of ca. 7.1° between the mean planes of the two lateral phenanthryl subunits.

The crystal packing of complexes **AuL1** and **ReL1** shows that the complexes form infinite columns (Figure 4) due to $\pi - \pi$ intermolecular interactions, evidenced by a close packing (short contact distances ca. 3.4–3.5 Å) between the two planar polyaromatic fragments. Within these columns, head-to-tail dimers are observed with a large overlay of the two interacting polyaromatic fragments (Figures 2 and 3). It can be noticed that these $\pi - \pi$ interactions are less efficient in the case of the **ReL1** complex due to the presence of a large Re(CO)₄Cl fragment hindering an efficient stacking between PAH ligands. Nevertheless, **ReL1** complex dimers, in turn, stack on each other via weaker π – π contacts, affording, once again, an infinite π -stacked columnar structure (Figure 4). Note that no Au–Au interactions are observed in the case of **AuL1**.

The complexes $\operatorname{Au}(L1)_2$, $\operatorname{Pd}(L2)_2^{23}$ and $\operatorname{Cu}(L1)_2$, having two PAH ligands in the coordination sphere, crystallize in the same space group \overline{PI} . Nevertheless, the different coordination sphere and coordination number of the metal ions allow different organization of the two ligands around the metal center and different solid-state organization.

As previously reported, derivative $Au(L1)_2$ crystallizes in the $P\overline{1}$ space group of the triclinic system (Tables 1 and S1). The asymmetric unit contains complex $Au(L1)_2$ resulting from the coordination of two ligands L1 on a Au(I) metal center (Figure 5). One $CF_3SO_3^-$ triflate counterion and three CH_2Cl_2 solvent molecules that do not show short contact interactions with the complex $Au(L1)_2$ complete the asymmetric unit. The Au(I)metal ion is located on the inversion center related with the $P\overline{1}$ space group, and therefore its coordination geometry is strictly linear in this solid-state structure. The two ligands L1 are symmetrically equivalent and form with the Au(I) metal center a stair-like structure, avoiding intramolecular $\pi - \pi$ interactions. The P–Au distance (d(P-Au), 2.3037(11) Å) is slightly longer in the derivative $Au(L1)_2$ compared to the derivative AuL1, which could be anticipated as a consequence of the formal replacement of the negatively charged Cl⁻ ligand by a second equivalent of neutral ligand L1. As observed for the complex AuL1, metric parameters centered on the ligands L1 are mostly comparable with those of the P-ligand (maximum deviation for

Table 2. Experimental and Calculated UV-Vis Absorption Data^a

	compound								
	L1	L2	AuL1	ReL1	$Au(L1)_2$	$Cu(L1)_2$	$Pd(L2)_2$		
λ_{\max} (nm)	472	472	509	494	516	502	510 578sh		
fwhm (cm ⁻¹)	3790	3800	3780	3533	5135	5390			
$\lambda_{ m vert}$ (nm)	479		512	482	529	534	527 578, 573		
$\lambda_{\rm vert}$ (PCM) (nm)	486		521	486	523	507	537 611, 555		

 ${}^{a}\lambda_{max}$ and λ_{vert} (in nm) refer to the measured maximum and the B3LYP/def2-TZVP-calculated first vertical excitation energy, respectively. λ_{vert} (PCM) are B3LYP/def2-TZVP data with dichloromethane solvent using the PCM solvent model.



Figure 7. Absorption spectra of compounds L1 (red), AuL1 (blue), ReL1 (light blue), Au(L1)₂ (orange), Cu(L1)₂ (green), and Pd(L2)₂ (violet) in CH₂Cl₂ (10^{-5} M). The TD-DFT-computed vertical excitation energies are presented above the experimental spectra. The size of the peaks representing the excitation energies is proportional to the calculated oscillator strength.

the mean plane including the P-center, ca. 0.08 Å). The coordinated P-centers bear a distorted tetrahedral geometry (angles are ca. 92.6° for the endocyclic C–P–C). Finally, in the crystal packing, infinite columns of molecules are observed due to intermolecular $\pi - \pi$ interactions (intermolecular contacts, ca. 3.5 Å) involving the peripheral unsaturated rings of the PAH core of the ligands L1 (Figures 4 and 5). Note that as no intramolecular $\pi - \pi$ interactions occur between the two ligands L1 within the molecular structure of Au(L1)₂ (Figure 5), likewise no infinite network of pure $\pi - \pi$ interactions is formed along such columnar stacked arrays. Again, no Au–Au interactions are observed similarly to the case of AuL1. This supramolecular structure represents, however, a nice example of the combination of coordination chemistry and $\pi - \pi$ interactions to afford organized structures.

Derivative $Cu(L1)_2$ crystallizes in the $P\overline{1}$ space group of the triclinic system (Table 1). The asymmetric unit contains the monocationic complex $Cu(L1)_2$ (Figure 6), a BF₄⁻ counterion, and four CH₂Cl₂ solvent molecules, which do not show short contact interactions with the complex $Cu(L1)_2$. The Cu(I) metal center has a distorted tetrahedral geometry (angles range between 95.97(11)° for the N-Cu-N angle and 113.87(4)°

for the P-Cu-P angle). The P-Cu bond lengths are classical for a phosphine σ^3 -P-center acting as two-electron donor on a Cu(I) metal center (*d*(P–Cu), 2.2524(11) and 2.2569(11) Å). Metric parameters observed for the two equivalents of the ligand L1 coordinated on the Cu(I) ion are mostly similar to those of the free ligand. This indicates that, as observed for the coordination on the Au(I) center, coordination of the P-center on Cu(I) does not induce a noticeable modification of the structure of the ligand L1. The coordinated P-centers in this complex have a distorted tetrahedral geometry. The π -surface of one of the PAH L1 is almost planar (maximum deviation for the mean plane including the P-center, ca. 0.09 Å), but the second ligand bears a larger deviation of planarity (maximum deviation for the mean plane including the P-center, ca. 0.65 Å) with a dihedral angle of ca. 5.4° between the mean planes of the two lateral phenanthryl subunits of the PAH core. The orientation of the two ligands L1 coordinated on the distorted tetrahedral metal center (angle of 47°) results in the location of the π -surfaces of these ligands in close proximity (Figure 6). Short contact interactions (ca. 3.2-3.3 Å) revealing intramolecular $\pi - \pi$ interactions are observed along large portions of the π -surfaces, while the mean planes of the polyaromatic cores

of each PAH L1 are almost parallel (interplanar angle, ca. 5.3°). As a consequence, the exocylic P-Ph moieties of each of the ligands are oriented outward from the central Cu(I) metal center. As observed in the case of the complex Pd(L2)₂, the coordination of two PAH L1/2 on a metal center allows organizing two PAHs involved in intramolecular $\pi - \pi$ interactions. In the crystal packing, complexes Cu(L1)₂ stack on each other with strong intermolecular $\pi - \pi$ interaction involving large portions of the π -surfaces. As a result, infinite columnar π -stacked networks are formed (Figure 4).

These examples show how coordination chemistry allows tuning supramolecular interactions between PAHs in the solid state. These interactions can be intramolecular, in the coordination sphere of the metal (compounds $Cu(L1)_2$ and $Pd(L2)_2$). Nevertheless, intermolecular interactions can also take place due to the π -stacking ability of the PAH ligand (compounds AuL1, ReL2, Au(L1)₂, and Cu(L1)₂). This property is very appealing considering the potential of this family of compounds for optoelectronic applications. Hence, using the same PAH -based ligand, a great diversity of solidstate structures can be obtained only by modification of the metallic ion. This unique property validates the strategy of inserting a coordinating atom such as P into a PAH.

Electronic Absorption Spectra and Computations. To evaluate the effect of the metal on the electronic properties of the compounds, the optical properties of complexes AuL1, ReL1, Au(L1)₂, Cu(L1)₂, and Pd(L2)₂ were investigated by UV-vis absorption in diluted CH₂Cl₂ solution. As previously reported, the UV-vis absorption spectrum of L1 displays a $\pi - \pi^*$ transition with classical PAH vibrational fine structures in the visible range (λ_{max} = 472 nm, see Table 2, Figure 7).¹⁵ For the AuL1 and ReL1 complexes, this absorption band with similar shape is red-shifted ($\Delta \lambda = 20-40$ nm) due to the Lewis acid character of the metal ions. This trend is similar to the effect of oxidation (or thio-oxidation) of the P-center that was previously observed for both P-containing PAHs and phosphole oligomers.^{15,26} This effect stabilizes the LUMO to a larger extent than the HOMO for the gold derivative (Figure 8), the latter having a nodal plane right at the phosphorus atom bound to the metal center.¹⁵ In the case of the ReL1 complex, the HOMO-LUMO difference remains virtually unaltered (note that the HOMO contains some Re d orbital participation as shown in Figure 8). Nevertheless, the frontier MOs of each



Figure 8. B3LYP/def2-tZVP//X-ray frontier MOs for **ReL1** and **AuL1** (L: B3LYP/def2-tZVP//B3LYP/6-31+G*).

complexes are located basically at the ligand, and the orbitals of the metal atoms have mainly some perturbing effect. Our TD-DFT calculations revealed that the lowest energy transitions of **AuL1** and **ReL1** are indeed basically the HOMO–LUMO excitations (see Supporting Information). Furthermore, these transitions are energetically well separated from the rest of the excitations. The B3LYP/def2-TZVP-calculated vertical excitation energies match favorably with the observed band maxima positions, showing a smaller bathochromic shift for the Re than for the Au complex (Figures 7 and 8).²⁷

Likewise, the orbitals of the ML₂-type complexes behave similarly: HOMO, HOMO-1 and LUMO, LUMO+1 (Figure S8 in the Supporting Information) are composed from the HOMOs and LUMOs of the two ligands, giving rise altogether to a pair of occupied and a pair of unoccupied orbitals. The absorption of the ML₂-type complexes is shifted somewhat in the bathochromic direction in comparison with ML-type complexes (Figure 7). The PAH vibronic fine structure can also be recognized; however, this feature is more diffuse and the bands are also getting broader, especially in the case of the Pd derivative, where even a new shoulder emerges at the lowenergy side. The TD-DFT calculations predict four close-lying transitions, which involve the admixture of the excitations from the HOMO-1 and HOMO to the LUMO and LUMO+1 orbitals (shown in Figure S8 of the Supporting Information). The numerical agreement between the calculated and the experimental results is the best in the case of $Pd(L2)_2$. Since the X-ray structure of $Pd(L2)_2$ was of poor quality, we have optimized the structure of Pd(L1)₂ at the M06-2X/LANL2DZ and ω B97X-D/LANL2DZ levels since these functionals account for dispersion effects, which is of high importance for π -stacked systems. The optimized structure was basically identical to that obtained by X-ray crystallography.²⁸ Thus, we have decided to use for the TD-DFT calculations the geometry obtained by X-ray crystallography, but using the smaller L1 ligand instead of the experimentally investigated L2. Since L1 and L2 have the same absorption band maxima (see Table 2), this simplification has only a minor effect. As an apparent consequence of the rather strong intramolecular π -stacking between the ligands of $Pd(L2)_{2}$, the four excitations are split in this case significantly, and accordingly the TD-DFT calculations predict two low-energy and medium-intensity transitions at 578 and 573 nm, in accordance with the shoulder at 578 nm on the low-energy side of the broad band with a maximum at 510 nm, which in turn is in reasonable agreement with the most intense transition for $Pd(L2)_2$ predicted at 527 nm. Complexes $Au(L1)_2$ and $Cu(L1)_2$ neither exhibit the low-energy spectral feature nor have a low-energy predicted transition energy. In these complexes, the two ligands are rotated away from each other, allowing weaker interactions between the two ligands. In order to test if the π -stacking is responsible for the low-energy feature in the spectrum, we have carried out TD-DFT calculations on $Cu(L1)_2$ with the two L1 ligands optimized at "cis" and "trans" position (neglecting the two acetonitriles), two extreme positions allowing strong or very weak interactions between the two ligands, respectively (the optimized geometries are presented in the Supporting Information). With the ligands in trans position the B3LYP/def2-tZVP//B3LYP/6-31G* calculations predict the four transition energies at 541, 530, 510, and 509 nm; in the case of the "cis" structure the vertical excitation energies are at 596, 578, 501, and 500 nm, showing that the splitting of the excitation energies is related to the π -stacked "*cis*" arrangement of the two ligands. This finding

gives further support to the X-ray structural arrangement of $Pd(L2)_2$. Since the two ligands L1 in the $Cu(L1)_2$ complex have a parallel displaced arrangement due to the distorted tetrahedral geometry of the copper center (angle of 47°), the interactions between the two ligands are not maximized, leading to absorption properties (Table 2) close to those calculated for the *trans* $Cu(L1)_2$ complex. Altogether, these tunable optical properties depending on the nature of the metal show the pertinence of introducing a P atom in a PAH backbone in order to take advantage of its coordination ability to modify its electronic properties.

CONCLUSION

In conclusion, we demonstrated that σ^3 , λ^3 -P-modified PAHs possess the classical "phosphine-like" reactivity toward different metal centers, allowing the preparation of five new complexes having specific absorption properties. The combination of coordination chemistry and π -stacking interactions allows obtaining a great diversity of solid-state structures, as evidenced by the X-ray diffraction studies. In some cases, infinite π -stacked columns were observed. Furthermore, new solid-state organization of phosphole-based PAHs can be envisaged since the phosphole ring possesses a tremendous variety of complexing modes (σ - and η -coordination modes).²⁵ This property is unusual for PAH compounds and is directly linked to the presence of the heteroatom in the 2D π -conjugated system. Considering the potential of P-containing PAHs for optoelectronic applications, this molecular engineering based on coordination chemistry might lead to new promising applications in this field.²

EXPERIMENTAL SECTION/CALCULATIONS

Chemicals and Instrumentations. All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly purified using MBraun SPS-800 drying columns. ¹H, ¹³ C, and ³¹P NMR spectra were recorded on a Bruker AM300 or AM400. ¹H and ¹³C NMR chemical shifts were reported in parts per million (ppm) relative to Me₄Si as external standard. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Compounds L1/2, AuL1, and Au(L1)₂ were synthesized according to a published procedure. ^{15,20} UV–visible spectra were recorded at room temperature on a Varian Cary 5000 spectrophotometer.

Synthesis. *Cu(L1)*₂. L1 (23 mg, 0.04 mmol, 1 equiv) was dissolved in 20 mL of dichloromethane. Cu(CH₃CN)₂BF₄ (0.04 mmol, 0.5 equiv) was then added. The solution was stirred at RT for 15 min; then the solvent was evaporated and the crude product was washed with pentane to afford Cu(L1)₂ as a red solid (50%). ¹H NMR (400 MHz, CD₂Cl₂): δ 2.33 (s, 6H, CH₃CN), 3.61 (s, 12H, OCH₃); 4.03 (s, 12H, OCH₃); 6.32 (d, 4H, ⁴J = 2 Hz, H_{aryl}); 6.58 (m, 4H, H_{aryl}); 7.14 (m, 4H, H_{meta}); 7.27 (m, 2H, H_{para}); 7.43 (m, 4H, H_{ortho}); 7.57 (dd, 4H, ³J(H,H) = 8 Hz, ³J(H,H) = 8 Hz, H_{aryl}), 8.00 (d, 4H, ³J(H,H) = 8 Hz, H_{aryl}); 9.03 (d, 4H, ³J(H,H) = 8 Hz, H_{aryl}). ³¹P NMR (160 MHz, CD₂Cl₂): δ -3.1 (brs). Due to solubility issues, no ¹³C spectrum could be recorded. HRMS (ESI): [M – 2CH₃CN]⁺ calcd for C₇₆H₅₄O₈P₂Cu 1219.2584, found 1219.2523.

Pd(*L2*)₂. L2 (29 mg, 0.04 mmol, 1 equiv) was dissolved in 20 mL of dichloromethane. PdCl₂(CH₃CN)₂ (0.04 mmol, 0.5 equiv) was then added. The solution was stirred at RT for 15 min; then the solvent was evaporated and the crude product was washed with pentane to afford **Pd**(*L2*)₂ as a red solid (75%). ¹H NMR (300 MHz, CDCl₃): δ 0.95 (t, 12H, ³*J*(H,H) = 6 Hz, -CH₃); 0.95 (t, 6H, ³*J*(H,H) = 6 Hz, -CH₃); 1.03 (t, 6H, ³*J*(H,H) = 6 Hz, -CH₃) 1.23-1.52 (m, 40H, -CH₂-); 1.74 (m, 16H, -CH₂-); 2.08 (m, 8H, -CH₂-); 3.92-4.31 (m, 16H,

O−CH₂−); 6.39 (d, 4H, ⁴J(H,H) = 2 Hz, H_{aryl}); 6.89 (m, 4H, H_{meta}); 7.07 (dt, 2H, ³J(H,H) = 8 Hz, H_{para}); 7.42 (dd, 4H, ³J(H,H) = 8 Hz, H_{aryl}); 7.48−7.62 (m, 8H, H_{ortho}+ H_{aryl}); 7.77 (d, 4H, ³J(H,H) = 8 Hz, H_{aryl}); 9.07 (d, 4H, ³J(H,H) = 8 Hz, H_{aryl}). ³¹P NMR (162 MHz, CDCl₃): δ +28.6 (s). Due to solubility issues, no ¹³C spectrum could be recorded. HRMS (ESI): $[M - Cl]^+$ calcd for C₁₁₆H₁₃₄O₈P₂PdCl 1857.8272, found 1857.8211.

ReL₁. L₁ (30 mg, 0.04 mmol, 1 equiv) was refluxed in 10 mL of toluene with Re(CO)₅Cl (1 equiv) for 1 h. The crude solution was evaporated, and the solid was washed with pentane to afford **10** as a red solid (60%). ¹H NMR (400 MHz, CDCl₃): δ 3.80 (s, 6H, OCH₃); 4.11 (s, 6H, OCH₃); 6.74 (m, 2H, H_{aryl}); 7.00 (m, 2H, H_{aryl}); 7.15–7.50 (m, 3H, H_{meta+para}); 7.81 (dd, 2H, ³J(H,H) = 8 Hz, ³J(H,H) = 8 Hz, H_{aryl}); 8.02 (m, 2H, H_{ortho}); 8.41 (d, 2H, ³J(H,H) = 8 Hz, H_{aryl}); 9.51 (d, 2H, ³J(H,H) = 8 Hz, H_{aryl}); ³¹P NMR (162 MHz, CDCl₃): δ + 3.4 (s). Due to solubility issues, no ¹³C spectrum could be recorded. HRMS (ESI): [M]⁺ calcd for C₄₂H₂₇O₈PCIRe 912.0684, found 912.0680.

Crystal Structure Determination. X-ray crystallographic data for Au(L1)₂ (CCDC 861179) were previously reported.¹⁵ Single crystals of ReL1, AuL1, and Cu(L1), suitable for X-ray crystal analyses were obtained by slow vapor diffusion of pentane into dichloromethane solutions. Single-crystal data collections were performed at 150 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo K α radiation (λ = 0.710 73 Å). Reflections were indexed and Lorentz-polarization corrected and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.³ Structure determinations were performed by direct methods with the solving program SIR97,³¹ which revealed all the non-hydrogen atoms. The SHELXL program³² was used to refine the structures by fullmatrix least-squares based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters

Single crystals of all these derivatives were always coated in Paratone oil once removed from the mother solution and mounted at low temperature on the diffractometer goniometer, and X-ray data collection was performed at low temperature. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.³³ 1487424, 1487422, 1487421, 1487423, and 861179 contain the supplementary crystallographic data for derivatives **ReL1**, AuL1, Cu(L1)₂, and Au(L1)₂, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Density Functional Calculations. B3LYP/def2-TZVP³⁴ and CAM-B3LYP/def2-TZVP³⁵ TD-DFT calculations of the complexes were carried out at the experimentally obtained geometries (in the case of the Pd complex using ligand L1 instead of L2), with the Gaussian 09 suite of programs.³⁶ Geometry optimizations were carried out at the M06-2X/LANL2DZ³⁷ and at the ω B97X-D/LANL2DZ³⁸ levels for the Pd(L1)₂ complex and at the B3LYP/6-31G* level for the Cu(L1)₂' complex. In the latter case the complex with the *cis* and *trans*-arranged L1 ligands was optimized. For the visualization of the Kohn–Sham MOs the VMD program³⁹ was used.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00715.

Additional information (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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