

Assembly of π -Conjugated Phosphole Azahelicene Derivatives into Chiral Coordination Complexes: An Experimental and Theoretical Study

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Abstract: Aza[*n*]helicene phosphole derivatives have been prepared from aza[*n*]helicene diynes by the Fagan–Nugent route. Their photophysical properties (UV/Vis absorption and emission behavior) have been evaluated. Their behavior as P,N chelates towards coordination to Pd^{II} and Cu^I has been investigated: metal-bis-(aza[*n*]helicene phosphole) assemblies are formed by a highly stereoselective coordination process, as demonstrated by X-ray crystallography. An aza[6]helicene phosphole bearing an enantio-

pure helicene part has been obtained, which allows the preparation of enantiopure Pd^{II} and Cu^I complexes with original topologies and high molar rotation (MR) and circular dichroism (CD). The structure–property relationship established from the experimental data has been studied in detail by theo-

retical studies (TDDFT calculations of UV/Vis, CD, and MR). Aza[*n*]helicene phosphole derivatives show π conjugation extended over the entire molecule, and its influence on the MR of aza[6]helicene phosphole **5c** has been demonstrated. Finally, it has been shown that the nature of the metal (coordination geometry and electronic interaction) can have a great impact on the amplitude of the chiroptical properties in metal-bis(aza[*n*]helicene phosphole) assemblies.

Keywords: chiroptical properties • density functional calculations • helical structures • palladium • P,N ligands

Introduction

Helicenes are fascinating molecules endowed with helical chirality and π -conjugated backbones.^[1] In recent years, the chemistry of these compounds has grown from the stage of an academic curiosity to an important field of research owing to their extraordinary optical and electronic properties provided by their unique helicoidal π structures. The

most appealing attribute of helicene derivatives is their huge chiroptical properties (optical rotation, circular dichroism)^[2] that make them promising building blocks for the synthesis of functional molecular materials (e.g., nonlinear optical materials,^[3a,h] chiral wave guides,^[3b] and so on). They also display interesting phosphorescent properties due to large spin–orbit coupling,^[4] a rather uncommon behavior for organic molecules. [*n*]Helicenes have also been used as organic catalysts for enantioselective transformations,^[3c,g] chiral derivatizing agents,^[3d] and building blocks for the design of chiral ligands for homogeneous transition metal catalysis.^[3e,f] The potential use of helicene derivatives in devices depends greatly on the facility of generating different frameworks to modulate and optimize their electronic and optical properties.^[5] Despite remarkable progress in helicene chemistry in the last decade, the development of short and efficient strategies to diversify helicene structures still remains a challenge to synthetic chemists.^[1,6]

An appealing alternative to stepwise organic chemistry for the construction of complex architectures is coordination chemistry.^[7] Indeed, metals are powerful templates for assembling π -conjugated ligands into well-defined molecular structures such as octupolar complexes,^[8] metallocyclophanes,^[9] and molecular knots,^[10] to name but a few. Consid-

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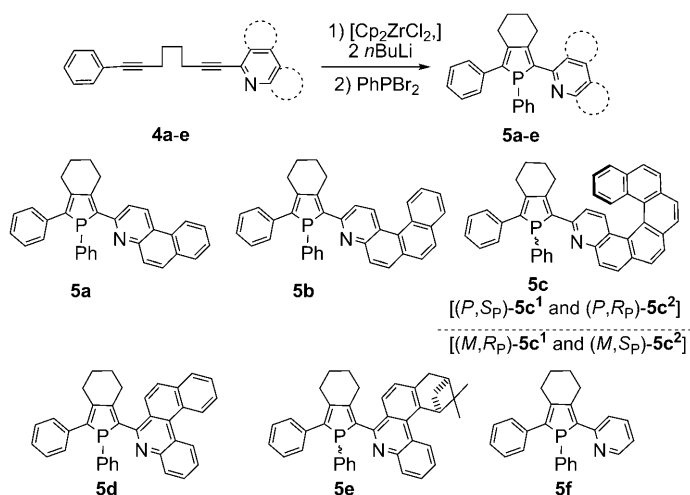
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ering a given target architecture, this approach simply involves careful design of the π -conjugated ligands guided by the basic concepts of coordination chemistry (*trans* effect, hemilability, etc.). Furthermore, coordination chemistry offers a simple way to tune the optical and electronic properties of the π ligands, since both the coordination-sphere geometry and the nature of the metal–ligand interaction can be readily modified by varying the metal center. Surprisingly, this general approach has rarely been used for the tailoring of helicoidal π -conjugated systems, and little is known about the coordination and organometallic chemistry of helicene derivatives.^[1a,3e,6b,11,12] We have therefore investigated the synthesis of helicene derivatives that could form stable metal bis(helicene) complexes. Compared to organic synthesis, this approach offers two main advantages. First, starting from one helicene-based ligand prepared according to a stepwise synthesis, it would be possible to readily generate structural variety simply by changing the metal template (e.g., variation of coordination geometry, electronic property, and charge number). Second, one can expect that the nature of the metal will impact the chiroptical properties of the helicene-based ligand. Note that this effect will be maximized if the donor atoms are included in the π -conjugated systems.

In spite of its apparent simplicity, the above approach poses a severe problem, that is, if a ligand bearing an enantiomerically pure helicene is used, the final metal–bis(helicene) assembly must be obtained as a single enantiomer. In other words, the coordination process leading to the target complexes must be highly stereoselective.^[13] To meet this requirement, a classical method in coordination chemistry is to tailor the electronic and steric properties of the ligand donor sites. Amongst the numerous types of ligands that have been developed, it is well established that heteroditopic donors such as P,N chelates are well suited to stereoselective coordination.^[14a] For example, the *trans* effect is particularly effective in square-planar d^8 metal centers and enables high *cis/trans* stereoselectivity.^[14b,c] Furthermore, heteroditopic ligands exhibit hemilabile behavior, a dynamic property which is very important for obtaining the thermodynamically more stable metal–bis(helicene) assembly. Therefore, we envisaged appending aza[n]helicenes with a phosphole ring to obtain rigid 1,4-P,N chelating ligands **5a–e** (Scheme 1). The phosphole moiety was selected because of its unique electronic properties.^[15] This heterole exhibits weak aromatic character, due to the pyramidal geometry of the P atom, which prevents the dienic moiety from efficiently interacting with the heteroatom lone pair. According to theoretical calculations, planar phosphole is not stable, although it has aromatic stabilization comparable to that of pyrrole (ca. 20–21 kcal mol^{−1}).^[16] In fact this aromatic stabilization is not sufficient to overcome the planarization barrier at the tricoordinate P atom (ca. 35 kcal mol^{−1}), but is responsible for the unusually low P-inversion barrier in phosphole (ca. 16 kcal mol^{−1}). The weakly aromatic character of the phosphole ring allows the dienic moiety of this heterole to be highly conjugated with aromatic substituents at the 2-



Scheme 1. Synthesis of mixed phosphole-azahelicene π -conjugated compounds **5a–e**, and known 2-(2-pyridyl)phosphole **5f**.

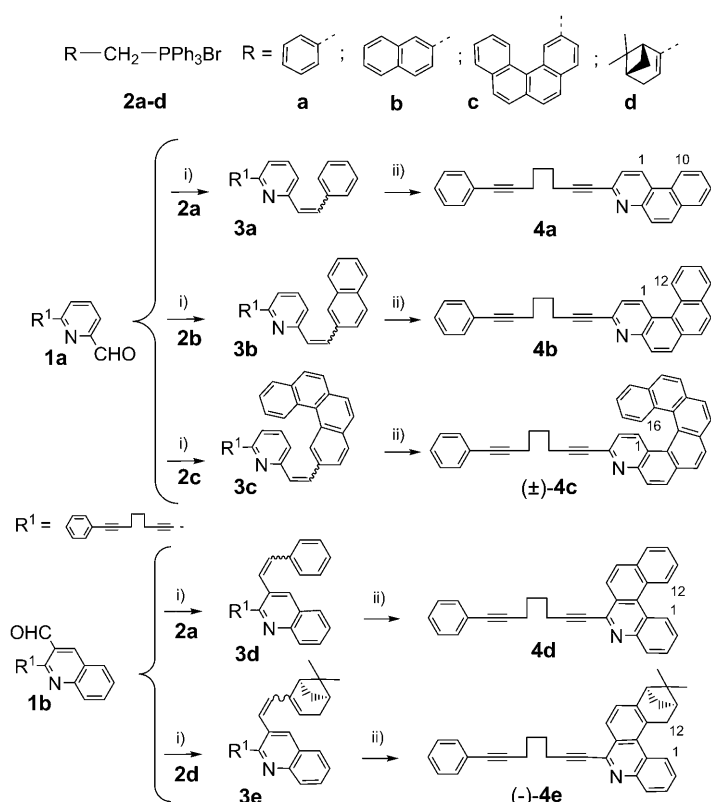
and 5-positions. The P atom is electronically coupled with this conjugated framework, as shown by the fact that chemical modifications, including coordination to metal centers, of the P center results in fine-tuning of the optical and electronic property of the π system.^[17]

Here we describe the synthesis, structural characterization, and elucidation of electronic (UV/Vis, fluorescence and phosphorescence spectroscopy) and chiroptical [molar rotation (MR), circular dichroism (CD)] properties by both experimental and theoretical methods of these novel mixed phosphole-aza[n]helicene π -conjugated systems (Scheme 1) and of the corresponding Cu^I and Pd^{II} bis(phosphole aza[n]helicene) complexes. The high stereoselectivity of the coordination process leading to the metal–bis(phosphole aza[n]helicene) assemblies is discussed on the basis of experimental and theoretical results. The study of this series of complexes bearing helicoidal ditopic ligands reveals that metallic ions can impact the optical rotations and CD of metal–bis(phosphole-aza[n]helicene) assemblies, which offers an unprecedented way to tune the chiroptical properties of [n]helicene derivatives.

Results

Synthesis and characterization of phosphole aza[n]helicene derivatives: Target σ^3 -phospholes **5a–e** bearing an aza[n]helicene substituent were prepared according to the Fagan–Nugent route^[18] from diynes **4a–e** (Scheme 1). Compounds **5a,b** and **5d–f** can be regarded as model molecules, since their azahelicene moiety is not configurationally stable in solution.

The diyne starting materials have two different structures with the pyridine moiety in the terminal (**4a–c**; Scheme 2) or at an inner position of the helix (**4d,e**; Scheme 2). They were obtained by classical synthetic routes. Sonogashira coupling of 1-phenyl-1,7-octadiyne^[17] with commercially avail-



Scheme 2. Synthesis of helicene-containing diynes **4a–e**. i) *n*BuLi, THF, Ar, RT, 3 h. ii) *hν*, cat I₂, toluene, RT, 15 h.

able 6-bromopyridine-2-carboxaldehyde and 2-chloro-3-quinoline carboxaldehyde afforded diynes **1a** (63 % yield) and **1b** (61 % yield; Scheme 2), respectively. These compounds were engaged in Wittig reactions with the appropriate phosphonium bromides **2a–d**, prepared according to literature procedures, to give olefins **3a–e** as *cis/trans* isomer mixtures (Scheme 2).

Sequential photocyclization and in situ oxidation^[1a] of stilbenoid derivatives **3a–e** was performed in toluene in the presence of catalytic amounts of iodine. Helicene-containing diynes **4a–e** (Scheme 2) were isolated in moderate yields (Table 1). Note that similar yields were obtained by using propylene oxide with stoichiometric quantities of iodine.^[19] All of the novel compounds gave satisfactory elemental analyses. They were fully characterized by high-resolution mass spectrometry, and the consistence of their NMR data with those of other diyne and azahelicene derivatives sup-

port the proposed structure. The most important spectroscopic information for compounds **4a–e** are 1) the presence of four singlets in the ¹³C{¹H} NMR spectra between $\delta = 79.0$ and 95.5 ppm, showing the presence of two unsymmetrical triple bonds, and 2) that protons, especially H¹ (see Scheme 2 for numbering), experience an anisotropic cone effect, a feature proving the formation of helices. For example, as observed for other azahelicene derivatives,^[6] H^{1,12}, which are at the inner positions of the benzo[*f*]quinoline and naphtho[1,2-*f*]quinoline moieties of aza[4]helicenes **4b** and **4d** (Scheme 2) display strongly deshielded ¹H NMR signals (Table 1). In contrast, aza[6]helicene diyne **4c** has a reversed anisotropic cone effect, and protons H^{1,16} display shielded chemical shifts (Table 1). Amongst these new derivatives, only **4c** bears a helicene moiety that is configurationally stable. This aza[6]helicene diyne was successfully resolved into its pure enantiomers by HPLC on a Chiralcel OD-H stationary phase.^[12a] Single crystals of the pure enantiomer (–)-**4c** suitable for X-ray diffraction study were grown from a heptane/AcOEt solution at room temperature and were studied by X-ray crystallography (Figure 1, Table 2). As observed for other helical conjugated molecules, (–)-**4c** aggregates in the solid state (Figure 1). This aggregation is due to a combination of intermolecular CH– π interactions between two helicene moieties (T-shaped organization; CH...Ph 3.5 Å) and the diyne arms and helicene fragments (CH...Ph 3.5 Å).

The next step towards the target mixed phosphole–helicene derivatives was oxidative coupling of diynes **4a–e** with zirconocene dichloride followed by [ZrCp₂]/PPh exchange (Scheme 1). This reaction sequence was conducted in THF according to a known procedure,^[17,18] giving rise to air-stable phospholes **5a–e** (Scheme 1), which were isolated in moderate yields (Table 1) after purification by column chromatography. The structures of phosphole derivatives **5a–e** were supported by high-resolution mass spectrometry and elemental analyses. They exhibited classical ¹H and ¹³C NMR data, with signals associated with the helicene moieties that compare well with those recorded for the corresponding diynes. Their ³¹P{¹H} NMR spectra showed sharp singlets in the range expected for *P*-aryl phospholes (Table 1),^[15,17] the signals for **5d** and **5e** being slightly deshielded, probably because the phosphole moiety is located in the anisotropy cone of the azahelicene.

The two stereogenic elements (P center, azahelicene) of **5a, b, d** (Scheme 1) undergo rapid inversion in solution, and only one set of NMR signals is observed at room temperature. For compound **5e**, two sets of NMR signals are observed due to the presence of the enantiomerically pure pinene substituent. Phosphole **5c** (Scheme 1), which is the only derivative featuring a configurationally stable aza[6]helicene moiety, was investigated in more detail. Its ³¹P{¹H} NMR

Table 1. Selected NMR data and yields for diynes **4a–e** (Scheme 2) and phospholes **5a–e** (Scheme 1).

Cmpd	$\delta(^1\text{H})^{[a]}$ [ppm]	Yield [%]	Cmpd	$\delta(^{31}\text{P}\{^1\text{H}\})^{[c]}$ [ppm]	Yield [%]
4a	8.81, 8.52 (H ¹ , H ¹⁰)	50	5a	+12.3	73
4b	9.17, 8.76 (H ¹ , H ¹²)	47	5b	+12.2	63
4c	7.81, 7.61 (H ¹ , H ¹⁶) ^[b]	48	5c	+14.0, +14.5	47
4d	9.09 and 8.96 (H ¹ , H ¹²)	62	5d	+20.7	45
4e	8.97 (H ¹)	25	5e	+20.4, +20.7	27

[a] At 300 MHz in CDCl₃. [b] At 500 MHz in CDCl₃. [c] At 81 MHz in CDCl₃.

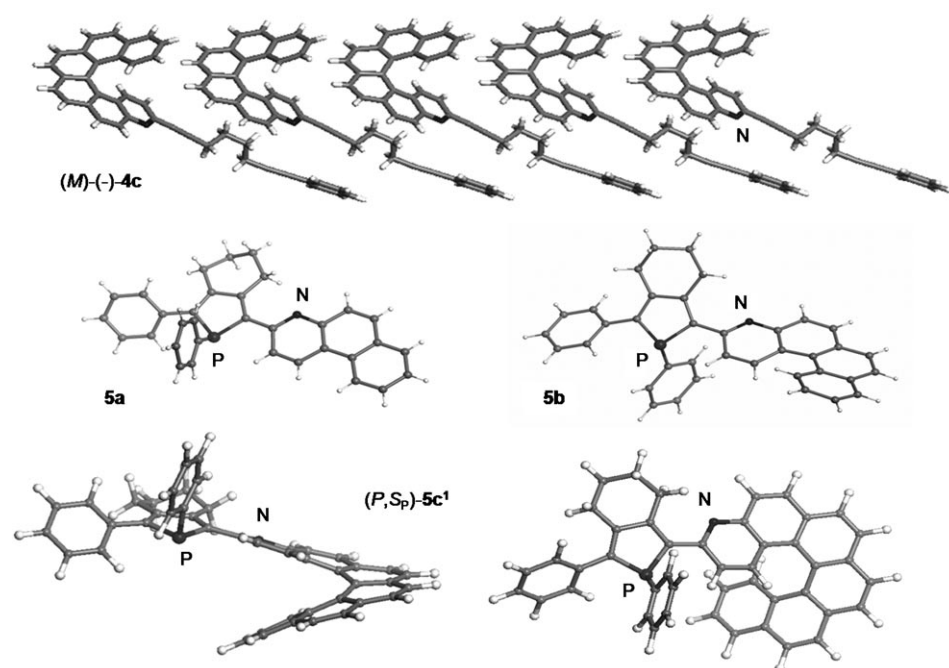


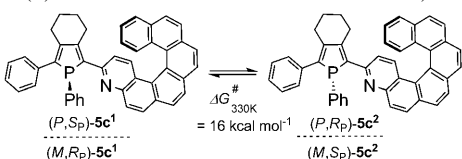
Figure 1. Packing of *M*-(-)-**4c** in the crystal along the *x* axis. Molecular structures of phospholes **5a–c** determined by X-ray crystallography.^[12]

Table 2. X-ray data of **4c**, **5a–c**.

	4c	5a	5b	5c
formula	C ₃₉ H ₂₇ N ₁	C ₃₃ H ₂₆ N ₁ P ₁	C ₃₇ H ₂₈ N ₁ P ₁	C ₄₅ H ₃₂ N ₁ P ₁
CCDC number	736269	736270	651119	707415
<i>M_r</i>	509.62	467.52	517.57	617.69
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> [Å]	9.233(1)	9.831(1)	9.5107(4)	9.701(2)
<i>b</i> [Å]	14.253(2)	13.655(1)	10.9272(5)	11.374(2)
<i>c</i> [Å]	11.032(1)	19.098(2)	14.1036(6)	14.341(2)
<i>α</i> [°]	90	74.935(4)	72.146(3)	78.216(10)
<i>β</i> [°]	111.861(1)	76.380(3)	70.845(3)	87.051(11)
<i>γ</i> [°]	90	83.273(3)	84.199(3) ^o	83.926(12)
<i>V</i> [Å ³]	1347.4(4)	2401.8(4)	1317.89(10)	1539.6(4)
<i>Z</i>	2	4	2	2
Color	colorless	yellow	yellow	yellow
crystal size [mm]	0.40 × 0.30 × 0.13	0.10 × 0.05 × 0.05	0.2 × 0.05 × 0.03	0.08 × 0.04 × 0.02
<i>ρ</i> _{calcd} [Mg m ⁻³]	1.256	1.293	1.304	1.332
<i>F</i> (000)	536	984	544	648
<i>μ</i> (MoK _α) [cm ⁻¹]	0.072	0.137	0.132	0.126
<i>λ</i> [Å]	0.71069	0.71069	0.71069	0.71069
diffractometer	APEX II Bruker-AXS	APEX II Bruker-AXS	APEX II Bruker-AXS	APEX II Bruker-AXS
index ranges <i>hkl</i>	−11 ≤ <i>h</i> ≤ 11, −13 ≤ <i>k</i> ≤ 17, −13 ≤ <i>l</i> ≤ 13	−12 ≤ <i>h</i> ≤ 12, −17 ≤ <i>k</i> ≤ 17, −24 ≤ <i>l</i> ≤ 24	−11 ≤ <i>h</i> ≤ 11, −12 ≤ <i>k</i> ≤ 12, −16 ≤ <i>l</i> ≤ 16	−12 ≤ <i>h</i> ≤ 12, −14 ≤ <i>k</i> ≤ 14, −12 ≤ <i>l</i> ≤ 18
<i>θ</i> range [°]	1.99 ≤ <i>θ</i> ≤ 26.38	2.12 ≤ <i>θ</i> ≤ 27.57	5.24 ≤ <i>θ</i> ≤ 24.71	1.45–27.56
reflections collected	9496	34837	18731	11764
independent reflections	2873	11042	4428	6896
reflections [<i>I</i> > 2σ(<i>I</i>)]	2633	7168	3255	3479
data/restraints/parameters	2873/1/362	11042/0/632	4428/0/352	6896/0/424
goodness of fit on <i>F</i> ²	1.134	1.028	1.022	1.022
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0364, <i>wR</i> 2 = 0.0776	<i>R</i> 1 = 0.0452, <i>wR</i> 2 = 0.1050	<i>R</i> 1 = 0.0393, <i>wR</i> 2 = 0.0795	<i>R</i> 1 = 0.0791, <i>wR</i> 2 = 0.1615
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0413, <i>wR</i> 2 = 0.0841	<i>R</i> 1 = 0.0892, <i>wR</i> 2 = 0.1257	<i>R</i> 1 = 0.0659, <i>wR</i> 2 = 0.0907	<i>R</i> 1 = 0.1713, <i>wR</i> 2 = 0.1921
absolute structure parameter	0(4)	—	—	—
largest diff. peak and hole [e Å ⁻³]	0.187 and −0.165	0.368 and −0.480	0.394 and −0.387	0.451 and −0.388

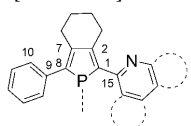
spectrum displays two sharp singlets of comparable intensity (Table 1). In fact, when starting with a diyne bearing an enantiomerically pure helix (for example *P* configuration), two diastereomeric phospholes (i.e., (*P,S_p*)-**5c**¹ and (*P,R_p*)-**5c**², Table 3) are obtained due to the presence of the stereogenic P atom. Their mirror images (i.e., (*M,R_p*)-**5c**¹ and (*M,S_p*)-**5c**², Table 3) were synthesized from the *M* azahelicene. Indeed, a variable-temperature ³¹P{¹H} NMR study revealed an inversion barrier between **5c**¹ and **5c**² of 16 kcal mol⁻¹ at 330 K. Phospholes **5a–c** were also characterized by an X-ray diffraction study confirming the proposed structures (Tables 2 and 4, Figure 1).

Table 3. Relative energies [kcal mol⁻¹] and corresponding mole fractions X_i at 298.15 K of four optimized configurations (gas phase: BP/SV(P) level; BP/SV(P) level with COSMO model for chloroform).



	Gas phase	X_i	COSMO	X_i
(<i>P,S_P</i>)- <i>s-trans</i> - 5c ¹	0.0	72.7	0.0	59.5
(<i>P,S_P</i>)- <i>s-cis</i> - 5c ¹	0.7	22.3	0.3	33.0
(<i>P,R_P</i>)- <i>s-trans</i> - 5c ²	2.0	2.4	2.4	1.1
(<i>P,R_P</i>)- <i>s-cis</i> - 5c ²	2.0	2.6	1.3	6.4

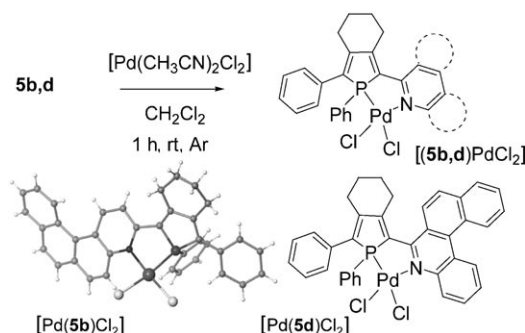
Table 4. Selected bond lengths [Å] and angles [°] for **5a–c** and the corresponding calculated values [in brackets] for **5c**.^[a]



	5a	5b	5c
P1–C1	1.816	1.794	1.816 [1.826]
C1–C2	1.3713	1.370	1.373 [1.398]
C2–C7	1.463	1.465	1.479 [1.468]
C7–C8	1.372	1.367	1.354 [1.390]
C8–P1	1.795	1.805	1.815 [1.827]
C8–C9	1.472	1.468	1.494 [1.469]
C1–C15	1.464	1.474	1.474 [1.470]
C7–C8–C9–C10	38.40(5)–42.82(6) ^[c]	–37.70(8)	–38.22(1) [–40.395]
N1–C15–C1–C2	–0.44(3) to 1.71(6) ^[c]	39.92(5)	–26.27(4) [–4.721]
Helical dihedral angle ^[b]	5.5	30.1	45.8 [48.6]

[a] Calculated structure (*P,S_P*)-*s-trans*-**5c**¹. [b] Angle between the planes defined by the terminal pyridyl and phenyl groups. [c] Two values found in the X-ray structure.

Ligand behavior of mixed azahelicene phosphole derivatives towards Pd^{II} and Cu^I centers: The neutral complexes [Pd(**5b**)Cl₂] and [Pd(**5d**)Cl₂] were obtained in high yields (> 85%) by treating [PdCl₂(CH₃CN)₂] with the corresponding phosphole derivative in CH₂Cl₂ solution (Scheme 3). The



Scheme 3. Synthesis of neutral complexes [Pd(**5b**)Cl₂] and [Pd(**5d**)Cl₂].

large ³¹P NMR downfield chemical shifts due to coordination ($\delta=60$ and 72 ppm) are consistent with the formation of five-membered palladacycles, and these complexes display similar ¹H NMR characteristics for the 1,5-diphenyl-2-(2-pyridyl)phosphole fragments to those of the related [(2-pyridyl)phosphole]PdCl₂ complexes.^[20] The proposed structures were confirmed by an X-ray diffraction study on [Pd(**5b**)Cl₂] (Tables 5 and 6, Scheme 3).

Compounds **5b–d** reacted in CH₂Cl₂ with [Pd(CH₃CN)₄](SbF₆)₂ (2:1 molar ratio) giving rise almost quantitatively to air-stable complexes [Pd(**5b**)₂](SbF₆)₂, [Pd(**5c**)₂](SbF₆)₂, and [Pd(**5d**)₂](SbF₆)₂, respectively (Scheme 4). Their elemental analyses are consistent with the formation of Pd–bis(phosphole azahelicene) assemblies. Their ³¹P{¹H} NMR spectra exhibit sharp singlets ([Pd(**5b**)₂]²⁺, $\delta=+76.6$ ppm; [Pd(**5c**)₂]²⁺, $\delta=+81.6$ ppm; [Pd(**5d**)₂]²⁺, $\delta=+75.0$ ppm) and only one set of ¹H signals attributable to the phosphole azahelicene ligands is observed. High-frequency ³¹P NMR chemical shifts are typical for dicationic Pd^{II} complexes bearing (2-pyridyl)phosphole ligands in a mutually *cis* configuration.^[12,20] The simplicity of these NMR data shows that these complexes are formed as single diastereomers. Complex [Pd(**5d**)₂]²⁺ was characterized by X-ray diffraction (Table 5 and 6, Scheme 4). A view showing the supramolecular arrangement of [Pd(**5d**)₂]²⁺ is provided in Figure 2.

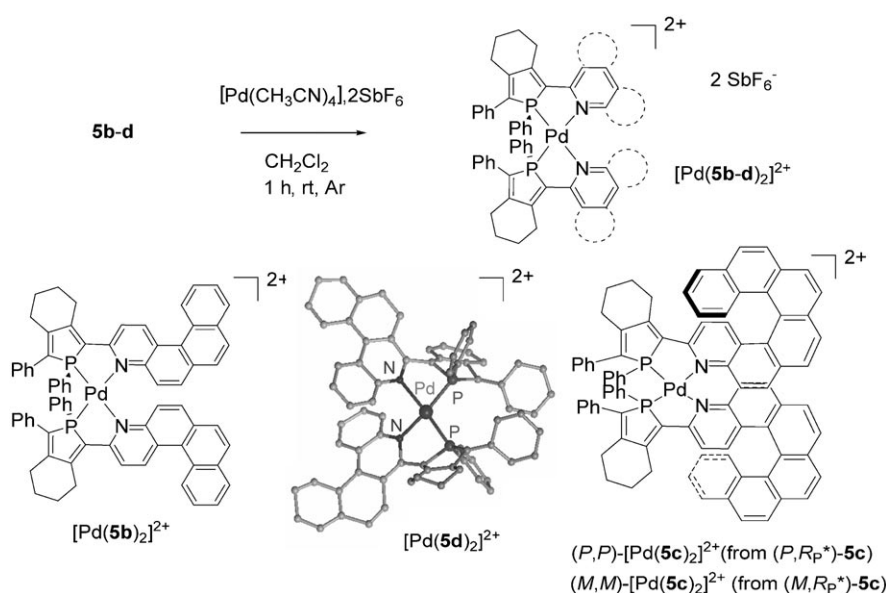
The reaction of **5b–d** with a Cu^I source (2:1 molar ratio) in CH₂Cl₂ solution at room temperature gave rise to the new complexes [Cu(**5b–d**)₂]⁺ (Scheme 5). The proposed structures were supported by elemental analysis, and complex [Cu(**5c**)₂]⁺ was characterized by HRMS. The ³¹P{¹H} NMR spectra of these derivatives in CH₂Cl₂ display a broad singlet at $\delta=5–6$ ppm ($\nu_{1/2}=85$ Hz), a typical shift for cationic Cu^I (2-pyridyl)phosphole complexes.^[20] Upon exposure to pentane vapors, air-stable single crystals of complexes [Cu(**5b**)₂]⁺ and [Cu(**5d**)₂]⁺ (Scheme 5, Tables 5 and 6) suitable for X-ray diffraction studies (Table 2) were obtained from the homogeneous reaction mixtures (yields > 77%).^[12b] Figure 2 shows the supramolecular organization of columns of [Cu(**5d**)₂]⁺ complexes.

Photophysical properties of azahelicene diynes, phospholes, and metal assemblies

Azahelicene diynes: Initially, the UV/Vis and luminescence properties of the structurally isomeric diynes **4b,d** (Scheme 2) were studied in detail to gain insight into the optical properties of this novel helicene series. The profiles of their UV/Vis spectra are characteristic of helicene derivatives, with intense absorptions at high energy ($\lambda_{\text{max}}=270–300$ nm, $\epsilon>10^4$ M⁻¹ cm⁻¹), and a series of well-defined weaker bands beyond 350 nm ($\epsilon\approx 10^3$ M⁻¹ cm⁻¹; Figure 3). In solution at room temperature, both compounds display highly structured fluorescence spectra (Figure 3 and Table 7), with vibrational progressions of 1300 and 1100 cm⁻¹ and emission quantum yields of 8 and 5% for **4b** and **4d**, respectively. The fluorescence lifetimes on the order of 5 ns are typical of extended aromatic π systems. In a rigid

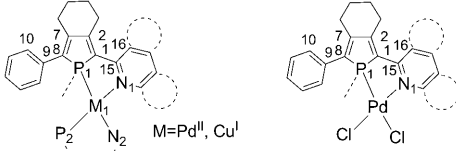
Table 5. X-ray structure determination summary of complexes $[\text{Pd}(\mathbf{5d})_2](\text{SbF}_6)_2$, $[\text{Cu}(\mathbf{5b})_2](\text{PF}_6)$, $[\text{Cu}(\mathbf{5d})_2]\text{Cl}$, and $[\text{Pd}(\mathbf{5b})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$.

	$[\text{Pd}(\mathbf{5d})_2](\text{SbF}_6)_2$	$[\text{Cu}(\mathbf{5b})_2](\text{PF}_6)$	$[\text{Cu}(\mathbf{5d})_2]\text{Cl}$	$[\text{Pd}(\mathbf{5b})\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$
formula	$\text{C}_{75.5}\text{H}_{59}\text{Cl}_3\text{Pd}_1\text{N}_2\text{P}_2\text{F}_{12}\text{Sb}_2$	$\text{C}_{76.5}\text{H}_{61}\text{Cu}_1\text{N}_2\text{P}_6\text{F}_6\text{Cl}_5$	$\text{C}_{133}\text{H}_{122}\text{Cu}_4\text{N}_4\text{P}_4\text{Cl}_{14}$	$\text{C}_{38}\text{H}_{28}\text{Cl}_4\text{N}_1\text{P}_1\text{Pd}_1$
CCDC number	651120	651121	651122	736271
M_r	1740.44	1455.97	2890.89	777.78
T [K]	100(2)	100(2)	100(2)	100(2)
crystal system	tetragonal	triclinic	monoclinic	orthorhombic
space group	$I4_1/a$	$P\bar{1}$	$C2/c$	$Pcab$
a [Å]	18.695(5)	14.431(2)	32.938(2)	12.586(2)
b [Å]	18.695(5)	21.614(3)	19.965(1)	22.480(3)
c [Å]	81.28(2)	22.007(3)	24.449(1)	23.240(3)
α [°]	90	82.315(4)	90	90
β [°]	90	85.456(5)	124.683(2)	90
γ [°]	90	75.858(4)	90	90
V [Å ³]	28 408(11)	6588.7(16)	13 221.0(12)	6575(2)
Z	16,	4	4	8
color	red	orange	yellow	red
crystal size [mm]	$0.2 \times 0.1 \times 0.05$	$0.1 \times 0.1 \times 0.03$	$0.2 \times 0.2 \times 0.1$	$0.20 \times 0.08 \times 0.04$
ρ_{calcd} [Mg m ⁻³]	1.628	1.468	1.452	1.571
$F(000)$	13 808	2988	5928	3136
$\mu(\text{MoK}\alpha)$ [cm ⁻¹]	1.240	0.672	0.102	0.968
λ [Å]	0.71069	0.71069	0.71069	0.71069
diffractometer	APEX II Bruker-AXS	APEX II Bruker-AXS	APEX II Bruker-AXS	APEX II Bruker-AXS
index ranges hkl	$-20 \leq h \leq 20$, $-17 \leq k \leq 20$, $-90 \leq l \leq 90$	$-16 \leq h \leq 16$, $-24 \leq k \leq 24$, $-20 \leq l \leq 24$	$-32 \leq h \leq 41$, $-24 \leq k \leq 24$, $-30 \leq l \leq 26$	$-15 \leq h \leq 15$, $-28 \leq k \leq 17$, $-27 \leq l \leq 27$
θ range [°]	$5.10 \leq \theta \leq 23.25^\circ$	$5.10 \leq \theta \leq 23.26^\circ$	$5.11 \leq \theta \leq 26.37^\circ$	$2.43 \leq \theta \leq 26.59^\circ$
reflections collected	86 356	37 977	68 081	34 974
independent reflections	10 112	18 196	13 411	6656
reflections $[I > 2\sigma(I)]$	5634	9642	10 702	3833
data/restraints/parameters	10112/397/1022	18196/788/1944	18196/325/969	6656/0/425
goodness of fit on F^2	1.128	1.028	1.028	1.083
final R indices $[I > 2\sigma(I)]$	$R1 = 0.1074$, $wR2 = 0.2213$	$R1 = 0.0793$, $wR2 = 0.1887$	$R1 = 0.0485$, $wR2 = 0.1187$	$R1 = 0.0834$, $wR2 = 0.1709$
R indices (all data)	$R1 = 0.1827$, $wR2 = 0.2542$	$R1 = 0.1628$, $wR2 = 0.2282$	$R1 = 0.0647$, $wR2 = 0.1302$	$R1 = 0.1551$, $wR2 = 0.1949$
absolute structure parameter	—	—	—	—
largest diff. peak and hole [e Å ⁻³]	1.324 and -1.249	0.842 and -0.911	1.580 and -1.127	1.580 and -1.127

Scheme 4. Synthesis of complexes $[\text{Pd}(\mathbf{5b-d})_2]^{2+}$. View of complex $[\text{Pd}(\mathbf{5d})_2]^{2+}$ established by X-ray diffraction study (H atoms, counteranions, and solvent molecules have been omitted). One of the two symmetrically independent complexes is shown.

glass at 77 K, the fluorescence is not shifted, and this reflects the rigidity of the π skeleton and the localized nature of the excited state. At this temperature, the fluorescence is accompanied by well-defined structured phosphorescence in the green region of the spectrum, with a vibrational progression of about 1500 cm^{-1} (Figure 3 and Table 7). The temporal decay of the phosphorescence is easily visible to the eye, occurring on a timescale of seconds. The singlet-state fluorescence is lower in energy for iso derivative $\mathbf{4d}$ than for its linear isomer $\mathbf{4b}$ ($\Delta E = 830 \text{ cm}^{-1}$), whereas the triplet phosphorescence shows the opposite trend ($\Delta E = 350 \text{ cm}^{-1}$): the singlet–triplet energy gaps are estimat-

Table 6. Selected bond lengths [Å] and angles [°] for [Pd(**5b**)₂]²⁺, [Cu(**5b**)₂]⁺, [Cu(**5d**)₂]⁺, and [Pd(**5b**)Cl₂].



	[Pd(5d) ₂] ²⁺ ^[a]	[Pd(5c) ₂] ²⁺ ^[b]	[Cu(5b) ₂] ⁺ ^[a]	[Cu(5d) ₂] ⁺ ^[a]	[Pd(5b)Cl ₂] ^[a]
P1–C1	1.753	1.835	1.783	1.801	1.789
C1–C2	1.322	1.380	1.361	1.359	1.347
C2–C7	1.504	1.485	1.498	1.468	1.490
C7–C8	1.360	1.385	1.349	1.359	1.343
C8–P1	1.801	1.835	1.804	1.809	1.810
C8–C9	1.495	1.478	1.468	1.475	1.484
C1–C15	1.509	1.453	1.463	1.466	1.464
C7–C8–C9–C10	58.765	55.227	52.806	51.629	12.73
C2–C1–C15–C16	54.299	53.03	39.085	52.447	41.123
helical dihedral angle ^[c]	28.46–32.90	49.91–53.22	21.92–22.3	28.52–28.84	33.14
P1–M1	2.248	2.302	2.280	2.295	2.239
N1–M1	2.136	2.200	2.084	2.105	2.096
P2–M1	2.248	2.319	2.295	2.298	–
N2–M1	2.109	2.188	2.083	2.090	–
N1–M1–P1	81.031	79.934	85.020	86.277	81.520
N1–M1–N2	96.248	98.612	117.964	120.280	–
N1–M1–P2	168.177	162.285	125.250	122.511	–
N2–M1–P2	81.572	79.725	87.514	86.330	–
N2–M1–P1	167.342	165.276	126.297	125.904	–
twist angle	17.96	24.75	83.58	86.35	–

[a] Data obtained by X-ray crystallography. [b] Data obtained by TDDFT.^[c] Angle between the planes defined by the terminal pyridyl and phenyl groups.

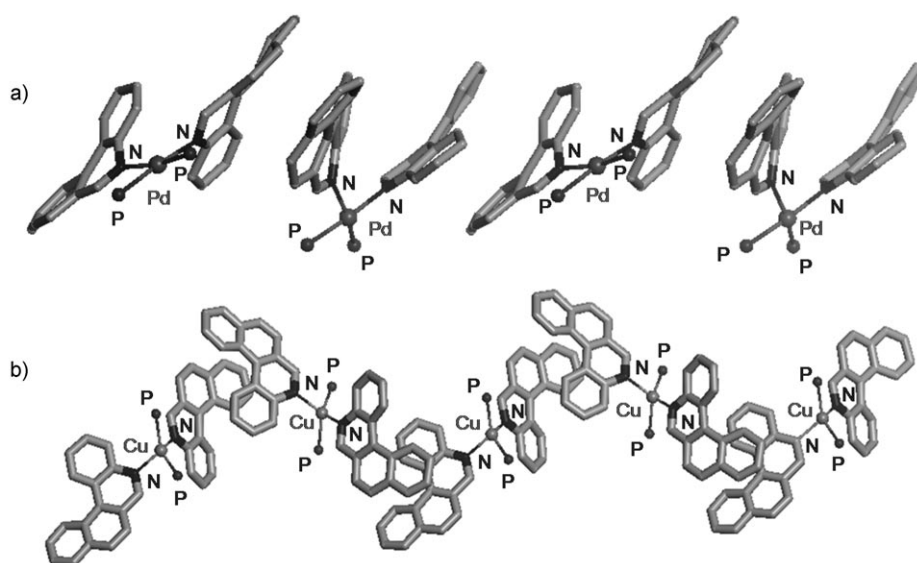


Figure 2. Simplified views of the supramolecular arrangement of complexes [Pd(**5d**)₂]²⁺ (a) and [Cu(**5d**)₂]⁺ (b).

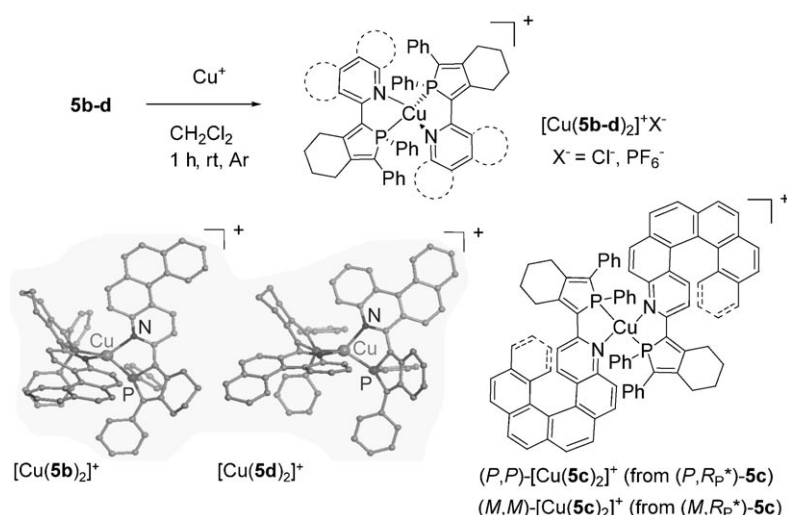
ed at 6300 and 5100 cm^{−1} for **4b** and **4d**, respectively. The more extended helicene diyne **4c** (Scheme 2) displays similar spectra to the shorter parent **4b**, but with a significant redshift in the absorption and fluorescence spectra indicating stabilization of the S₁ state by around 2000 cm^{−1} upon

elongating the chromophore. The influence on the triplet state is smaller (ca. 650 cm^{−1}), based on the shift in the phosphorescence spectrum.

Azahelicene phospholes: The UV/Vis spectra (CH₂Cl₂, 5 × 10^{−5} M) of **5a–e** (Scheme 1) display strong absorption in the visible range of the electronic spectrum (Table 7, Figure 4). According to theoretical calculations, these bands can be assigned to π–π* transitions (vide infra). A detailed analysis of the structure/absorption property relationship is provided in the Discussion section. The study on the emission properties of mixed phosphole–azahelicene derivatives started with investigations on the known 1,2-diphenyl-5-(2-pyridyl)-phosphole (**5f**)^[17] (Scheme 1) as a model compound with which comparison can be made. In solution at 298 K, **5f** displays a structureless, broad fluorescence band centered at 475 nm (Φ = 3 %, τ < 1 ns) with a large Stokes shift of 7000 cm^{−1}. At 77 K, the fluorescence emission is blueshifted (λ = 436 nm, τ = 4.7 ns) and no phosphorescence could be detected. At room temperature, phosphole **5b** bearing the linear aza[4]helicene moiety (Scheme 1) displays a broad fluorescence emission centered at 499 nm (Φ = 8 %, τ ≈ 0.8 ns), irrespective of the excitation wavelength, with a good match between the absorption and excitation spectra (Figure 5). At 77 K, the behavior is more complicated. Upon excitation at short wavelengths (ca. 350 nm), helicene-like fluorescence is observed (λ = 378 nm, τ = 12 ns) accompanied by a broad, rather

ill-defined emission between 450 and 600 nm (Figure 5).

The emission decay in this region displays short-lived components on the order of 10 ns, but also a long-lived component of 1.5 s. The latter is comparable to the phosphorescence displayed by the azahelicene diynes, and the time-re-



Scheme 5. Synthesis of cationic complexes $[\text{Cu}(\mathbf{5b-d})_2]^+$. Solid-state structure of complexes $[\text{Cu}(\mathbf{5b})_2]^+$ and $[\text{Cu}(\mathbf{5d})_2]^+$ (one stereoisomer; H atoms, counteranions, and solvent molecules have been omitted for clarity).

solved emission spectrum recorded at time delays greater than 100 μs is also similar to the phosphorescence of the azahelicene unit. Thus, it appears that, under these conditions at low temperature, emission can emanate from helicene-like excited states, as well as from lower-energy singlet states delocalized across the molecule.

Its isomer **5d** bearing the iso-helicene substituent (Scheme 1) displays similar behavior at 77 K. In this case, however, the dual emission is also evident at 298 K (Figure 6). Thus, excitation at 350 nm leads to structured helicene-like bands around 400 nm, in addition to a

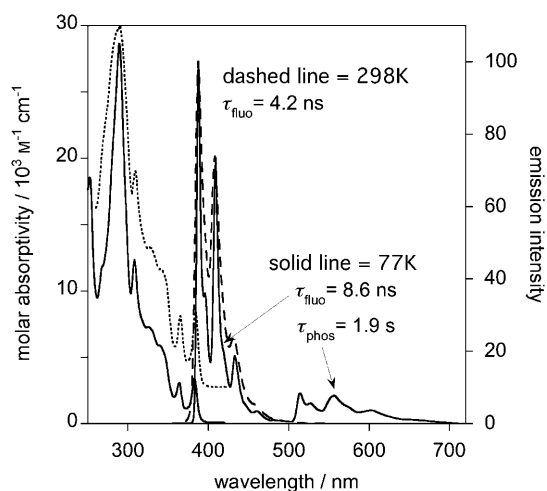


Figure 3. Absorption (solid line, left), excitation ($\lambda_{\text{em}}=410$ nm, dotted line) and emission ($\lambda_{\text{ex}}=360$ nm, dashed line) spectra of diyne **4b** in CH_2Cl_2 at 298 K, and the emission spectrum (solid line, right) in a diethyl ether/isopentane/ethanol (2:2:1 v/v) glass at 77 K.

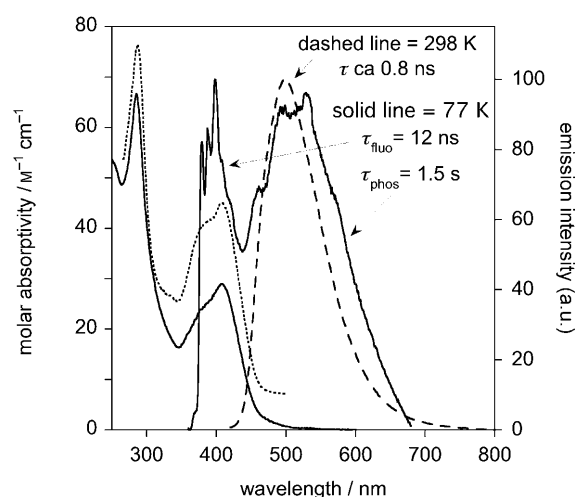


Figure 5. Absorption (solid line, left), excitation ($\lambda_{\text{em}}=500$ nm, dotted line) and emission ($\lambda_{\text{ex}}=360$ nm, dashed line) spectra of **5b** in CH_2Cl_2 at 298 K, and the emission spectrum in a diethyl ether/isopentane/ethanol (2:2:1 v/v) glass at 77 K (solid line, right).

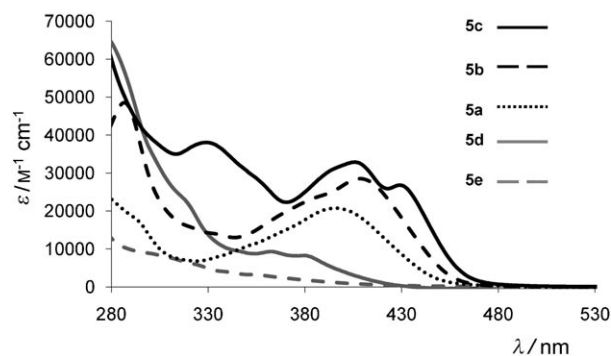


Figure 4. Electronic spectra of mixed azahelicene phosphole derivatives **5a-e** in CH_2Cl_2 .

broader emission band at 460 nm. The emission bands have different lifetimes (Table 7) and significantly different excitation spectra, confirming that the units responsible for the two emission bands are not fully coupled. Phosphole **5c** (Scheme 1) similarly displays a broad fluorescence emission centered at 500 nm at 298 K, with biexponential decay kinetics (Table 7). At 77 K, the emission spectrum of **5c** consists of a broad band centered at 490 nm ($\tau=2.6$ ns, with a long phosphorescence component of 1.3 s also detectable in the low-energy tail), together with some structured, helicene-like emission to higher energy ($\lambda=425$ nm, $\tau=8.5$ ns).

Pd^{II} and Cu^I complexes: Compared to the spectrum of free ligands **5b,d**, the $\pi-\pi^*$ transitions of the corresponding

Table 7. Photophysical data for azahelicene diynes **4b–d**, azahelicene phospholes **5b–d** (with pyridyl phosphole **5f** for comparison), and their Pd^{II} and Cu^I complexes. Data at 298 K in CH₂Cl₂; at 77 K in diethyl ether/isopentane/ethanol (2:2:1 v/v).

Derivatives	$\lambda_{\text{max}}^{\text{abs}}$ [nm] (ϵ [M ⁻¹ cm ⁻¹])	$\lambda_{\text{fluor}}^{\text{RT}}$ [nm]	$\Phi_{\text{RT}}^{\text{fluor}}$ [%]	$\tau_{\text{RT}}^{\text{fluor}}$ [ns]	$\lambda_{\text{fluor}}^{77\text{K}}$ [nm]	$\tau_{\text{fluor}}^{77\text{K}}$ [ns]	$\lambda_{\text{phos}}^{77\text{K}}$ [nm]	$\tau_{\text{phos}}^{77\text{K}}$ [ns]
4b	289 (28600), 308 (12300), 326 (7290), 364 (3070), 382 (3300)	388, 408, 432	8	4.2	388, 409, 433	8.6	514, 556, 602	1.9
4c	265 (48700), 321 (18000), 331 (17500), 352 (8510), 393 (1560), 416 (1270)	422, 446, 472	6	5.9	420, 445, 473	9.3	532, 578, 626	1.5
4d	285 (43800), 313 (12800), 334 (4680), 351 (2340), 370 (3550), 388 (3670)	401, 419, 444	5	4.9	401, 423, 449	7.8	505, 546, 592	1.0
5b	285 (66600), 406 (28800)	499	8	0.8	378, 398	12	ca. 500	1.5
5c1,c2	265 (67500), 326 (21000), 395 (15900), 430 (12700)	502	–	6, 1.2	425 and 490	8.5, 2.6	ca. 550	1.3
5d	266 (36200), 357 (5780), 375 (4900)	389, 404 (sharp) 456 (broad)	–	3	406	8	475	2.5
5f	364 (7650)	475	3	0.5	436	4.7	–[a]	–[a]
5b -PdCl ₂	478 sh (2400)	480	–	2.5, 6.3	[b]	[b]	–[a]	–[a]
5d -PdCl ₂	482 sh (2120)	470	–	3.5, 14	460	3.6, 7.2	–[a]	–[a]
[Pd(5b) ₂] ²⁺	399 (11600), 525 (1400)	382 and 445	–	8.3, 2.4	–	–	540	1.5
[Pd(5d) ₂] ²⁺	402 (15400), 500 (3400)	380 and 454	–	4.8, 3	450	5	550	2.3
[Cu(5b) ₂] ⁺	384 (16600), 403 (17400)	400 and 450	–	10, 3.3	417	15	510	1.9
[Cu(5d) ₂] ⁺	368 (29900), 403 (24800)	410 and 490	–	3.6, 3	410	6.5	ca. 530	1.8

[a] No phosphorescence detected. [b] Series of ill-defined peaks.

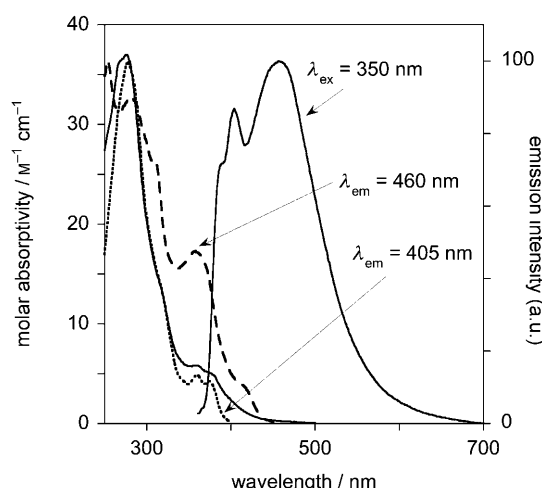


Figure 6. Absorption and emission ($\lambda_{\text{ex}} = 350$ nm) spectra of **5d** in CH₂Cl₂ at 298 K (solid lines, left and right), and the excitation spectra registered at 405 and 460 nm (dotted and dashed lines respectively).

PdCl₂ complexes [Pd(**5b**)Cl₂] and [Pd(**5d**)Cl₂] are much weaker, and new absorptions of low intensity at about 480 nm are observed (Table 7). These transitions can be assigned to charge transfers (CT) involving the metal and the azahelicene phosphole ligand, as already observed in related Pd^{II} 2-pyridylphosphole complexes (vide infra).^[20] The absorption behavior of dicationic Pd(phosphole azahelicene)₂ assemblies [Pd(**5b**)₂]²⁺ and [Pd(**5d**)₂]²⁺ is essentially comparable to that of the corresponding PdCl₂ complexes. Upon coordination to the Pd^{II} center, the intensity of the π - π^* transitions of the free ligands decreases and new transitions of low intensity are observed at longer wavelengths (Table 7, Figure 7). The position of the absorption maxima

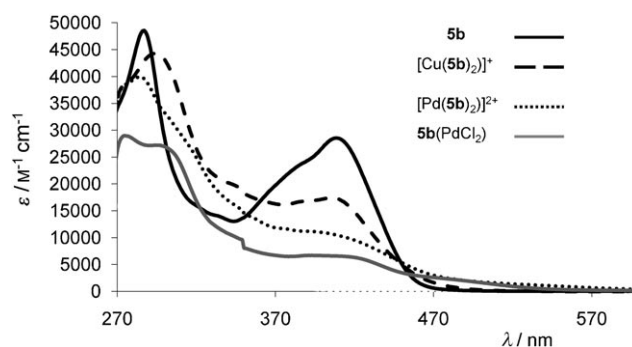


Figure 7. Electronic absorption spectra of compound **5b** and complexes [(**5b**)PdCl₂], [Pd(**5b**)₂]²⁺ and [Cu(**5b**)₂]⁺ (5×10^{-5} M in CH₂Cl₂).

of the Cu^I- and Pd^{II}(phosphole azahelicene)₂ assemblies are essentially comparable, with the Cu complexes having higher molar extinction coefficients (Table 7, Figure 7). The most notable difference between the absorption spectra of these two series of complexes is the absence of long-wavelength absorptions for the Cu^I(phosphole azahelicene)₂ complexes [Cu(**5b**)₂]⁺ and [Cu(**5d**)₂]⁺ (Table 7, Figure 7).

The emission displayed by both series of complexes at 298 K is very weak, whilst the behavior at 77 K is complicated by dual emissions. It is thus difficult to draw a clear picture of the emission properties. In the case of [Pd(**5b**)Cl₂], a broad structured emission band centered at 480 nm is observed, independent of the excitation wavelength, the temporal decay of which exhibits two components on the order of 2.5 and 6.3 ns. Note that the data for the complex **5d** are largely comparable to those of **5b**. For [Pd(**5b**)₂]²⁺ at 298 K, excitation at short wavelengths (<350 nm) gives rise predominantly to structured helix-like fluorescence ($\tau = 8.3$ ns) bands (Figure 8). For longer excitation wavelengths,

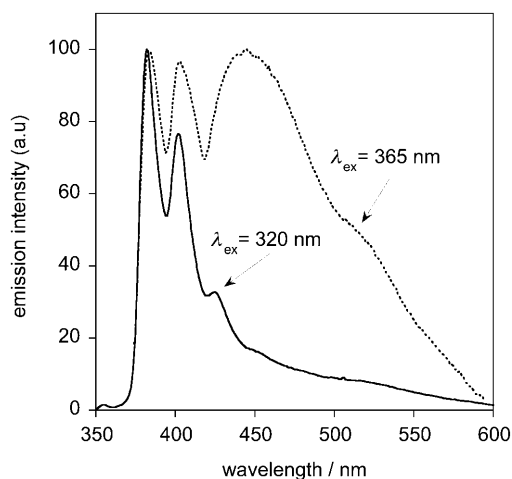


Figure 8. Normalized emission spectra of $[\text{Pd}(\mathbf{5b})_2]^{2+}$ in CH_2Cl_2 at 298 K following excitation at the wavelengths indicated.

a broad band centered around 445 nm appears ($\tau = 2.4$ ns, Figure 8). On the other hand, excitation into the low-energy CT absorption bands gives rise to no detectable emission. At 77 K, long-lived phosphorescence centered at 540 nm is observed ($\tau = 1.5$ s, Table 7).

The emission behaviors of Cu^{I} complexes $[\text{Cu}(\mathbf{5b})_2]^+$ and $[\text{Cu}(\mathbf{5d})_2]^+$ are essentially similar to those of the corresponding Pd^{II} assemblies (Table 7). At 298 K, these complexes are weakly fluorescent ($\tau = 2.4$ – 10.0 ns, Table 7), while at 77 K the spectra again seem to result from a superimposition of fluorescent and phosphorescent bands (Table 7).

Chiroptical properties (molar rotation and circular dichroism) of azahelicene diynes, phospholes, and metal complexes: The specific molar rotations (MR in $\text{deg cm}^2 \text{dmol}^{-1}$) of enantiopure compounds were determined in CH_2Cl_2 solutions at concentrations around 0.01 g/100 mL at 23 °C with the sodium D line. The + and – enantiomers display mirror-image values within an error of $\pm 2\%$. Enantiopure aza[6]helicene diyne *P*-**4c** (Scheme 2) displays a high MR value of $[\phi]_{\text{D}}^{23} = +10240$ (Table 8), comparable to that of *P*-hexacarbohelicene ($[\phi]_{\text{D}}^{23} = 11950$).^[21a] The specific MR of phosphole *P*-**5c**^{1,2} is lower ($[\phi]_{\text{D}}^{23} = +8200$) and corresponds to a mixture of diastereomers (*(P,S_p)*-**5c**¹ and *(P,R_p)*-**5c**²). In comparison, complex *(P,P)*- $[\text{Pd}(\mathbf{5c})_2]^{2+}$ displays a huge specific MR ($[\phi]_{\text{D}}^{23} = +23100$), which is much larger than that of its Cu^{I} analogue *(P,P)*- $[\text{Cu}(\mathbf{5c})_2]^+$ ($[\phi]_{\text{D}}^{23} = 13100$). The MR of diyne **4e** and phosphole **5e** are very weak, since they exhibit central chirality.

Table 8. Experimental and calculated molar rotations of enantiopure compounds.

	<i>P</i> - 4c	(9 <i>S</i> ,11 <i>R</i>)- 4f	(9 <i>S</i> ,11 <i>R</i>)- 5f	<i>P</i> - 5c	<i>(P,P)</i> - $[\text{Pd}(\mathbf{5c})_2]^{2+}$	<i>(P,P)</i> - $[\text{Cu}(\mathbf{5c})_2]^+$
$[\phi]_{\text{D}}^{23[\text{a,b}]}$	+10240	–195	–62	+8200	+23100	+13150
	<i>(P,P,R_pR_pΔ_{Pd})-[Pd(5c¹)₂]²⁺</i>		<i>(P,P,R_pR_pΔ_{Cu})-[Cu(1c¹)₂]²⁺</i>		<i>(P,P,R_pR_pΔ_{Cu})-[Cu(1c¹)₂]²⁺</i>	
$[\phi]^{[\text{c}]}$	+26660		+13230		+30340	

[a] Measured in CH_2Cl_2 . [b] In $\text{deg cm}^2 \text{dmol}^{-1}$ and within an error of $\pm 2\%$. [c] TDDFT calculation on diastereomer **5c**¹.

The CD spectra were recorded in CH_2Cl_2 solutions at concentrations around 5×10^{-5} M and display mirror-image values for the + and – enantiomers. The CD spectrum of *P*-**4c** (Figure 9) shows two bands with high $\Delta\epsilon$ values around

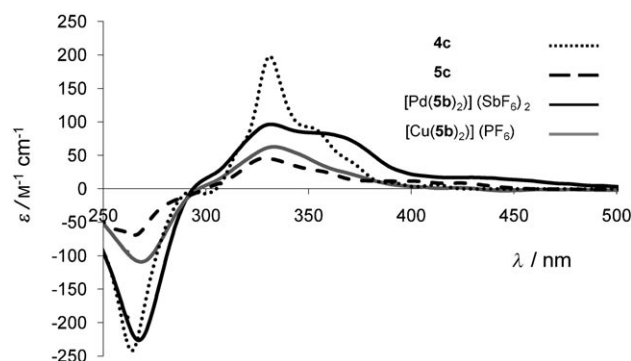


Figure 9. CD spectra of compounds **4c**, **5c**, $[\text{Pd}(\mathbf{5c})_2](\text{SbF}_6)_2$, and $[\text{Cu}(\mathbf{5c})_2](\text{PF}_6)$ (blue) having *P*-configured helices.

270 nm (–) and around 330 nm (+), which allow unambiguous assignment of the absolute configuration by comparison with previously known helicenes.^[21a,b] For phosphole **5c**, the mixture of diastereomers (*(P,S_p)*-**5c**¹ and *(P,R_p)*-**5c**² gives lower CD values together with additional very small CD bands at $\lambda > 370$ nm. Moreover, the CD spectra of *(P,P)*- $[\text{Pd}(\mathbf{5c})_2]^{2+}$ and *(P,P)*- $[\text{Cu}(\mathbf{5c})_2]^+$ are quite different. They both display two intense CD bands around 270 nm (–) and around 330 nm (+). However, the magnitude of the CD spectrum of Pd^{II} complex **3** is much larger than that of Cu^{I} complex **4** (Figure 9). The CD spectrum of *(P,P)*- $[\text{Pd}(\mathbf{5c})_2]^{2+}$ displays additional intense bands at about 370 nm as well as weak bands at longer wavelengths (410–450 nm) that are not observed for *(P,P)*- $[\text{Cu}(\mathbf{5c})_2]^+$ (Figure 9).

Theoretical study: Theoretical calculations were performed on phosphole *P*-**5c** and its complexes *(P,P)*- $[\text{Pd}(\mathbf{5c})_2]^{2+}$ and *(P,P)*- $[\text{Cu}(\mathbf{5c})_2]^+$ to gain more insight into the structure–chiroptical property relationships. The most stable structures of **5c** and its complexes were first determined by DFT calculations, and then the molecular orbitals were obtained and the UV/Vis and CD spectra calculated by time-dependent (TD) DFT. Finally, the MR at 589 nm was computed. In this section, molar rotations (in units of $\text{deg cm}^2 \text{dmol}^{-1}$) are scaled by a factor of 1:1000, that is, molar rotations are reported in units of $10^3 \text{ deg cm}^2 \text{dmol}^{-1}$, which we abbreviate as mru.

During the course of this study we discovered that the ligands themselves are highly interesting, flexible systems with strong chiroptical properties. We show below that the main role of the metal atom is to direct the geometry of the ligands. Therefore, to better understand the chiroptical proper-

ties of the metal complexes it is necessary to perform a detailed analysis of the azahelicene phosphole ligands first.

Computational details: All structures were optimized with the Turbomole 5.7.1 program^[22a] using the double- ζ SV(P) basis set,^[23] which includes polarization functions on all of the atoms in the system except hydrogen, and the Becke–Perdew (BP) functional,^[24] by using the RI-DFT method and accompanying auxiliary basis sets.^[22b,c] Absorption (UV/Vis) and circular dichroism (CD) excitation spectra, as well as optical rotations (ORs) at the sodium D line wavelength (589.3 nm) were calculated with the Becke half-and-half functional (BHLYP)^[25] and SV(P) basis set. Benchmark calculations showed that this basis set/functional combination describes the valence excitations in the UV/Vis range reasonably well.^[12a] All spectra were broadened with Gaussian functions with a σ value of 0.26 eV. Solvation effects for the phosphole ligands were investigated by inclusion of the conductor-like screening model (COSMO)^[26] for chloroform (dielectric constant of 4.8). Further investigations of the electronic structure of the Pd and Cu phosphole complexes were performed by using the NBO^[27] analysis capabilities of the Gaussian 03^[28] code (at the same BHLYP/SV(P) level of theory).

In some cases a sum-over-states (SOS) analysis [Eq. (1)] was applied to the optical rotations

$$[\phi]_w^k = 91.43028 \omega^2 \sum_{n=1}^k \frac{R_{0n}}{\omega_{0n}^2 - \omega^2} \quad (1)$$

where $[\phi]$ is the molar rotation in units of $\text{deg cm}^2 \text{ mol}^{-1}$, ω the angular frequency of light, ω_{0n} the frequency of the n th excitation, R_{0n} is the rotatory strength of the n th excitation in units of $10^{-40} \text{ esu}^2 \text{ cm}^2$ (c.g.s. system), and k the number of excitations included in the SOS. The optical rotations computed directly (referred to as linear-response optical rotations from now on) correspond to the SOS limit whereby k covers all excitations that are possible with a given basis set.

We also analyzed some CD spectra in terms of MO-to-MO and LMO-to-LMO (LMO=localized molecular orbital) contributions. In the present study, natural LMOs (NLMOs) were used, as devised by Weinhold et al.^[29] In the context of this work, the analysis in terms of LMOs allows for convenient identification of the metal orbitals in each excitation without referring to the primitive or contracted basis set. In linear-response TDDFT, the transition density for an excitation can be calculated from a density matrix and the Kohn–Sham MOs, assumed here to be real, as Equation (2)

$$\rho_{0 \rightarrow j} = \sum_{ai} P_{ai}(\omega_j) \varphi_i \varphi_a \quad (2)$$

where ω_j is the excitation frequency. It is convenient to write the density perturbation in terms of ordered pairs ai , where a is an unoccupied and i an occupied orbital, and to

consider separately a symmetric part $P_{ai}^S = (X + Y)_{ai}$ and an antisymmetric part $P_{ai}^A = (X - Y)_{ai}$, from which the transition density and current density can be computed in the MO basis.^[21b,30] TDDFT programs typically determine the coefficients $X_{ai} = P_{ai}$ and $Y_{ai} = P_{ia}$, or alternatively their sum and difference, for each transition.^[31,32] The normalization is such that^[33] Equation (3) holds.

$$\sum_a^{\text{unocc}} \sum_i^{\text{occ}} (X + Y)_{ai} (X - Y)_{ai} = 1 \quad (3)$$

Thus, each excitation can be analyzed conveniently in terms of contributions from occupied–unoccupied MO pairs adding up to 1 (100%). A relatively pure transition may have a contribution on the order of about 80% or higher from a single pair $\varphi_i \varphi_a$. Many of the coefficient products for the occ–unocc pairs will be small; however, typically there are dominant contributions in low-lying transitions. For example, an excitation with 85% HOMO-to-LUMO character has $(X + Y)_{\text{HOMO-LUMO}} (X - Y)_{\text{HOMO-LUMO}} = 0.85$. Most TDDFT programs print contributions from this, or a related, analysis of the transitions.

Consider next an orthonormal set of LMOs λ along with the transformation that describes the canonical MOs in the localized orbital basis [Eq. (4)].

$$\varphi_j = \sum_k \lambda_k T_{kj} \quad (4)$$

Instead of the NLMOs one may use other localized sets such as obtained from the Boys,^[34a] Edmiston–Ruedenberg,^[34b] or von Niessen^[34c] criteria, or Pipek–Mezey^[34d] LMOs, to name a few alternatives. Substituting Kronecker δ terms into Equation (3) yields Equation (5), where $a, b, c \in \text{unocc}$ and $i, j, k \in \text{occ}$, where a, b, i, j are MO indices and c, k indices for the localized orbitals.

$$1 = \sum_{ai} (X + Y)_{ai} (X - Y)_{bj} \sum_b^{\text{unocc}} \delta_{ab} \sum_j^{\text{occ}} \delta_{ij} \\ = \sum_{ai} \sum_{bckj} (X + Y)_{ai} (X - Y)_{bj} T_{ca} T_{cb} T_{ki} T_{kj} \quad (5)$$

We define A_{ck}^S and A_{ck}^A in Equations (6), which are the symmetric and antisymmetric components of the transition density matrix in the LMO basis

$$A_{ck}^S = \sum_{ai} (X + Y)_{ai} T_{ca} T_{ki} \quad (6a)$$

$$A_{ck}^A = \sum_{bj} (X - Y)_{bj} T_{cb} T_{kj} \quad (6b)$$

and the LMO analogue of Equation (3) is now Equation (7).

$$\sum_c^{\text{unocc}} \sum_k^{\text{occ}} A_{ck}^S A_{ck}^A = 1 \quad (7)$$

Equation (7) can be used to analyze occ–unocc LMO contributions for a given excitation. In general, for a larger molecule this procedure may yield many contributions with relatively small weights, but it is now easy to group contributions from a particular atom or functional group, or analyze in terms of specific one-, two-, or delocalized multicenter orbitals. For a metal atom, or other subgroup, contributions can also be extracted from the MO–MO terms by grouping MO coefficients with respect to the AO basis at each center. However with multi- ζ polarized metal basis sets it would not be as simple, for example, to extract which metal orbital contributes, in particular if the metal environment is not highly symmetric, as is the case here. For the present work we have written a program that analyzes the TDDFT results from Turbomole computations in terms of LMOs according to the occ–unocc LMO contributions of Equation (7).

Calculated UV and CD spectra of aza[6]helicene phosphole **5c¹:** Starting from the crystal structure of ligand **5c**¹ (Figure 1 and Table 2), Figure 10 shows some changes in the

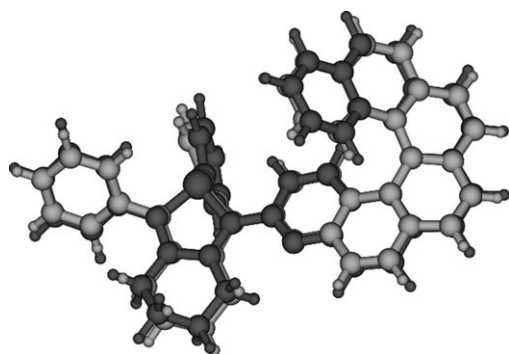


Figure 10. Overlay of the (darker) BP/SV(P) optimized structure and the (lighter) crystal structure for **5c**¹ (hydrogen atoms added).

geometry occur upon optimization with the SV(P) basis. Overall, however, the optimized and single-crystal X-ray structures match well, and the differences were tentatively attributed to crystal-packing effects. We proceeded to use the optimized geometry, as it may better represent the structure in solution. Further optimization with the more flexible TZVP^[35] basis and additional calculations with TZVP and the COSMO solvation model showed that the geometry remained virtually unchanged from the SV(P) calculation. Thus, the more economic SV(P) basis was used for subsequent computations.

Four configurations were studied: (*P,S_p*)-*s-trans*-**5c**¹, the structure with an inverted phosphole (*P,R_p*)-*s-trans*-**5c**², and both of these with the phosphole rotated 180° about the C–C bond of N–C–C–P, that is, (*P,S_p*)-*s-cis*-**5c**¹ and (*P,R_p*)-*s-cis*-**5c**², respectively. Their relative BP/SV(P) optimized energies in both gas phase and COSMO calculations are given in Table 3.

Figure 11 shows the simulated BHLYP/SV(P) UV/Vis absorption spectrum averaged over the various conformers,

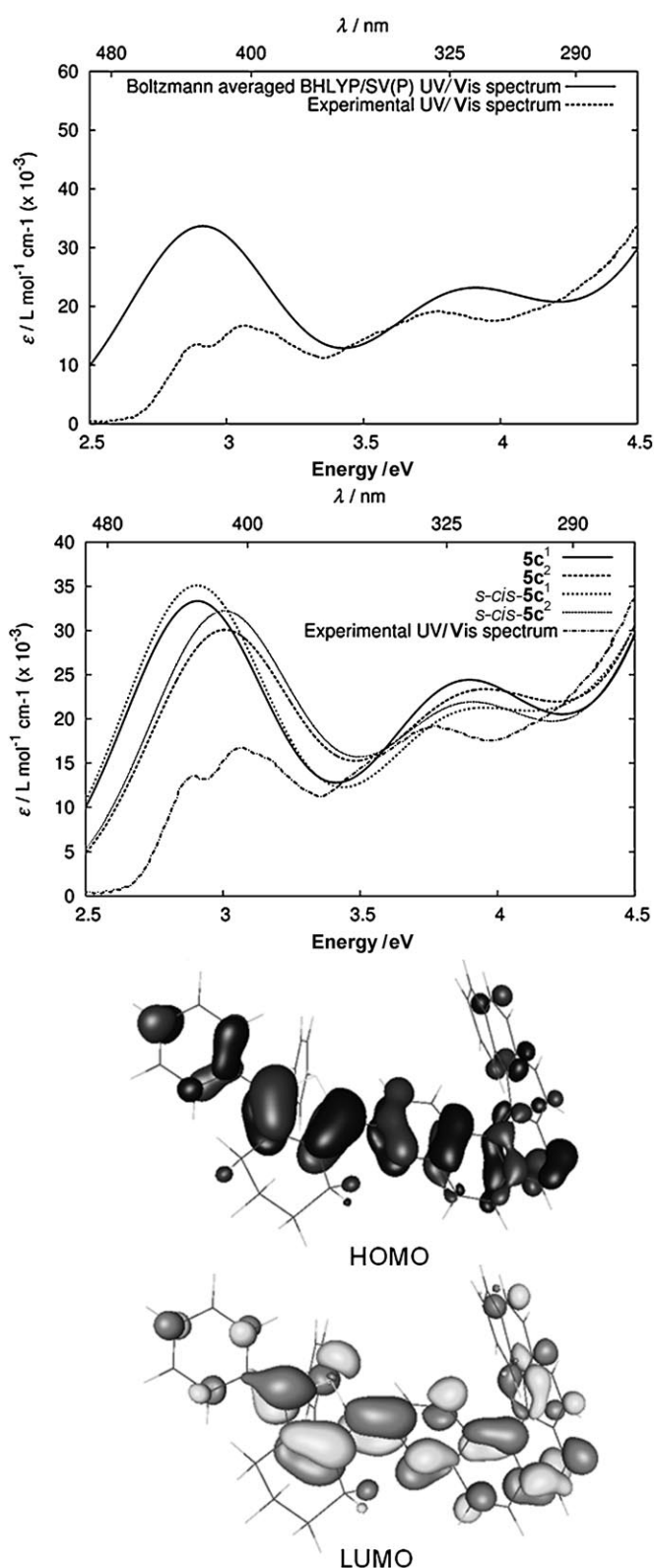


Figure 11. Boltzmann averaged BHLYP/SV(P) absorption spectrum of the phosphole ligands (top) and the spectra of the individual components (bottom). All calculated spectra are redshifted by 0.25 eV and Gaussian-broadened ($\sigma=0.26$). View of the HOMO and LUMO of (*P,S_p*)-*s-trans*-**5c**¹.

and of the individual conformers. The computed “stick” spectra were redshifted by 0.25 eV and Gaussian-broadened ($\sigma=0.26$). Absolute intensities are known to be difficult to reproduce computationally, and a deviation by a factor of two for absorption spectra is quite typical at the TDDFT level of theory. Likewise, spectral shifts on the energy scale of a few tenths of an electron volt are also not uncommon. Therefore, overall the calculated averaged spectrum agrees well with experiment within the predictive limits of the computational model. The analysis of the MOs involved in the main UV/Vis bands of **5c**^[36] is provided in Table 9. The

Table 9. UV/Vis analysis of optimized **5c**^[36] structure.^[a]

Excitation	Energy [eV]	Osc. str.	From-to	%
1	2.90	74.7	162–163	85.4
4	3.76	16.2	160–164	41.2
			162–165	12.0
			162–166	10.3
5	3.84	22.3	162–164	22.8
			161–164	17.0
			161–163	13.9
19	4.82	20.2	161–166	29.5
21	4.95	62.8	157–164	20.2
			159–164	17.3

[a] 157, 164 (PH); 159, 160, 162, 163, 165 (BPH); 161, 166 (H). BPH designates the categorization of the orbital: B(enzene)/P(hosphole)/H-(elicene). Excitation energies have been redshifted by 0.25 eV, and oscillator strengths scaled by a factor of 100.

HOMO–LUMO (162–163) are also depicted in Figure 11 and discussed below. The frontier orbitals of each ligand conformation appear quite similar; all are conjugated from the helicene through the phosphole and into the C-phenyl group.

As shown in Figure 12, within acceptable error bars for the intensities and overall energy shift, the calculated CD spectrum also agrees well with experiment. This computationally large system requires calculation of a significant number of excitations to cover the experimentally accessible frequency range. For BHLYP/SV(P), 120 calculated excitations extend only to the upper end of the experimentally recorded spectrum. Additional excitations were calculated to ensure that there is no influence from the higher-lying excitations near the high-energy cutoff of the spectrum.

The data from Figure 12 show a noticeable difference in intensity of the CD from **5c**¹ in the low energy regime. Compounds *s-cis*-**5c**¹ and *s-trans*- and *s-cis*-**5c**² have similar CD band positions and intensities with the applied broadening, but **5c**¹ has a much more intense and redshifted peak. There are also sizeable differences in the calculated MRs at 589.3 nm. The MR for *trans*-**5c**¹ is roughly 27 mru, whereas that of *cis*-**5c**¹ is about 17 mru; *trans*-**5c**² and *cis*-**5c**² have calculated MR values of approximately 11.7 and 16.4 mru, respectively. Below we investigate the reasons for these pronounced differences.

Influence of conjugation and substituents: The structure/chiroptical property relationship was investigated in detail for

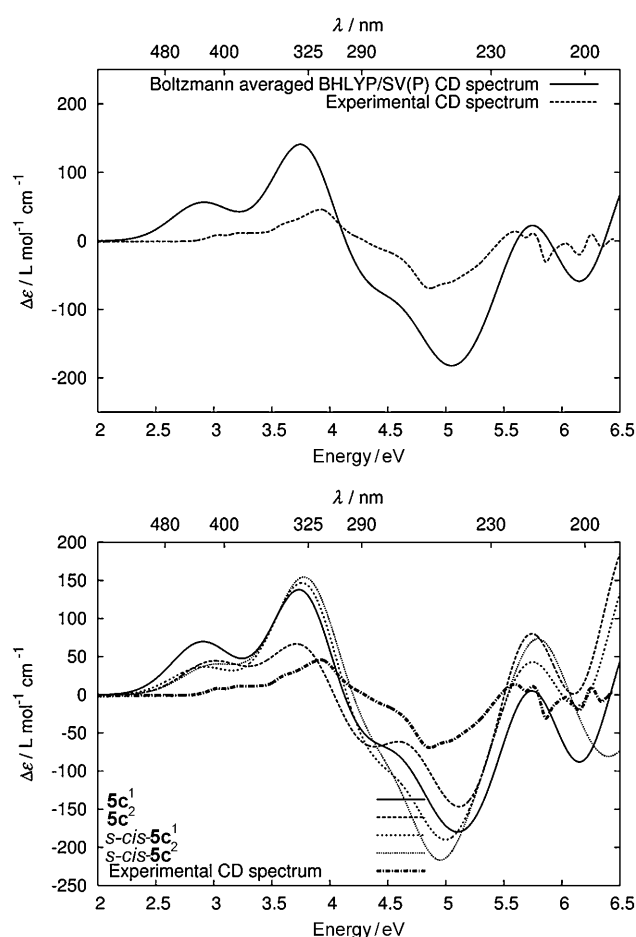


Figure 12. BHLYP/SV(P) CD spectrum of the Boltzmann-averaged phosphole ligands (top) and the individual components (bottom). All spectra are redshifted by 0.25 eV and Gaussian-broadened ($\sigma=0.26$).

mixed phosphole–azahelicene ligand **5c**. Four key features that significantly affect the molar rotation were theoretically studied, which we discuss individually below.

- 1) Conjugation of the ligand π system with the C-phenyl substituent of the phosphole ring: To study how the length of conjugation affects the MR, the terminal phenyl group of optimized **5c**¹ structure was rotated in 10° intervals (Figure 13). No further optimizations were performed at any of the rotation steps, and at each point the MR was calculated. There are two pronounced troughs when the C-phenyl group is not conjugated with the phosphole group (70–80° and 240–260°) and two peaks when the two moieties are conjugated (140–160°, 310–320°) in the rotation cycle. It is apparent in Figure 13 that the MR maxima have somewhat different values because the phenyl group is not perfectly symmetric with respect to the rotation axis (the atoms of the phenyl group at α and $\alpha+180^\circ$ have similar but not exactly the same locations). Taking the difference between the maximum and minimum peak values, the orientation of the C-phenyl group can contribute up to approximately 5 mru to the variations in the calculated MR.

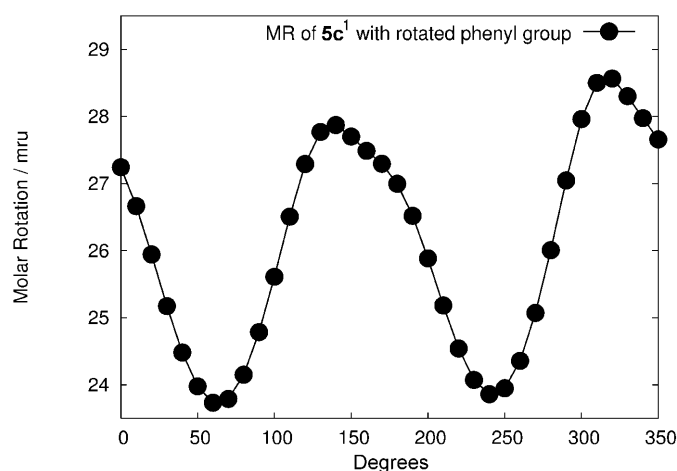


Figure 13. Molar rotation (589.3 nm) as a function of the rotation of the C-phenyl group for the optimized $5c^1$ ligand.

2) Conjugation of the helicene π system with the phosphole: To study the effect of the conjugation of the helicene π system with the phosphole, the optimized $5c^{1[36]}$ ligand was taken as a starting point. Subsequently, the phosphole group was rotated about the C–C bond of the N–C–C–P linking segment in 10° intervals. As before, no further optimizations were performed at any of the rotation steps, and at each interval the MR was calculated (Figure 14). We also considered scenarios in which the C-phenyl group has been rotated to be roughly parallel with the phosphole group (denoted $5c^{1\alpha}$), and approximately perpendicular (denoted $5c^{1\beta}$). These two models represent the extreme cases of allowing the conjugation of the π system to continue through the 5-phenyl group. All three systems have two peaks and two troughs in the

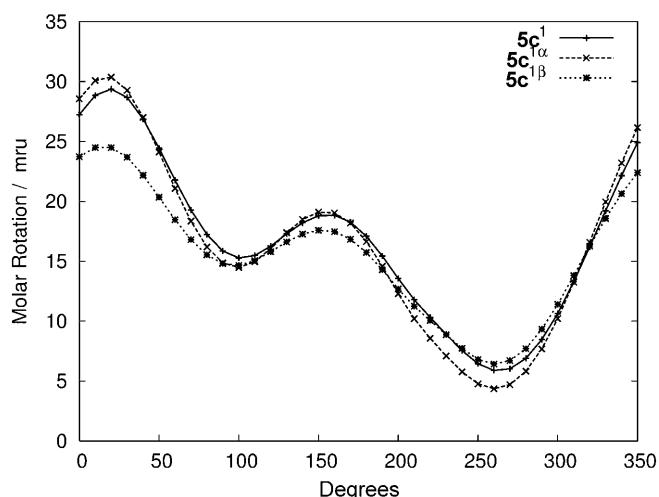


Figure 14. Molar rotation as a function of the rotation of the phosphole group about the C–C bond of N–C–C–P for the optimized $5c^1$ ligand. $5c^{1\alpha}$ indicates that terminal phenyl group is roughly parallel with the phosphole group, and $5c^{1\beta}$ indicates a perpendicular orientation.

rotation cycle. The geometries, which correspond to the phosphole groups being perpendicular to the helicene π system (cutting off the conjugation between the helicene and phosphole moieties), exhibit the lowest MRs. The effect is very pronounced, causing overall variations of about 25 mru.

3) Substituents attached to the phosphole moiety: To investigate how the *P*-phenyl group and the cyclohexane group fused to the phosphole influence the MR, we performed the same type of calculations as under point 2 while considering three different cases: a) the *P*-phenyl group is removed, b) the cyclohexane group is removed, c) both groups are removed. In each case the dangling bonds were hydrogen-capped with no further optimizations performed on any of these systems. The MRs for these structures as a function of the rotation angle of the phosphole moiety relative to the helicene, in comparison to $5c^1$ rotation, are shown in Figure 15. Clearly, the model without the cyclohexane group (i.e., with the *P*-phenyl group still attached) follows the response of the unaltered ligand the closest (see Discussion).

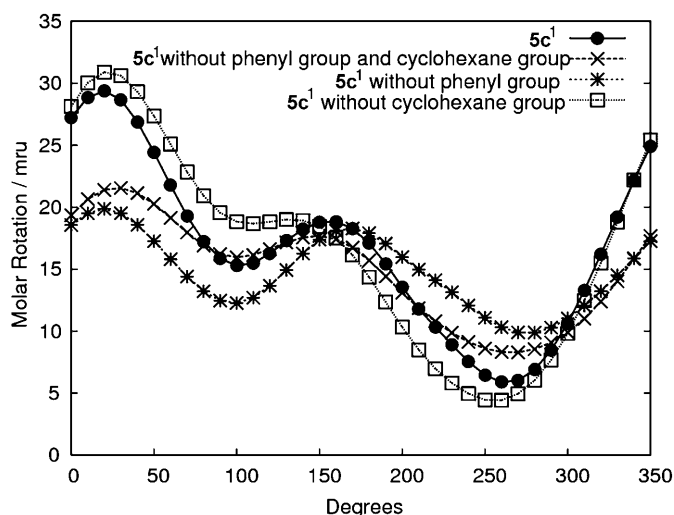


Figure 15. Molar rotation at 589.3 nm as a function of the rotation of the phosphole group about the C–C bond of N–C–C–P for the optimized $5c^1$ ligand, $5c^1$ with the cyclohexane group removed, $5c^1$ with the phenyl group (attached to P) removed, and $5c^1$ with both groups removed.

4) Location of the *P*-phenyl substituent relative to the helicene chromophore: Another key piece of information is how the same series of calculations turns out for the $5c^2$ derivative (phosphole inversion). The N–C–C–P dihedral angles of the $5c^1$ and $5c^2$ structures optimized to the same value within a few degrees. Therefore, the main difference between these isomers is the location of the *P*-phenyl group. Figure 16 shows the influence on the MR of the rotation of the phosphole moiety relative to the helicene moiety for $5c^1$ and $5c^2$. Diastereomers $5c^1$ and $5c^2$ have similar troughs and a similarly strong peak in the molar rotation for angles between 150 and 200°.

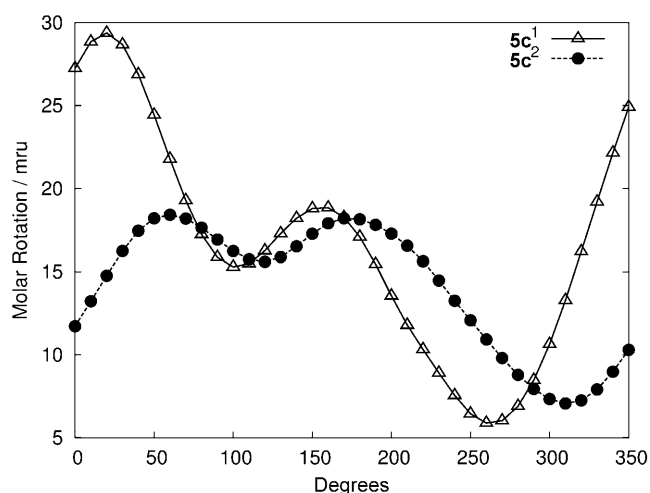


Figure 16. Molar rotation as a function of the rotation of the phosphole and helicene moieties about the C–C bond of N–C–C–P for the optimized **5c¹** and **5c²** ligands.

However, there is a distinctively large difference in the $0 \pm 60^\circ$ range. We therefore suggest that the location of the phenyl group is one of the main factors responsible for the lower MR of the optimized **5c²** structure compared to **5c¹**.

To further probe the influence of the location of the *P*-phenyl group on the MR, the optimized **5c¹** and **5c²** structures were each separated into two molecules, one azahelicene and one benzene (*P*-phenyl), kept where their carbon frameworks would be positioned in the optimized ligand structures and with the dangling bonds capped with hydrogen. The benzene moieties were then rotated with respect to the azahelicene in the same manner as the other rotation models (i.e., about what would be the C–C bond of the N–C–C–P dihedral angle). Figure 17 shows the calculated MRs as a function of the rotation angle. For comparison, the MR of an azahelicene molecule with a geometry as adopted in the **5c¹** ligand is approximately 11.9 mru, which is close to the experimental^[21a] value of 12.0 mru for *P*-hexahelicene. The B3LYP/SV(P)//BP/SV(P) calculated MR value for *P*-hexahelicene is also 12.0 mru.

Figure 18 depicts this model and demonstrates that the azahelicene substructures in **5c¹** and **5c²** are similar enough to compare directly. Figure 19 depicts the starting positions of the benzene rings in the model with respect to the azahelicene in the *R*-(**5c²**) and *S*-(**5c¹**) configurations of the ligands, viewed along the axis of rotation. Figure 17 shows the troughs for the **5c²**-like configuration to be in the $350 \pm 50^\circ$ range, and for the **5c¹**-like configuration at the $250 \pm 50^\circ$ range. Comparing this information to Figure 19, it is apparent that when **5c²** is in the 0° range, it is in the same quadrant as the azahelicene. The same is also true when the **5c¹**-like configuration is in the 270° range. The main inference is that when the phenyl group is spatially close to the terminal ring of the azahelicene then the MR will drop significantly.

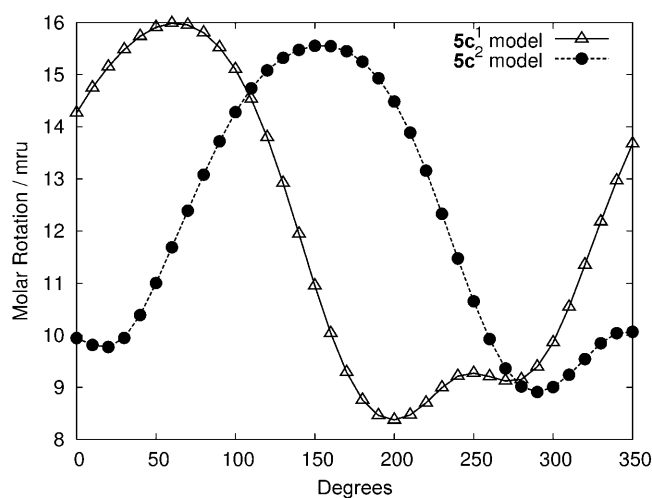


Figure 17. Molar rotation as a function of the rotation of benzene relative to azahelicene about an axis that would be the C–C bond of N–C–C–P for the optimized **5c¹** and **5c²** ligands.

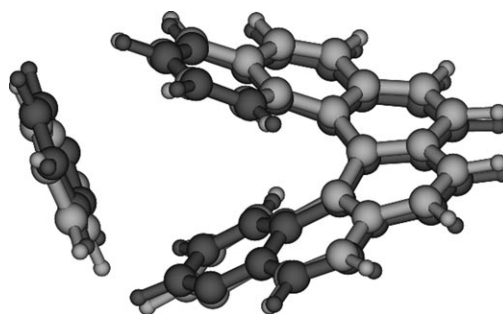


Figure 18. Benzene rotating around azahelicene; an overlay of the models derived from **5c¹** at 270° (lighter) and **5c²** at 0° (darker).

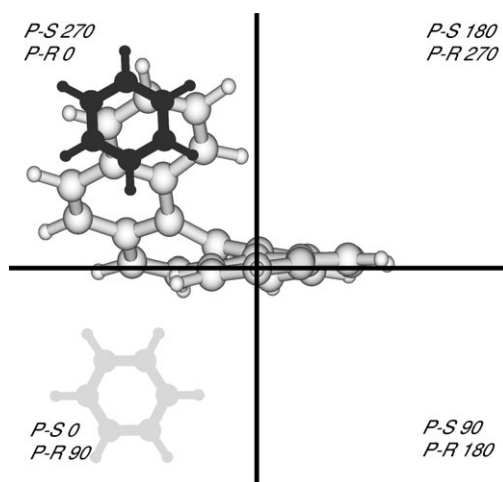


Figure 19. Depiction of the starting positions of benzene with respect to the helicenes for the rotation in the model of Figure 18 corresponding to **5c¹** (*P*–*S*, lighter) and **5c²** (*P*–*R*, darker). Locations at other rotation angles are also indicated by text. The view direction is along the axis of rotation. The molar rotations calculated as a function of the rotational angle are shown in Figure 17.

Structural analysis of $[\text{Cu}(\mathbf{5c})_2]^+$ and CD/MR calculations:

The Cu^{I} bis(aza[6]helicene phosphole) complex was examined in detail. Because no crystal structure of $[\text{Cu}(\mathbf{5c})_2]^+$ has been obtained, the geometry was built from two of the optimized $\mathbf{5c}^{\text{I}[36]}$ ligands, which were placed around the Cu center and further optimized. The copper center adopts a distorted tetrahedral geometry, so two metal configurations were considered: One structure has a Δ configuration with

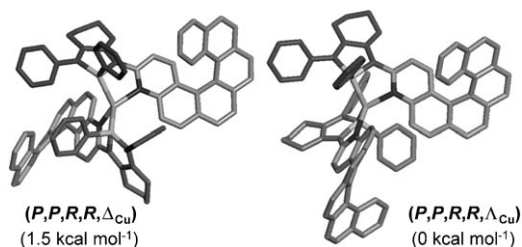


Figure 20. Optimized structures and relative energies for $[\text{Cu}_\Delta(\mathbf{5c}^{\text{I}})_2]^+$ and $[\text{Cu}_\Lambda(\mathbf{5c}^{\text{I}})_2]^+$ by DFT calculations.

respect to the metal center $[\text{Cu}_\Delta(\mathbf{5c}^{\text{I}})_2]^+$ and the other a Λ -configuration $[\text{Cu}_\Lambda(\mathbf{5c}^{\text{I}})_2]^+$ (Figure 20). At the BP/SV(P) level of theory (gas phase) $[\text{Cu}_\Lambda(\mathbf{5c}^{\text{I}})_2]^+$ is more stable than $[\text{Cu}_\Delta(\mathbf{5c}^{\text{I}})_2]^+$ by $1.5 \text{ kcal mol}^{-1}$. The energy difference is small. Within the error bars of DFT we cannot conclude that one of these conformers forms preferentially over the other. Next, CD calculations were performed. Comparing the calculated and experimental CD spectra, and considering the performance of the computations for the isolated ligand, the computations for both configurations can be considered to be in good agreement with experiment (Figure 21a). The result is that the calculations both for the Λ and the Δ Cu configurations are in similar agreement with the experimental CD spectrum. Based on the relative stability and similarity of the spectra, both species might be present in solution unless the synthesis yields one of the isomers preferentially.

We shall now discuss the contribution of the metal to the main transitions. Plots of selected MOs and the Cu-, P-, and N-centered natural localized molecular orbitals (NLMOs)

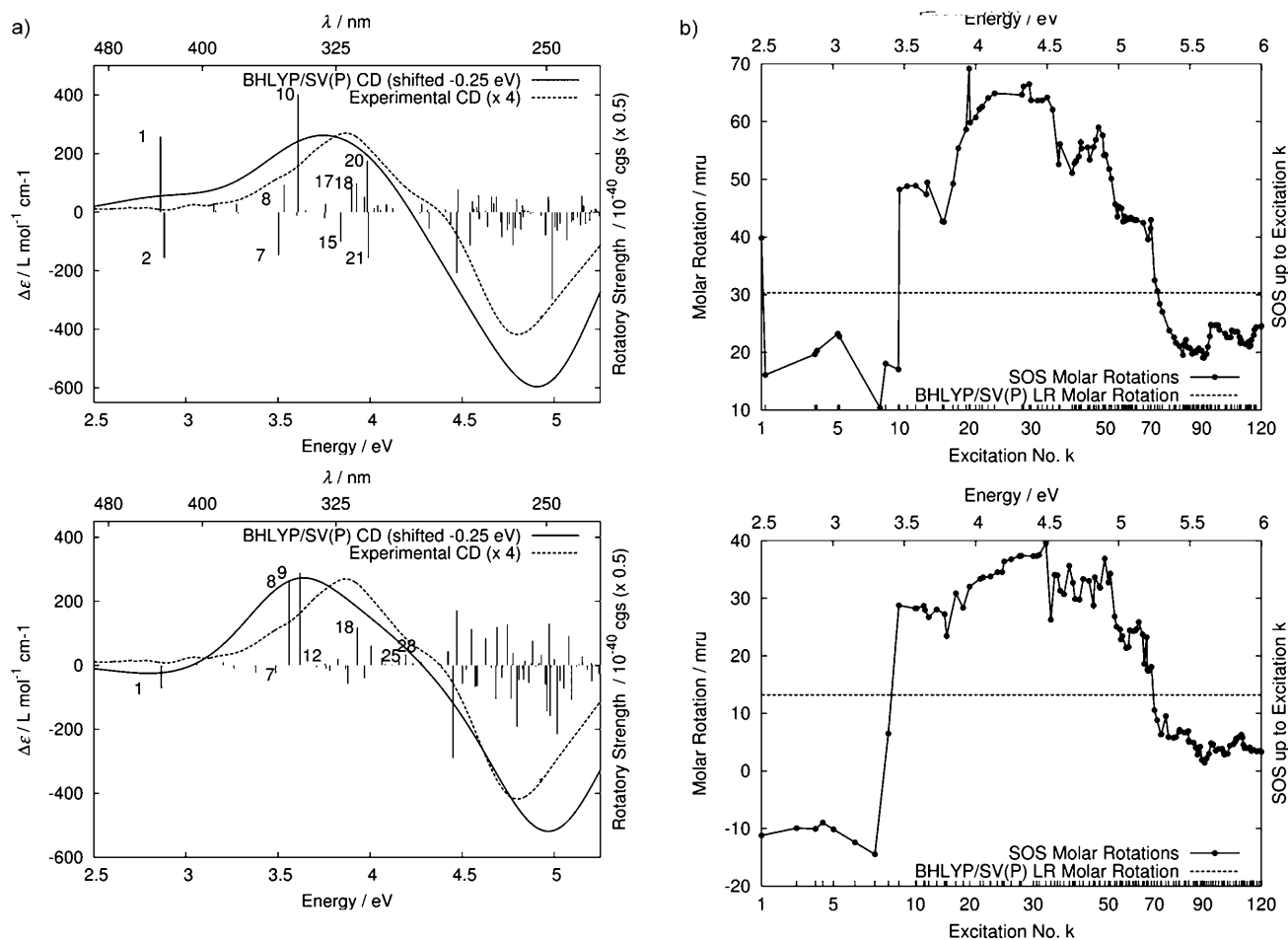


Figure 21. a) BHLYP/SV(P) CD spectrum of $[\text{Cu}_\Lambda(\mathbf{5c}^{\text{I}})_2]^+$ (top) and $[\text{Cu}_\Delta(\mathbf{5c}^{\text{I}})_2]^+$ (bottom). Numbered excitations are those selected for MO and SOS analysis. All calculated spectra are redshifted by 0.25 eV and Gaussian-broadened ($\sigma=0.26$). b) Partial SOS molar rotation for the $[\text{Cu}_\Lambda(\mathbf{5c}^{\text{I}})_2]^+$ (top) and $[\text{Cu}_\Delta(\mathbf{5c}^{\text{I}})_2]^+$ (bottom) configurations [Eq. (1)] plotted as a function of k , the number of excitations included in the SOS. The converged linear response BHLYP/SV(P) result is indicated by a dotted line.

are provided in the Supporting Information. Plots of the canonical MOs involved in some of the more intense transitions indicate that the Λ complex has more metal involvement than the Δ configuration. The NLMOs of the ground-state electronic structures of the two complexes show that the qualitative aspects of the metal–nitrogen and metal–phosphorus bonds are similar for both complexes. Although there are no formal Cu–N/P bonds assigned by the NBO program, the ligand “lone pair” orbitals pointing directly at the metal center clearly represent ligand–metal bonds, and therefore these NLMOs are identified with the metal–nitrogen bonds. The NBO procedure indicates little s–d mixing for Cu in the N/P–Cu bonds; the metal hybrid AOs involved in the bonds have more than 95 % s character in both $[\text{Cu}_\Lambda(\mathbf{5c}^1)_2]^+$ and $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$. The NBO algorithms assign the configuration of the metal center as $3d^{10}4s^{0.3}$ in both stereoisomers, that is, charge donation occurs from the ligands to the Cu^1 ion.

The metal contribution to each important transition and to the final MR was calculated for both the $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$ and the $[\text{Cu}_\Lambda(\mathbf{5c}^1)_2]^+$ diastereomers. By selecting the transitions involving the metal center and using an SOS method [Eq. (1)], the contributions to the optical rotation due to metal-centered excitations can be identified. After visually inspecting the MOs involved in these transitions they can be categorized as “partially metal centered”, delocalized “helicene–phosphole–benzene” (HPB), and any combination of delocalized “helicene/phosphole/benzene” (H/P/B) orbitals. “Helicene–phosphole–benzene” means that there are fragment orbitals involved from each of these groups to form extended conjugated MOs in the complex. Here, “partially metal centered” means considerable participation from one or more metal orbitals in addition to “helicene/phosphole/benzene”, as there are no purely metal frontier orbitals. Considering the second major positive CD band after the shoulder in the $[\text{Cu}_\Lambda(\mathbf{5c}^1)_2]^+$ complex (around 340 nm), eight excitations strongly contribute to the spectrum (rotatory strengths of at least $150 \times 10^{-40} \text{ esu}^2 \text{ cm}^2$). In the occunocc MO analysis, four of the excitations afford a contribution from a metal-centered MO that is greater than 10 % [per Eq. (3)]. Two of the excitations have a greater than 10 % contribution from π orbitals of the conjugated HPB backbone, and the other two contain no single MO-to-MO transition contributing 10 % or more. The strong mixing of MOs in the excitations was already seen in the ligand spectrum. The calculated partial MR of these eight excitations from the SOS method at the sodium D line is 33.7 mru, with a breakdown of 8.1 from partially metal centered MO transitions, 1.2 from HPB MO transitions, and 24.4 from numerous small contributions. From this data, approximately 24 % of the MR magnitude can be attributed to low-lying excitations with some metal involvement, a contribution of 3.5 % comes from the HPB-centered MOs, and the bulk of 73.5 % comes from numerous excitations that are not easily analyzed. Including all calculated excitations [$k=120$ in Eq. (1)] yields a reduction of the SOS rotation to 24.6 mru, as shown in Figure 21 b. The converged linear response value for this

isomer is 30.3. The experimental MR is only 13, which suggests the other isomer is likely dominant in solution.

Considering the lowest-energy positive CD band in the Δ complex, we find that there are no intense transitions, similar to above, that involve any of the partially metal centered orbitals. There are four weaker transitions in the calculated CD spectrum involving metal MO contributions greater than 10 %. Including these weak metal-centered transitions along with the intense transitions which do not involve a metal-centered orbital (see Figure 21 a, bottom), the SOS method yields a partial MR value of approximately 38.0 mru of which the metal-centered transitions contribute only -1.1 . For $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$ the dominant SOS contributions to the MR are transitions from the HPB backbone. Therefore, there must be negative partial MRs from numerous low-intensity transitions and/or higher lying excitations that bring the MR down to near the calculated value. Including all calculated excitations [$k=120$ in Eq. (1)], the SOS MR for the Δ complex from the experimentally accessible frequency range of the CD spectrum is on the order of 3.3 (see Figure 21 b). The converged calculated linear-response molar rotation is 13.2, which is close to the experimental value (13.1 mru).

The SOS results above do not completely quantify the metal involvement in the optical activity, because many of the partially metal centered (pMc) MOs extend over a large part of the conjugated ligand backbone, making it difficult to assess the metal contribution from the MO analysis. In addition to looking at the percentage contribution of the transitions from MO to MO [Eq. (3)], we also analyzed the excitations in terms of NLMO-to-NLMO contributions [Eq. (11)]. The individual percentages are small and the analysis yields many terms, but it helps to quantify the metal involvement in these transitions. For example, for excitation 7 of $[\text{Cu}_\Lambda(\mathbf{5c}^1)_2]^+$ the sum contribution of all transitions originating from occupied metal one-center NLMOs (metal lone pairs, one-center refers to the NLMO centered around one atom) is 14 %, that from metal two-center NLMOs (metal–ligand bonds) is 21 %, and that to the metal lone-pair one-center NLMOs is less than 1 %. The metal orbitals contribute a total of 35 % to this excitation. A truncated table of NLMO percentage contributions for the three complexes can be found in Tables 10–12. Note that the metal one-center unoccupied NLMOs (Table 10) include the formally unoccupied metal orbitals as identified by the NBO analysis, as well as some more diffuse Cu/Pd NLMOs that the program specifically identified as metal-centered. The tables indicate that, overall, the metal centers themselves do not contribute significantly to the intense CD excitations.

Experimentally, the low-energy CD band is very weak for the Cu complex, and compared to the Pd complex the Cu system has a much smaller MR. The SOS of the five lowest calculated excitations for $[\text{Cu}_\Lambda(\mathbf{5c}^1)_2]^+$ is 23.25, and for $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$ it is -10.13 mru. These excitations, which have less than 2 % total NLMO contribution from the metal, as mentioned above, distinguish the Λ and Δ configurations with an MR difference of over 30 mru. The experimentally

Table 10. NLMO-to-NLMO percentage contributions for selected transitions of $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$.^[a]

Excitation	Metal 1-center [%]	Metal-(N,P) 2-center [%]	Total [%]
1	1	1	2
2	1	1	2
7	14	21	35
8	16	22	38
10	1	1	2
15	2	2	4
17	9	9	18
18	6	7	13
20	3	4	7
21	2	2	4

[a] 1-center refers to the NLMO centered around 1 atom (i.e., a Cu lone pair). 2-center refers to a centering of 2 atoms (i.e., a Cu–N bond). All metal 1-center unocc. contributions for the above excitations are <1%, and have been omitted.

Table 11. NLMO-to-NLMO percentage contributions for selected transitions for $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$.^[a]

Excitation	Metal 1-center [%]	Metal 2-center [%]	Total [%]
1	1	1	2
2	1	1	2
7	16	27	43
8	1	2	3
9	0	1	1
12	11	16	27
18	4	5	9
25	6	8	14
28	4	5	9

Note: All metal 1-center unocc. contributions for the above excitations are <1%, and have been omitted.

Table 12. NLMO-to-NLMO percentage contributions for selected transitions for $[\text{Pd}_\Delta(\mathbf{5c}^1)_2]^{2+}$.

Excitation	Metal 1-center [%]	Metal 2-center [%]	Total [%]
1	0	0	0
2	0	0	0
9	5	18	23
17	0	1	1
18	1	2	3
19	1	1	2
20	0	0	0
23	0	0	0
32	0	0	0
35	0	0	0
36	1	3	4
38	0	1	1
50	0	0	0
58	1	0	1
59	0	0	0
60	1	0	1
62	0	0	0
70	1	0	1
72	1	1	2
83	1	2	3
87	0	0	0
90	1	3	4

[a] The majority of the metal 1-center unocc. contributions for the above excitations are <1% and have been omitted.

measured MR is about 13.1. The calculated linear-response MR for $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$ and $[\text{Cu}_\Delta(\mathbf{5c}^1)_2]^+$ are 13.23 and 30.34 mru, respectively, which are equivalent to the complete SOS within the excitation space allowed by the basis set. Figure 21a indicates that the excitations in this range dominate the MR at 589.3 nm. Overall, the data suggest that the involvement of the metal is relatively weak and does not directly contribute to the MR in a significant manner (see Discussion). However, the metal configuration dictates the structure of the ligand in the complex.

Using our helicene–benzene model from the ligand analysis (point 4), we can hypothesize that the MR is much higher for the Δ configuration, since it does not have any *P*-phenyl groups crowding near the helicene moiety, and that the MR is much lower for the Δ configuration, as it has a *P*-phenyl and a *C*-phenyl group (from the other ligand) spatially close to it.

Structural analysis of $[\text{Pd}(\mathbf{5c}_2)]^{2+}$ and CD/MR calculations:

For the structural stability calculations, NO crystallographic data of $[\text{Pd}(\mathbf{5c}_2)]^{2+}$ was available; therefore, the coordinates were built from two of the optimized $\mathbf{5c}^1$ ligands,^[36] which were placed around the Pd center and further optimized at the BP/SV(P) level of theory giving $[\text{Pd}_\Delta(\mathbf{5c}^1)_2]^{2+}$. A $[\text{Pd}_\Delta(\mathbf{5c}^2)_2]^{2+}$ complex was also built and optimized in the same manner. The geometry around Pd is distorted square-planar, so there is less room for the bound ligands than in the distorted tetrahedral copper complexes, which leads to significantly more steric repulsion. As a consequence, $[\text{Pd}_\Delta(\mathbf{5c}^1)_2]^{2+}$ is calculated to be approximately 19.4 kcal mol^{−1} more stable than $[\text{Pd}_\Delta(\mathbf{5c}^2)_2]^{2+}$, which shows a predisposition for two $\mathbf{5c}^1$ ligands binding to the Pd $_\Delta$ center over two $\mathbf{5c}^2$ ligands (Figure 22). Note that we did not converge a distorted

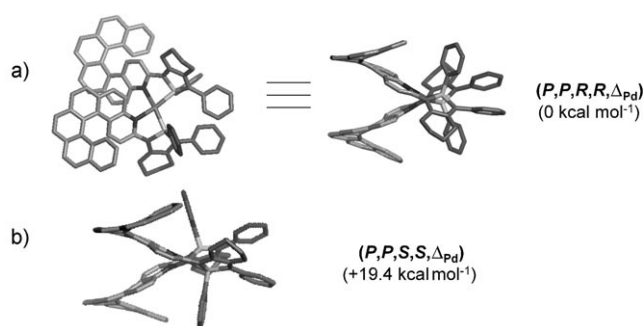


Figure 22. Optimized structures and relative energies for $[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ and $[\text{Pd}(\mathbf{5c}^2)_2]^{2+}$ from DFT calculations.

square-planar Pd center having a Δ configuration from two *P*-helicenes, which suggests that the helix configuration dictates the stereochemistry at the Pd^{II} center.

From the analysis of the calculated excitations,^[12a] the results confirm that the dominant contributions to the CD spectrum (Figure 23) are from π – π^* transitions involving phosphole/helicene/benzene MOs for the excitations having

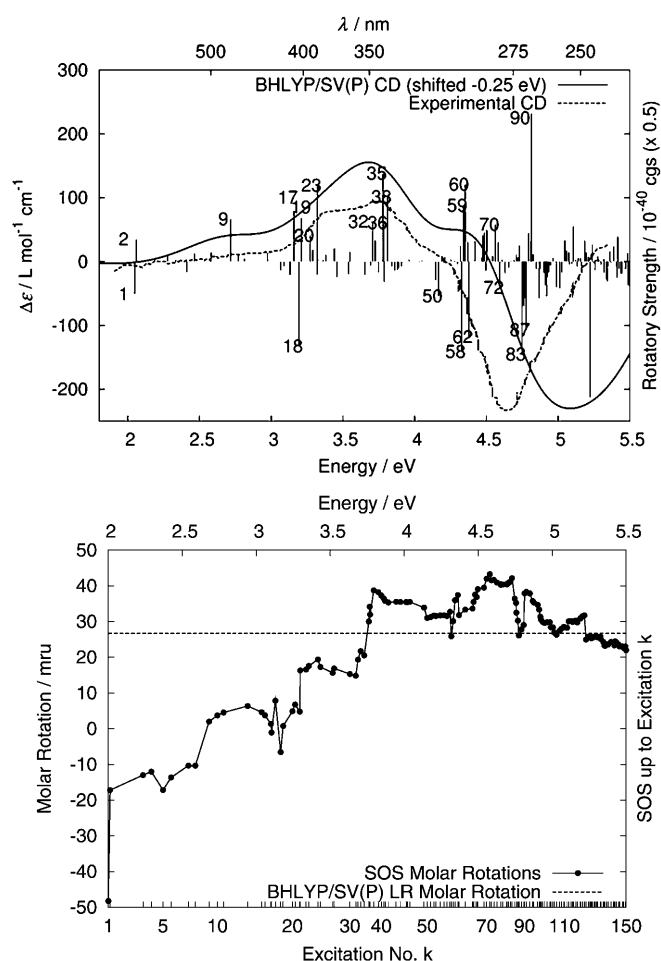


Figure 23. (Top) B3LYP/SV(P) CD spectrum of $[\text{Pd}_A(\mathbf{5c}^1)_2]^{2+}$ compared with experiment. Numbered excitations are those selected for MO and SOS analysis. (Bottom) Partial SOS molar rotation for $[\text{Pd}_A(\mathbf{5c}^1)_2]^{2+}$. Equation (1), plotted as a function of k , the number of excitations included in the SOS. The converged linear response B3LYP/SV(P) result is indicated by a dotted line. All calculated spectra are redshifted by 0.25 eV and Gaussian-broadened ($\sigma=0.26$). Compared to our previous communication^[12a] a larger number of excitations has been computed for this work, which affects the high-energy cut-off of the spectrum.

the strongest rotatory strength. There are numerous metal orbitals involved in various excitations, but with low percentage contributions. It is also noticeable that the CD strengths of the transitions that have the largest percentage of pMc MOs in the transition vectors tend to be relatively weak. Most of these excitations can be assigned as metal bonding to metal antibonding (LUMO) excitations.

As done for the copper complexes, we performed an NBO calculation and analyzed the NLMOs for the Pd complex. Several metal-centered NLMOs are illustrated in the Supporting Information. Again, the orbitals assigned by the NBO algorithms as ligand “lone pairs” pointing directly at the metal center represent the ligand–metal bonds. The NBO analysis indicates s–d mixing at the palladium center; the hybrid metal AOs involved in the bonds have 23 % s and 77 % d character. The NBO code assigns the configura-

tion of the metal center as $4d^95s^{0.4}$, that is, there is significant accumulation of electronic charge at the metal center compared to the formal Pd^{II} d^8 configuration, but the d shell is not completely filled. The MO analysis of the excitations correspondingly identified excitations with unoccupied orbitals having some metal 4d character.

Using the NLMO-to-NLMO percentage contributions to analyze the transitions previously investigated in terms of MO contributions^[12a] (Table 12) suggests that in the palladium complex metal orbitals contribute less to the intense excitations than was found for the Cu complex. Only one intense transition contains 23 % total contribution from metal-centered NLMOs; the rest have less than 5 %. The lowest eight excitations of $[\text{Pd}_A(\mathbf{5c}^1)_2]^{2+}$ have less than 2 % metal contribution according to the NLMO percentage contribution analysis. Using the SOS analysis, these first eight excitations yield a partial MR of -10.36 mru; adding in the ninth gives a partial MR of 1.97. The lowest 11 excitations, which make up the first CD band, give a partial MR of 4.52, and with all calculated excitations [$k=150$ in Eq. (1)] the partial MR is 21.95 mru. The bottom panel of Figure 23 shows that the first pair of calculated excitations contributes strongly to the MR, on the order of -20 mru. Both of these excitations have sizeable rotatory strengths, but they strongly cancel due to an excitation-energy difference of only 0.01 eV. The MO analysis shows that each of these excitations is dominated by a pair of HOMO- and HOMO–1-to-LUMO transitions (helicene-to-phosphole). The NLMO analysis (Table 12), indicates that there is $\ll 1\%$ metal contribution in either of these excitations even though the LUMO contains a metal-orbital contribution. Inclusion of additional calculated excitations slowly converges the SOS MR closer to the linear-response value. Considering the partial MRs, the calculated linear response MR of 26.66, and the NLMO analysis, the data suggest that the metal has little involvement in the MR at 589.3 nm.

The location of the phenyl groups with respect to the helicenes is the main correlation we can make between the optimized structures of $[\text{Pd}_A(\mathbf{5c}^1)_2]^{2+}$, $[\text{Cu}_A(\mathbf{5c}^1)_2]^+$, and $[\text{Cu}_A(\mathbf{5c}^1)_2]^+$. Looking at the relative helicene–helicene orientations of these three structures reveals no striking similarities that would allow us to make another analogy between the Pd and Cu complexes. Considering the previous discussion on how the phenyl groups of the phosphole ligands, and therefore of the copper complexes, affect the computed MR, we notice that in the $[\text{Pd}_A(\mathbf{5c}^1)_2]^{2+}$ structure phenyl groups attached to the P center are close to the azahelicene. They are not as close as in the $[\text{Cu}_A(\mathbf{5c}^1)_2]^+$ complex but not quite as far away as in $[\text{Cu}_A(\mathbf{5c}^1)_2]^+$. Since the phenyl–helicene orientation of $[\text{Pd}_A(\mathbf{5c}^1)_2]^{2+}$ is closer to that of $[\text{Cu}_A(\mathbf{5c}^1)_2]^+$, the calculated value of 26.60 falls in line with the results expected from this model. Within this model, it is the flexibility of Cu to adopt a distorted tetrahedral geometry which allows the phenyl groups to pack in next to the helicenes (in the Cu Δ configuration), and cause a lower MR than would be possible from a distorted square-planar geometry. It is also this flexibility that allows the phenyl

groups to position themselves further away from the helicenes (as in the Cu Λ configuration) in a manner that is similarly possible for a distorted square-planar configuration.

Discussion

Metal-mediated oxidative coupling of functional 1, n -diynes ($n=6,7$) followed by metal–dihalogenophosphine exchange is a versatile synthetic route towards phosphole derivatives.^[17] Considering that our target compounds are mixed phosphole azahelicenes that can act as 1,4-chelating ligands (Scheme 1), this general synthetic approach firstly requires the preparation of diynes bearing azahelicene substituents. This novel family of helicenes, including 4-azahelicenes substituted by a diyne at the 3-position and 5-azahelicenes substituted at the 6-position, was obtained by using a Sonogashira coupling–photocyclization–Wittig reaction sequence (Scheme 2). Note that functionalized azahelicenes are still rare,^[6] and that these results show that it is possible to conduct the photocyclization–oxidation sequence in the presence of potentially reactive triple bonds. The solid-state analysis of (–)-**4c** (Figure 1) reveals that the helical angle (angle between the terminal pyridyl and phenyl rings, 56.7°) as well as the C≡C distances (1.191–1.194 Å) are classical.^[6,17] These compounds display photophysical properties typical of regular helicenes (fluorescence at room temperature; fluorescence and phosphorescence at low temperature).^[4] Chiral diynes **4c,e** display different optical rotations. The specific rotation of compound **4e** is quite low ($[\alpha]_{\text{D}}^{23}=42.9$), as expected from its small helicoidal moiety, whereas that of **4c** is much higher ($[\alpha]_{\text{D}}^{23}=1660$) and comparable to those recorded for other aza[6]helicene derivatives.^[6]

Among the prepared mixed phosphole azahelicene derivatives (Scheme 1), **5a,b,d** can be regarded as model molecules, since their helicene moiety inverts at room temperature. The impact of the helicoidal system length on the helicoidal curvature (angle between the two terminal aromatic rings, hc), and therefore on the helicene inversion barrier, is nicely illustrated by comparison of the solid-state structures within the **5a–c** series (Tables 2 and 4, Figure 1). The benzo[f]quinoline part of **5a** is completely planar, the naphtho[1,2- f]quinoline part of **5b** displays a helical geometry with an hc of only 30.1°, while the hc of the aza[6]helicene fragment in **5c** is much more pronounced (45.8°; Figure 1). For all compounds, the P atom of the phosphole ring is pyramidalized (Σ angles around P, 296–302°) and, as is usually observed for 2-pyridylphosphole derivatives,^[17] the P and N atoms have an *s-trans* conformation in the solid state (Figure 1). The twist angles between the central phosphole ring and its aza[n]helicene and C-phenyl substituents are small enough ($<40^\circ$, Table 4) to allow electronic interaction between the three phenyl–phosphole–azahelicene π systems. Interestingly, only one pair of enantiomers is observed in the solid state for phospholes **5b,c** (Scheme 1), which exist as interconverting diastereomers in solution. Furthermore, the (P^*,S_p^*)-**5c**¹ diastereomer that crystallizes is that which

is predicted to be the most stable by the theoretical calculations (Table 3). In fact, there is roughly a 2.0–2.5 kcal mol^{–1} difference in energy between **5c**¹ and **5c**² (Table 3). These energies are sufficiently close (considering the error bars of relative DFT energies) to support the experimental observation of both phosphole configurations in solution by NMR spectroscopy. Note that the low inversion barrier at P determined by NMR spectroscopy for **5c** (16 kcal mol^{–1} at 330 K) is typical for those recorded in 1-phenylphospholes.^[15] The fact that P^* -phospholes exist as two isomers of comparable energy that interconvert at room temperature is a key property of this heterole that is of great importance for the diastereoselective formation of metal–bis(azahelicene phosphole) assemblies (vide infra).

The UV/Vis data of compounds **5a–e** (Figure 4) were investigated in order to probe the electronic interaction between the phosphole ring and the aza[n]helicene moieties. The presence of extended π systems in **5a–e** is suggested by the fact that their λ_{max} are bathochromically shifted compared to those of their 1,7-diyne precursors (Table 7). The absorption spectra of phospholes **5a,b** (bearing terminal azahelicenes) are considerably redshifted compared to those of **5d,e**, which have an inner pyridine moiety (Table 7, Figure 4). This behavior can be attributed to the fact that the former have longer, more extended π -conjugated systems than branched compounds **5d,e** (Scheme 1). It is noteworthy that a regular bathochromic shift occurs upon increasing the size of the pyridine-based π system (see the series 2-(2-pyridyl)phosphole **5f**/aza[4]helicene derivative **5b**/aza[6]helicene derivative **5c**; Scheme 1, Table 7). These differences clearly show the impact of the helicene composition on the optical properties of mixed phosphole azahelicene derivatives and indicate that these two π subunits are electronically coupled.

The above conclusion based on experimental data is confirmed by TDDFT calculations with the B3LYP functional and the SV(P) basis set that were conducted on **5c**, which bears the largest helicene moiety (Scheme 1). The calculated UV/Vis spectrum of the more stable (P,S_p)-*s-trans* isomer of **5c** (Table 3, Figure 1) well reproduces the experimental one, given a shift of –0.25 eV (Figure 11). Note that the Maxwell–Boltzmann averaged calculated spectrum (taking into account the relative contribution of all isomers of **5c**, Table 3) is similar to the experimental spectrum presented in Figure 11, within the error range of such calculations (see the Supporting Information). Strong calculated UV/Vis excitations of **5c**^{1,2} were analyzed (in and slightly above the experimental frequency range). For all stereoisomers, the lowest excitation (which is also responsible for the lowest positive CD band; vide supra) is predominantly a HOMO-to-LUMO transition of the π system (80% or greater contribution). Interestingly these molecular frontier orbitals involve both the azahelicene and the phosphole fragments (Figure 11). Likewise, all the other UV/Vis excitations are π – π^* transitions involving combinations of molecular orbitals of the π -system (HOMO–7 to LUMO+7 MOs) spreading over the helicene and phosphole moiety

(Figure 11). Surprisingly, even the high-energy transition at 4.7 eV, which is normally the π - π^* transition fingerprint of helicenes (see, for example, compounds **4b–d**, Table 7), is not pure but involves a complex mixture of molecular π orbitals that include the phosphole moiety (HOMO, HOMO–1, ...; see Supporting Information). Therefore, the different absorption bands cannot be attributed to localized excitations in the helicene or the phosphole moiety separately. This theoretical study therefore confirms the conclusion drawn from the UV/Vis experimental data that the π subunits of mixed azahelicene phosphole derivatives are strongly electronically coupled. The theoretical calculations reveal that the lowest absorption bands of *cis*- and *trans*-**5c**¹ are redshifted with respect to the corresponding bands of *cis*- and *trans*-**5c**². These data suggest that the configuration at the P atom impacts on the HOMO–LUMO gap of phosphole-based π -conjugated systems. Indeed, the calculated HOMO–LUMO gaps for *cis*- and *trans*-**5c**¹ (4.95 and 4.92 eV) are smaller than that of *cis*- and *trans*-**5c**² (5.05 eV). To the best of our knowledge, this is the first time that the influence of the configuration at P on the optical properties of phosphole-based π -conjugated systems has been demonstrated.

The emission behavior of mixed azahelicene phosphole derivatives **5b–d** is essentially comparable to that of the corresponding helicenes (fluorescence at RT; fluorescence plus phosphorescence at low temperature from helicene part) with an additional contribution of the fluorescent phosphole moiety. Note that the quantum yields of these phospholes bearing azahelicene substituents are much higher than that of the simple phosphole-(2-pyridyl) derivative **5f** (Table 7).

The coordination chemistry of phospholes **5b–d** was then examined. Before investigating the synthesis of rather sophisticated metal-bis(phosphole-aza[n]helicene) assemblies, it was necessary to check that phosphole-modified azahelicene bearing either a terminal (**5b**, Scheme 1) or an inner (**5d**, Scheme 1) P,N moiety can act as 1,4-chelating ligands towards transition metal centers such as PdCl₂ (Scheme 3). The NMR data of complexes [Pd(**5b/d**)Cl₂] are consistent with coordination of the mixed phosphole azahelicene ligands through their P and N atoms. This was confirmed by an X-ray diffraction study on [Pd(**5b**)Cl₂] (Scheme 3). The Pd^{II} center has an almost square-planar geometry with angles and bond lengths in the metallacycle comparable with those reported for other Pd^{II} complexes bearing 2-(2-pyridylphosphole) chelates.^[20] For example, the small twist angle between the phosphole ring and the azahelicene (18.1°) allows electronic interaction between these two π units. The helical shape of the aza[4]helicene part is not perturbed upon complexation, since the twist angle between the two terminal aromatic rings of the aza[4]helicene (33.1°) is comparable to that of the free ligand (30.1°). The phenyl substituent of the P atom and the aza[4]helix have a mutual *anti* arrangement with respect to the Pd^{II} coordination plane in order to minimize steric repulsion between these two phosphole substituents (Scheme 3). These results confirm that mixed phosphole azahelicene derivatives act as 1,4-che-

lating ligands towards metal centers and illustrate that, due to the ease of inversion at P, they can adapt their configuration in metal coordination spheres to minimize steric interactions.

The reaction of Pd²⁺ with two equivalents of phosphole pyridine derivatives **5b–d** affords the corresponding metal-bis(azahelicene phosphole) assemblies as single diastereomers according to multinuclear NMR data (Scheme 4). The stereoselective organization of the P,N ligands in the Pd^{II}-coordination sphere was investigated in detail by an X-ray diffraction study of complex [Pd(**5d**)₂]²⁺ (Tables 5 and 6) and theoretical calculations performed on complex [Pd(**5c**¹)₂]²⁺ (Table 6). The Pd^{II} center of complex [Pd(**5d**)₂]²⁺ shows a highly distorted square-planar geometry (vide infra) and, in accordance with the *trans* effect,^[12] the P and N atoms have a mutual *trans* arrangement (Scheme 4). The angle between the two N–Pd–P planes is 17.3°. This distortion, which is due to overlap of the two coordinated azahelicene moieties, results in a chiral coordination sphere around the Pd^{II} center with either a Λ or Δ configuration.^[12b] It is likely that the configuration at the metal is maintained in solution due to the overlap of the helices (Scheme 4), which prevents “flopping” of the ligands. Remarkably, amongst the numerous possible stereoisomers (2⁶), only one pair of enantiomers is obtained in the solid state ($M_{\text{helix } 1}, M_{\text{helix } 2}, S_{\text{P}1}, S_{\text{P}2}, \Delta_{\text{Pd}}$) and ($P_{\text{helix } 1}, P_{\text{helix } 2}, R_{\text{P}1}, R_{\text{P}2}, \Delta_{\text{Pd}}$). For obvious steric reasons, the phenyl substituents of the phosphole ligands are in *trans* position with respect to the PdN₂P₂ coordination plane, and the two azahelicene moieties are homochiral (Scheme 4). Indeed, as observed for [Pd(**5b**)Cl₂], the phosphole ring can adapt its configuration at P to minimize steric repulsion. This solid-state analysis shows that both electronic (*trans* effect) and steric (repulsion of phosphole substituents) features participate in the high stereoselectivity of the coordination process leading to Pd^{II}(phosphole aza[n]helicene)₂ assemblies (Scheme 4). It is furthermore likely that the hemilabile nature of P,N chelates **5b–d** is a clue to obtaining the more thermodynamically stable complex by establishing coordination–decoordination equilibria.

The structure of the aza[4]helicene moieties is not perturbed by their assembly into the dicationic Pd bis(phosphole azahelicene) complex. For example, the angles between the two terminal aromatic rings in [Pd(**5d**)₂]²⁺ (30.7 and 34.9°) are comparable to those of [Pd(**5b**)Cl₂] (30.1°). Finally, the rather large distance between the two helicenes (shortest inter-ring distance, 4.1 Å) indicates that no intramolecular π - π interaction takes place. An additional interesting point is the organization of complex [Pd(**5d**)₂]²⁺ into heterochiral columns in which each molecule stacks with its enantiomeric neighbor (Figure 2). This type of supramolecular organization, which is due to π stacking of the azahelicene moieties, is well known in helical molecules.^[1] This result shows that the presence of the metal center does not prevent metal phosphole aza[n]helicene complexes from behaving as regular helicene derivatives.

The formation of complex [Pd(**5c**)₂]²⁺ (Scheme 4) deserves discussion, since in this case the phosphole ligand

bears optically pure helix moieties. The fact that complex $[\text{Pd}(\mathbf{5c})_2]^{2+}$ is obtained as a single enantiomer starting from $(P,R_p^*)\text{-}\mathbf{5c}$ or $(M,R_p^*)\text{-}\mathbf{5c}$ shows that the configuration of the helix controls the configuration of the other stereogenic centers, that is, the phosphole P and Pd atoms. This is nicely confirmed by the fact that calculations at the BP/SV(P) level of theory performed for the ligand having a *P*-helix revealed that the $[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ assembly, in which the P atom has *R* configuration and the configuration around the Pd center is Δ , is 19.4 kcal mol⁻¹ more stable than its $S_P\Delta_{Pd}$ diastereomer $[\text{Pd}(\mathbf{5c}^2)_2]^{2+}$ (Figure 22). Furthermore, the complex having a Λ_{Pd} configuration (*P*-helix, R_P) is not a minimum on the potential-energy surface. This theoretical study confirms the high stereoselectivity of the coordination process and allows one to establish unambiguously that only $(P,P,R_P,R_P\Delta_{Pd})\text{-}[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ and $(M,M,S_P,S_P\Lambda_{Pd})\text{-}[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ complexes were formed (Scheme 4). The large energy difference between the different diastereomers (Figure 22) can be attributed to steric factors, as suggested by the fact that the square-planar Pd^{II} coordination sphere of $[\text{Pd}(\mathbf{5c}^2)_2]^{2+}$ is much more distorted than that of $[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ (twist angle between the N-Pd-P planes: $[\text{Pd}(\mathbf{5c}^2)_2]^{2+}$, 54.8°; $[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$, 24.7°). In fact, the metric data of the PdN₂P₂ core of $[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ (Figure 22) fit well with those of complex $[\text{Pd}(\mathbf{5b})_2]^{2+}$ established by X-ray diffraction studies (Table 6).^[12b] These data suggest that there is no steric stress associated with the assembly of phosphole-modified [6]helicene ligand **5c** in the Pd coordination sphere. The curvature of the helices is retained in the coordination sphere of the metal (**5c**, 45.8°; theoretical calculations, 49.5°), and the two twist angles between the coordinated phosphole and the pyridine rings of 19.4 and 23.4° allow electronic interaction between the phosphole and the azahelicene π systems to take place. In conclusion, the coordination of the mixed phosphole azahelicene derivatives to a d⁸ Pd^{II} center is highly stereoselective due to a unique combination of specific electronic (*trans* effect), steric (presence of the bulky helicene and *P*-substituent), and dynamic (fast inversion at P) properties. This result clearly shows that, in spite of their peculiar structures and the presence of sterically demanding azahelicene substituents, the heteroditopic P,N chelating moieties including a phosphole moiety dictate the coordination behavior of **5b–d** towards the square-planar Pd²⁺ ion and allow a highly stereoselective coordination process to take place.

The next step was to investigate whether, using the same azahelicene phosphole ligands, metal-bis(phosphole-aza[*n*]helicene) assemblies with different topologies could be obtained by varying the nature of the metal center. For this purpose d¹⁰ tetrahedral Cu^I complexes were prepared (Scheme 5). The chiral Cu^I centers display a distorted tetrahedral geometry with the two azahelicenes having an almost perpendicular arrangement (angle between the two N-Cu-P planes: $[\text{Cu}(\mathbf{5b})_2]^+$, 83.7°; $[\text{Cu}(\mathbf{5d})_2]^+$, 86.4°; Scheme 5). The Cu–P and Cu–N distances, as well as the P,N bite angles, are unremarkable (Tables 5 and 6). Note that the Cu^I atoms are stereogenic centers with spiro-type chirality, leading to

either Λ or Δ configuration.^[38] Among the numerous theoretically possible diastereomers, only two for complex $[\text{Cu}(\mathbf{5b})_2]^+$ and one for $[\text{Cu}(\mathbf{5d})_2]^+$ were found in the solid state. Furthermore, the two diastereomers of $[\text{Cu}(\mathbf{5b})_2]^+$ differ only by the conformation of the flexible $-(\text{CH}_2)_4-$ moiety grafted onto the phosphole rings. Therefore, if one focuses on the metal coordination sphere, only the $(M_{\text{helix1}}, P_{\text{helix2}}, R_{P1}, R_{P2}, \Delta_{\text{Cu}})$ and $(P_{\text{helix1}}, M_{\text{helix2}}, S_{P1}, S_{P2}, \Lambda_{\text{Cu}})$ diastereomers are observed. These solid-state studies speak for the fact that the coordination process leading to the Cu^I complexes is stereoselective. However, it is difficult to draw helpful conclusion from these experimental data, since these complexes contain two heterochiral helicene moieties, whereas our approach is to use optically pure helicene ligands that will afford complexes with homochiral helicene moieties. In fact, DFT calculations at the BP/SV(P) level revealed that the energy difference between the diastereomeric Λ and Δ $[\text{Cu}(\mathbf{5c}^1)_2]^+$ complexes bearing the P,N ligands with an enantiomerically pure *P*-helix is quite small (ca. 1.5 kcal mol⁻¹).

These results demonstrate that modification of azahelicenes by a phosphole moiety to generate chelating P,N fragments that can coordinate to metal centers is a versatile approach to readily generate structural diversity. In fact, starting from one programmed heteroditopic P,N helicene, air-stable chiral metal-bis(phosphole-aza[*n*]helicene) assemblies can be readily obtained on coordination to metal ions having different coordination geometries. Theoretical and experimental results show that the coordination is highly stereoselective in the case of square-planar metal centers.

Complexes $[\text{Pd}(\mathbf{5c})_2]^{2+}$ and $[\text{Cu}(\mathbf{5c})_2]^+$ exhibit very different chiroptical properties. The former has a much higher specific molar rotation than the latter (Table 8). Likewise, the CD spectrum of the palladium complex is globally more intense than that of the copper analogue (Figure 9). Furthermore, the CD spectrum of Pd^{II} assembly $[\text{Pd}(\mathbf{5c})_2]^{2+}$ displays intense bands at about 370 nm as well as weak bands at low-energy wavelengths (410–450 nm) that are not observed for $[\text{Cu}(\mathbf{5c})_2]^+$ (Figure 1). These results clearly show that 1) it is possible to perform coordination-driven tuning of chiroptical properties of phosphole-modified azahelicenes, and that 2) it is more efficient to organize these heteroditopic ligands around a d⁸ square-planar metal center than around a tetrahedral one.

Regarding the optical activity of these metal-bis(phosphole-aza[6]helicene) assemblies, the main questions are: 1) do metal orbitals directly participate in the excitations, or is the only role of the metal to keep the ligands in their relative positions? 2) If so, does the metal boost the molar rotation? 3) Does the nature of the metal dictate specific relative arrangements of the ligands that may boost or quench the optical activity in the complex? The confrontation between the experiments and the theoretical calculations enabled us to resolve all these questions.

The computed^[12a] CD spectrum of $[\text{Pd}(\mathbf{5c}^1)_2]^{2+}$ calculated for the most stable diastereomer $(P,P,R_P,R_P\Delta_{Pd})$ agrees very well with the experimental CD of $(+)\text{-}[\text{Pd}(\mathbf{5c})_2]^{2+}$ after a

redshift of 0.25 eV (Figure 23). Therefore the absolute configuration (*P,P,R_pR_pΔ_{Pd}*)-(+)) can be ascertained for Pd^{II}-bis-(aza[6]helicene phosphole) assemblies. The over-/underestimation of the CD intensity of the bands at 330 and 250 nm, respectively, is similar to the case of free hexahelicene.^[21] On the other hand, the computed CD of diastereomers (*P,P,R_pR_pΔ_{Cu}*)-[Cu(**5c**¹)₂]⁺ and (*P,P,R_pR_pΛ_{Cu}*)-[Cu(**5c**¹)₂]⁺ both reproduce reasonably well the experimental CD spectrum of (+)-[Cu(**5c**)₂]⁺ (after a redshift of 0.25 eV, Figure 21a), so that the absolute configuration of Cu^I-bis-(aza[6]helicene phosphole) assemblies cannot be determined by means of CD calculations. Interestingly, the CD spectra of the two diastereomeric Cu^I complexes are similar. An important aspect is that, both in the Pd^{II}- and the Cu^I-bis-(aza[6]helicene phosphole) assemblies, the most intense CD bands involve essentially π-π* transitions of the extended phosphole-azahelix π systems. In the MO-MO transitions having the highest CD values, the metal centers contribute to many transitions (Tables 10–12 and Supporting Information) but to a smaller extent than the phosphole azahelix π system. In the [Pd(**5c**)₂]²⁺ complex, the Pd^{II} center contributes in particular to the low-energy tail of the first CD band through partial metal-to-ligand charge transfer (excitation 9, Table 12 and Figure 23). However, there is no such contribution in the case of [Cu(**5c**)₂]⁺, for which low-energy CD bands involving the metal center are not observed (excitations 1 and 2, Tables 10 and 11 and Figure 21a). These results show that overall the metal contribution to the CD is much more important for the Pd than for the Cu assemblies.

The molar rotations of Pd^{II}- and the Cu^I-bis-(aza[6]helicene phosphole) assemblies were investigated by TDDFT calculations. The experimental molar rotation for the Pd complex (*P,P,R_pR_pΔ_{Pd}*)-[Pd(**5c**¹)₂]²⁺ of 23 mru compares well with the calculated value for molar rotation of (*P,P,R_pR_pΔ_{Pd}*)-[Pd(**5c**²)₂]²⁺ built from two phospholes (*P,S_p*)-**5c**¹ (26.7 mru). If we use the structure built/optimized from phosphole (*P,R_p*)-**5c**², then a molar rotation of -9245 is obtained. These results not only confirm the absolute configuration assignment (*P,P,R_pR_pΔ_{Pd}*)-(+)) for [Pd(**5c**)₂]²⁺, but more importantly bring to light the high sensitivity of the molar rotation to the diastereomeric structure of Pd^{II}-bis-(aza[6]helicene phosphole) assemblies. This is also true in the case of Cu^I-bis-(aza[6]helicene phosphole) assemblies, for which (*P,P,R_pR_pΔ_{Pd}*)-[Cu(**5c**¹)₂]⁺ has a calculated MR value of 30 mru, while the calculated MR of (*P,P,R_pR_pΔ_{Pd}*)-[Cu(**5c**¹)₂]⁺ of 13.2 mru is very close to the experimental value (13.1 mru). In fact, the latter diastereomer displays the topology encountered for [Cu(**5b**)₂]⁺ and [Cu(**5d**)₂]⁺ in the solid state (Scheme 4). Nevertheless, it is difficult to conclude on the stereochemical assignment of [Cu(**5c**)₂]⁺ only on the basis of molar rotation calculations. The results indicate that the isomer with the smaller metal contribution in the orbitals and in the intense excitations has the lower molar rotation and agrees well with experiment. However, since the overall participation of the metal orbitals in the optical activity of the Cu complex does not appear dominant, the question arises whether the role of the metal is

more important in the sense that it also dictates the relative positions of the ligands. Indeed, the fact that the MR depends significantly on the stereochemistry and the shape of the complex is an important issue that is evidenced in our TDDFT calculations, and this conclusion encouraged us to go back to the phosphole structure, which is easier to investigate by theoretical calculations.

The key to better understanding the optical properties of the copper and palladium complexes lies predominantly in the characteristics of the π system and the conformational flexibility of the phosphole ligands. By studying the aspects that affect the MR of the ligand, we can notice trends and offer valuable insight into the metal complexes. Among a variety of possibilities, we have identified four key features that significantly affect the MR of the ligands and have implications for the optical activity of metal-bis(aza[6]helicene phosphole) assemblies.

First, the MR calculations on aza[6]helicene phosphole **5c** show that the optimized diastereomeric structures have very different MR values (*trans*-**5c**¹, 11.7 mru; *cis*-**5c**², 16.4 mru). Furthermore, conjugation through the 5-phenyl group can quite significantly impact the MR value of **5c**, although not in the same magnitude as the conjugation between the phosphole and the aza[6]helicene moieties, for which the MR values span a range of approximately 25 mru (as compared to only about 5 from 5-phenyl rotation in Figures 13 and 14). The maximum MRs are obtained when the phosphole group is in conjugation with the helicene π system. If we consider the **5c**¹ structure, there are two other groups which can perturb the system: the *P*-phenyl group and the cyclohexyl group fused to the phosphole. From Figure 15 it is clear that the extent of conjugation within the molecule with the cyclohexane group removed (i.e., the *P*-phenyl group still present) follows the MR of **5c**¹ more closely over the range of rotations. From investigating the ligands, removal of the *P*-phenyl group (PPh→PH) seems to have a more profound effect in relation to its proximity to the azahelicene group. The HOMOs of the optimized ligands have a node in the π system located at the P atom (see Supporting Information). The *P*-phenyl carbon atom, however, makes some contribution to the LUMO of the optimized ligands. On the other hand, the cyclohexane group does not significantly contribute either to the HOMO or to the LUMO. Unlike the *P*-phenyl group, its removal does not impact the frontier orbitals of the π system which we consider to dominate the MR. To summarize, conjugation from the helicene through the phosphole group can noticeably affect the molar rotations, and even more so if the conjugation continues through the terminal phenyl group. The substituents on the phosphole group also affect the MR, both via direct electronic effects on the frontier orbitals of the conjugated π system, and more indirectly via through-space interactions with the helicene moiety. Indeed, we have observed that the *P*-phenyl group plays a particularly important role, causing the MR to drop significantly in magnitude when it is in spatial proximity to the azahelicene. This suggests that the location of the phenyl group is one of the

main factors responsible for the lower MR of the optimized **5c**² structure compared to **5c**¹.

At this stage, we can correlate the factors influencing the MR of the [Cu_Δ(**5c**)₂]⁺ and [Cu_Λ(**5c**)₂]⁺ complexes with the position of their phenyl groups relative to the helicene moieties. If we consider the four points influencing the CD of phosphole **5c**, some interesting results might be expected. Considering the structure of [Cu_Λ(**5c**¹)₂]⁺ (Figure 20) the phenyl groups are not stacked next to the helicene moiety. The models from the previous sections would predict that 1) removing the phenyl groups attached to the P center should not dramatically alter the MR, since there is no phenyl group near the azahelicene lowering the MR, and 2) further removing the terminal phenyl groups should make the MR lower due to decreasing the extent of π conjugation. This is exactly the trend seen from the calculations. The MR values for [Cu_Λ(**5c**¹)₂]⁺ with the *P*-phenyl groups removed (PPh→PH), and then with further removal of the terminal phenyl groups are 30.3, 33.5, and 23.2 mru, respectively.

In the optimized [Cu_Δ(**5c**¹)₂]⁺ structure, on the other hand, two phenyl groups are in close proximity to the azahelicene (Figure 20). This could be the cause of the low MR for this isomer. It is actually the terminal phenyl group of one ligand that is closest to the azahelicene of the other ligand. Considering these facts, the ligand model would predict that 1) removing the phenyl groups attached to the P center should increase the MR, since there is a phenyl group near the azahelicene lowering the MR, and 2) further removing the 5-phenyl groups should make the MR even higher because it is these groups that are closest to the azahelicene (despite having shortened the length of conjugation). This is, again, exactly the trend seen from the calculations. The MR values for [Cu_Δ(**5c**¹)₂]⁺ with *P*-phenyl groups removed, and then with further removal of the terminal phenyl groups are 13.2, 26.9, and 37.7 mru, respectively. Considering these phenyl-group configurations, a ligand without phenyl groups would cause MRs of the Δ and Λ isomers that are more similar than those calculated for the full systems. However, these isomers would still be quite unique: with all phenyl groups removed the MRs of the two isomers still differ by more than 10 mru.

The Pd system was investigated by us in a previous short communication,^[12a] mainly to assign the CD spectrum. It was noted that the low-energy tail of the CD spectrum involved MO contributions with some metal character, but so far it has been unclear what the exact role of the metal orbitals in the molar rotation of the complex is. The experimentally measured MR for [Pd(**5c**¹)₂]²⁺ is approximately +23.1 mru. The computed MR value for [Pd_Δ(**5c**¹)₂]²⁺ is 26.6, and that for [Pd_Δ(**5c**²)₂]²⁺ −9.2 mru. These results clearly indicate that the structure of the Pd complex in solution can be unambiguously assigned as containing two **5c**¹ centers and a Δ configuration at the Pd center and shed light on the high stereoselectivity of formation of the Pd^{II}–bis(aza[6]helicene phosphole) assembly.

Conclusion

A series of aza[*n*]helicene phospholes has been prepared, and the photophysical properties of these π -conjugated compounds investigated. The chiroptical properties of aza[6]helicene phosphole **5c** were examined in detail. The influence of the π substituents on the chiroptical properties of aza[6]helicene phosphole **5c** is examined theoretically. Indeed, 1) by modifying the dihedral angles between the phosphole ring and the substituents in the 2- and 5-positions of **5c** (aza[6]helicene and phenyl), the conjugation path is varied and influences the molecular rotation (MR); 2) the position of the *P*-phenyl group relative to the aza[6]helicene, depending on the *S_p* or *R_p* configuration, shows a significant influence on the MR. We found that the azahelicene phospholes are interesting systems not only in their own right but also as ligands in metal complexes. The coordination chemistry of aza[*n*]helicene phospholes as new 1,4-P,N chelating ligands enabled the preparation of Pd^{II}– and Cu^I–bis(aza[*n*]helicene phosphole) assemblies. In the case of the Pd complexes, experimental and theoretical studies revealed high stereoselectivity thanks to a combination of electronic (*trans* effect) and steric (repulsion of the *P*-Ph substituents and the azahelicenes) factors in the metal coordination sphere. The chiroptical properties of [Pd(**5c**)₂]²⁺ and [Cu(**5c**)₂]⁺ have been compared by means of TDDFT calculations, which showed that the metal makes small contributions to the CD absorption values and that the role of the metal atom in such complexes is to organize the aza[6]helicenes in space relative to each other. Indeed, it has been demonstrated that the proximity in space of the phenyl groups to the helicene moieties significantly influences the MR values of the metal–bis(aza[6]helicene phosphole) assemblies.

Experimental Section

General information: All experiments were performed under an atmosphere of dry argon by using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). PPhBr₂ was prepared as described in the literature.^[40a] Irradiation reactions were conducted with a Heraeus TQ 150 mercury vapor lamp. Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016 A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063–0.200 mm) in 3.5–20 cm columns. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker AM300 and DPX200 spectrometers. ¹H and ¹³C NMR chemical shifts are reported in parts per million (ppm) relative to Me₄Si as external standard. ³¹P NMR downfield chemical shifts are expressed with a positive sign in ppm, relative to external 85% H₃PO₄ and are proton-decoupled. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1. CD Specific rotations (in deg cm² g^{−1}) were measured in a 1 dm thermostated quartz cell on a Jasco-P1010 polarimeter. Circular dichroism (in m^{−1} cm^{−1}) was measured on a Jasco J-815 Circular Dichroism Spectrometer. Derivatives **2c** to **5c** and their Pd^{II} and Cu^I complexes were prepared as described in ref. [12a].

Determination of optical data: UV/Vis spectra were recorded at room temperature on a UVIKON 942 or a Biotek Instruments XS spectrophotometer in quartz cuvettes of 1 cm path length.

Steady-state luminescence spectra were measured on a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube; the spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Samples for emission measurements were contained within quartz cuvettes of 1 cm path length modified with appropriate glassware to allow connection to a high-vacuum line. Degassing was achieved by a minimum of three freeze–pump–thaw cycles whilst connected to the vacuum manifold; final vapor pressure at 77 K was $<5 \times 10^{-2}$ mbar, as monitored with a Pirani gauge. Luminescence quantum yields were determined by the method of continuous dilution, with quinine sulfate in 1 M H_2SO_4 or $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (bpy = 2,2'-bipyridine) in air-equilibrated aqueous solution as standard ($\phi = 0.548$ and 0.028 respectively); estimated uncertainty in ϕ is $\pm 20\%$ or better.

Luminescence lifetimes shorter than 10 μs were measured by time-correlated single-photon counting (TCSPC) following excitation at 374.0 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at 90° with a Peltier-cooled R928 photomultiplier tube after passage through a monochromator. Phosphorescence lifetimes longer than 10 μs were measured by multichannel scaling following excitation with a pulsed xenon lamp. Measurements at 77 K were carried out in a diethyl ether/isopentane/ethanol (2:2:1 v/v) matrix in 4 mm o.d. tubes in a liquid-nitrogen dewar.

6-(8-Phenylocta-1,7-diyn-1-yl)pyridine 2-carboxaldehyde (1a): $[\text{PdCl}_2(\text{PPh}_3)_2]$ (94 mg, 134 μmol , 5%), CuI (25 mg, 134 μmol , 5%), and $i\text{Pr}_2\text{NH}$ (11 mL, 97 mmol) were added to a stirred solution of 2-bromopyridine-carboxaldehyde (500 mg, 2.68 mmol) in anhydrous THF (10 mL) at room temperature under argon. After 5 min, 1-phenyl-octa-1,7-diyne (489 mg, 2.68 mmol) was added. The resulting mixture was stirred overnight. Evaporation of the solvents under reduced pressure and purification by column chromatography over silica gel (heptane/ CH_2Cl_2 1:1 as eluent) afforded **1a** as a brown product (470 mg, 63%). R_f (heptane/ CH_2Cl_2 1:1) = 0.1; ^1H NMR (300 MHz, CDCl_3): δ = 7.82 (m, 2H), 7.59 (dd, J = 7.4 Hz, J = 1.1 Hz, 1H, H_{py}), 7.40 (m, 2H), 7.27 (m, 3H), 2.53 (m, 4H, $\text{C}=\text{CCH}_2$), 1.84 ppm (m, 4H, $\text{C}=\text{CCH}_2$); ^{13}C NMR (75 Hz, CDCl_3): 193.1, 152.7, 144.4, 137.2 (CH), 131.5 (CH), 131.5 (CH), 131.0 (CH), 128.2 (CH), 128.2 (CH), 123.8 (CH), 120.0 (CH), 92.3 (C $\equiv$), 89.6 (C $\equiv$), 81.1 (C $\equiv$), 79.8 (C $\equiv$), 27.9 (C $\equiv\text{CH}_2$), 27.4 (C $\equiv\text{CH}_2$), 19.03 (C $\equiv\text{CH}_2\text{CH}_2$), 19.0 ppm (C $\equiv\text{CH}_2\text{CH}_2$); elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{17}\text{NO}$ (287.36): C 83.60, H 5.96, N 4.87; found: C 83.27, H 5.96, N 4.87; HRMS (EI): m/z : calcd for $\text{C}_{20}\text{H}_{17}\text{NO}$: 287.13101; found: 287.1315.

2-(8-Phenylocta-1,7-diyn-1-yl)quinoline 3-carboxaldehyde (1b): $[\text{PdCl}_2(\text{PPh}_3)_2]$ (91 mg, 130 μmol , 5%), CuI (25 mg, 130 μmol , 5%), and $i\text{Pr}_2\text{NH}$ (11 mL, 97 mmol) were added to a stirred solution of 2-chloro-3-quinoline carboxaldehyde (500 mg, 2.6 mmol) in anhydrous THF (10 mL) at room temperature and under argon. After 5 min 1-phenyl-octa-1,7-diyne (475 mg, 2.6 mmol) was added. The resulting mixture was stirred overnight. Evaporation of the solvents under reduced pressure and purification by column chromatography over silica gel (heptane/EtOAc 9:1 as eluent) afforded **2b** as an orange oil (533 mg, 61%). R_f (heptane/AcOEt 9:1) = 0.19; ^1H NMR (300 MHz, CDCl_3): δ = 10.71 (s, 1H, CHO), 8.71 (s, 1H, H^1), 8.14 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.86 (ddd, J = 8.7 Hz, 7.1 Hz, 1.5 Hz, 1H), 7.63 (ddd, J = 8.3 Hz, 6.8 Hz, 1.1 Hz, 1H), 7.40–7.65 (m, 2H, H Ph), 7.27–7.31 (m, 3H, H Ph), 2.69 (t, J = 6.8 Hz, 2H, $\text{C}=\text{CCH}_2$), 2.53 (t, J = 6.8 Hz, 2H, $\text{C}=\text{CCH}_2$), 1.67–1.97 ppm (m, 4H, $\text{C}=\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3): 190.9 (CHO), 149.9 (C), 144.2 (C), 136.8 (CH), 132.8 (CH), 131.5 (CH $\times$ 2), 129.6 (CH), 129.1 (CH), 128.7 (C), 128.2 (CH $\times$ 2), 127.9 (CH), 127.6 (CH), 126.2 (C), 123.8 (C), 97.5 and 89.5 (C $\equiv\text{CH}_2$), 81.2 and 77.8 (C $\equiv\text{CH}_2$), 28.0 and 27.3 (C $\equiv\text{CH}_2$), 19.3 and 19.0 ppm (C $\equiv\text{CH}_2\text{CH}_2$); HRMS (EI): m/z : calcd for $\text{C}_{25}\text{H}_{19}\text{N}$ [$M-\text{CO}$] $^+$: 309.15175; found: 309.1513.

6-(8-Phenylocta-1,7-diyn-1-yl)-2-(2-phenylethenyl)pyridine (3a): $n\text{BuLi}$ (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was added dropwise to a stirred suspension of benzylphosphonium bromide **2a** (904 mg, 2.1 mmol) in anhydrous THF (15 mL) cooled to -78°C under argon. The reaction mixture

was warmed to room temperature and stirred for 30 min. Then the reaction mixture was cooled to -78°C and a solution of aldehyde **1a** (500 mg, 1.74 mmol) in anhydrous THF (5 mL) was added dropwise. After stirring under argon at room temperature for three hours, the reaction mixture was filtered over Celite. Evaporation of the solvent and column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **3a** (600 mg, 95%) as a mixture of *Z/E* isomers. *trans* isomer (first-eluted): ^1H NMR (300 MHz, CDCl_3): δ = 7.25–7.68 (m, 14H), 7.18 (d, J = 16.2 Hz, 1H, $=\text{CH}$), 2.53 (m, 4H, $\text{C}=\text{CCH}_2\text{CH}_2$), 1.85 ppm (m, 4H, $\text{C}=\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 Hz, CDCl_3): 155.9, 143.6, 136.6, 133.4, 131.6, 128.8, 128.4, 128.25, 127.6, 127.2, 125.3, 124.0, 120.5, 90.3 (C $\equiv$), 89.9 (C $\equiv$), 81.1 (C $\equiv$), 81.0 (C $\equiv$), 29.8 (C $\equiv\text{CH}_2$), 28.0 (C $\equiv\text{CH}_2$), 19.2 (C $\equiv\text{CH}_2\text{CH}_2$), 19.1 ppm (C $\equiv\text{CH}_2\text{CH}_2$). *cis* isomer (second-eluted): ^1H NMR (300 MHz, CDCl_3): δ = 7.25–7.43 (m, 11H), 7.19 (d, J = 7.6 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 6.85 (d, J = 12.4 Hz, 1H, $=\text{CH}$), 6.69 (d, J = 12.4 Hz, 1H, $=\text{CH}$), 2.51 (m, 4H, $\text{C}=\text{CCH}_2\text{CH}_2$), 1.82 ppm (m, 4H, $\text{C}=\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 Hz, CDCl_3): 156.6, 143.6, 136.6, 135.7, 133.5, 131.6, 130.5, 128.9, 128.4, 128.2, 127.6, 124.9, 123.9, 90.3 (C $\equiv$), 89.7 (C $\equiv$), 80.7 (C $\equiv$), 80.7 (C $\equiv$), 27.9 (C $\equiv\text{CH}_2$), 27.5 (C $\equiv\text{CH}_2$), 19.0 (C $\equiv\text{CH}_2\text{CH}_2$), 19.0 ppm (C $\equiv\text{CH}_2\text{CH}_2$); elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{23}\text{N}$ (361.478): C 89.71, H 6.41, N 3.87; found: C 89.77, H 6.47, N 3.62; HRMS (EI): m/z : calcd for $\text{C}_{27}\text{H}_{23}\text{N}$: 361.18305; found: 361.1798.

2-(8-Phenylocta-1,7-diyn-1-yl)benzo[*f*]quinoline (4a): A toluene solution (340 mL) of substituted pyridine **3a** (200 mg, 0.55 mmol) containing catalytic amounts of iodine was irradiated overnight with a Heraeus TQ 150 mercury vapor lamp. Evaporation of the solvent followed by purification by column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **4a** (100 mg, 50%) as a beige solid. ^1H NMR (500 MHz, CDCl_3): δ = 8.81 (d, J = 8.5, 1H, H^1), 8.52 (d, J = 8.0 Hz, 1H, H^{10}), 7.99 (d, J = 9.1 Hz, 1H, H^5 or H^6), 7.95 (d, J = 9.1 Hz, 1H, H^5 or H^6), 7.9 (d, J = 7.5 Hz, 1H), 7.66 (m, 2H), 7.62 (d, J = 8.5 Hz, 1H, H^2), 7.45 (m, 2H), 7.30 (m, 3H), 2.62 (t, J = 6.7 Hz, 2H, $\text{C}=\text{CCH}_2\text{CH}_2$), 2.53 (t, J = 6.67 Hz, 2H, $\text{C}=\text{CCH}_2\text{CH}_2$), 1.83–1.93 ppm (m, 4H, $\text{C}=\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 Hz, CDCl_3): 148.1, 143.3, 131.7, 131.6, 131.4, 130.85, 129.3, 128.7, 128.2, 127.7, 127.6, 127.5, 127.2, 124.5, 124.2, 123.9, 122.7, 91.7 (C $\equiv$), 89.75 (C $\equiv$), 81.2 (C $\equiv$), 81.1 (C $\equiv$), 28.0 (C $\equiv\text{CH}_2$), 27.5 (C $\equiv\text{CH}_2$), 19.2 (C $\equiv\text{CH}_2\text{CH}_2$), 19.1 ppm (C $\equiv\text{CH}_2\text{CH}_2$); HRMS (EI): m/z : calcd for $\text{C}_{27}\text{H}_{21}\text{N}$: 359.16740; found: 359.1674; UV/Vis (CH_2Cl_2): λ (ϵ) = 280 (35000), 290 (26000), 304 (13400), 326 (6310), 342 (6780), 360 nm (8800).

1-Phenyl-2-(benzo[*f*]quinol-2-yl)-5-phenyl-3,4-butanophosphole (5a): $n\text{BuLi}$ (1.6 M in hexanes, 0.9 mL, 1.47 mmol) was added dropwise to a THF solution (20 mL) of diyne **4a** (220 mg, 0.61 mmol) and $[\text{Cp}_2\text{ZrCl}_2]$ (179 mg, 0.61 mmol) under argon at -78°C . The reaction mixture was warmed to room temperature and stirred overnight. Freshly distilled PhPBr_2 (139 μL , 0.67 mmol) was added to this solution at -50°C . The reaction mixture was allowed to warm to room temperature and was stirred for 30 h. The mixture was then filtered over basic alumina (THF as eluent) under inert atmosphere and the volatile substances were removed in vacuo. Final purification by column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded phosphole **5a** (210 mg, 73%) as a yellow solid. Single crystals were grown by slow diffusion of pentane into a chloroform solution. M.p. 205°C ; R_f (heptane/AcOEt 8:2) = 0.75; ^{31}P NMR (81 MHz, CDCl_3): δ = 12.3 ppm; ^1H NMR (300 MHz, CDCl_3): δ = 8.81 (d, J = 8.7 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 7.9–8.0 (m, 4H), 7.79 (d, J = 8.7 Hz, 1H), 7.58–7.69 (m, 2H), 7.47 (d, J = 8 Hz, 2H), 7.34 (t, J = 7.7 Hz, 4H), 7.21 (t, J = 7.3 Hz, 1H), 7.1 (m, 2H), 3.6–3.79 (m, 1H), 2.88–3.1 (m, 2H), 2.72–2.79 (m, 1H), 1.65–1.92 ppm (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): 155.9 (C), 155.7 (C), 149.4 (C), 149.3 (C), 148.1 (C), 148.1 (C), 146.0 (C), 145.9 (C), 144.7 (C), 144.6 (C), 142.4 (C), 142.4 (C), 137.3 (C), 137.0 (C), 133.65 (CH), 133.4 (CH), 132.2 (C), 132.0 (C), 131.4 (C), 130.6 (CH), 130.5 (CH), 129.7 (C), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (C), 126.9 (CH), 126.7 (CH), 126.5 (CH), 122.8 (C), 122.4 (CH), 122.1 (CH), 122.0 (CH), 29.7 (CH $_2$), 29.0 (CH $_2$), 28.2 (CH $_2$), 23.2 ppm (CH $_2$); HRMS (EI): m/z : calcd for $\text{C}_{33}\text{H}_{26}\text{NP}$: 467.18029; found: 467.1785; UV/Vis (CH_2Cl_2): λ (ϵ) = 271 (25600), 291 (18200), 348 (10900), 393 nm (21200); elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{26}\text{NP}$: C 84.77, H 5.61, N 3.00; found: C 85.73, H 5.60, N 3.02.

[(Z,E)-2-(2-Naphthyl)ethenyl]-6-(8-phenylocta-1,7-diyn-1-yl)pyridine (3b)

(3b): *n*BuLi (1.6 M in hexanes, 0.85 mL, 1.32 mmol) was added dropwise to a stirred suspension of 2-naphthylmethylphosphonium bromide **2b** (600 mg, 1.2 mmol) in anhydrous THF (15 mL) cooled to -78°C under argon. The reaction mixture was warmed to room temperature and stirred for 30 min. Then the reaction mixture was cooled to -78°C and a solution of aldehyde **1b** (300 mg, 1 mmol) in anhydrous THF (10 mL) was added dropwise. After stirring under argon at room temperature for three hours, the reaction mixture was filtered over Celite. Evaporation of the solvent and column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **3b** (377 mg, 92%) as a *Z/E* isomer mixture. ^1H NMR (300 MHz, CDCl_3): δ = 7.94 (s, 0.46 H), 7.79–7.83 (m, 4.38 H), 7.58 (t, J = 7.9 Hz, 0.5 H), 7.45–7.49 (m, 3.8 H), 7.22–7.35 (m, 5.8 H), 7.07 (d, J = 7.5 Hz, 0.5 H), 7.02 (d, J = 12 Hz, 0.5 H, =CH *Z* isomer), 6.82 (d, J = 12 Hz, 0.5 H, =CH *Z* isomer), 2.49–2.61 (m, 4 H, $\equiv\text{CCH}_2$), 1.80–1.91 ppm (m, 4 H, $\equiv\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3): 156.6 (C), 155.9 (C), 143.7 (C), 143.6 (C), 136.6 (CH), 135.7 (CH), 134.2 (C), 134.1 (C), 133.6 (CH), 133.5 (C), 133.5 (CH), 133.4 (C $\times$ 2), 132.8, 131.6, 130.7 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH $\times$ 2), 127.8 (CH), 127.7 (CH $\times$ 2), 127.6 (CH), 126.9 (CH), 126.4 (CH $\times$ 2), 126.2 (CH $\times$ 2), 125.3 (CH), 125.0 (CH), 124.0 (C), 123.7 (CH), 122.8 (CH), 120.6 (CH), 90.4 (C $\times$ 2), 89.8 (C), 81.1 (C $\times$ 2), 81.8 (C), 28.0 (C $\equiv\text{CCH}_2\text{CH}_2$), 27.6 (C $\equiv\text{CCH}_2\text{CH}_2$), 19.2 (C $\equiv\text{CCH}_2\text{CH}_2$), 19.1 ppm (C $\equiv\text{CCH}_2\text{CH}_2$); HRMS (EI): m/z : calcd for $\text{C}_{31}\text{H}_{25}\text{N}$: 411.19870; found: 411.1983.

2-(8-Phenylocta-1,7-diyn-1-yl)naphtho[1,2-*f*]quinoline (4b): A toluene solution (570 mL) of substituted pyridine **3b** (649 mg, 1.58 mmol) containing catalytic amounts of iodine was irradiated overnight with a Heraeus TQ 150 mercury vapor lamp. Evaporation of the solvent followed by purification by column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **4b** (304 mg, 47%) as a beige solid. M.p. 104°C . R_f (heptane/EtOAc 8:2) = 0.4; ^1H NMR (300 MHz, CDCl_3): δ = 9.17 (d, J = 8.8 Hz, 1 H), 8.76 (d, J = 7.4 Hz, 1 H), 8.12 (d, J = 8.8 Hz, 1 H), 7.98 (d, J = 8.9 Hz, 2 H), 7.86 (d, J = 8.5 Hz, 1 H), 7.75 (d, J = 8.6 Hz, 1 H), 7.56–7.64 (m, 3 H), 7.45–7.48 (m, 2 H), 7.28–7.31 (m, 3 H), 2.64 (t, J = 6.6 Hz, 2 H, $\equiv\text{CCH}_2$), 2.54 (t, J = 6.6 Hz, 2 H, $\equiv\text{CCH}_2$), 1.82–1.98 ppm (m, 4 H, $\equiv\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3): 148.7 (C), 142.6 (C), 135.4 (CH), 133.5 (C), 131.6 (CH $\times$ 2), 131.1 (CH), 131.0 (C), 129.9 (C), 128.8 (CH), 128.4 (CH), 128.3 (CH $\times$ 3), 127.5 (CH), 127.2 (CH), 126.7 (CH), 126.6 (CH), 126.5 (C), 126.3 (CH), 124.1 (C), 124.0 (C), 123.5 (CH), 91.8 and 89.8 (C $\equiv\text{CCH}_2$), 81.3 and 81.1 (C $\equiv\text{CCH}_2$), 28.1 and 27.6 (C $\equiv\text{CCH}_2$), 19.2 and 19.1 ppm (C $\equiv\text{CCH}_2\text{CH}_2$); HRMS (EI): m/z : calcd for $\text{C}_{31}\text{H}_{23}\text{N}$: 409.18305; found: 409.1837; UV/Vis (CH_2Cl_2): λ (ϵ) = 289 (33 700), 307 (14 100), 324 (7 700), 340 (6 000), 363 (3 000), 382 nm (3 300).

1-Phenyl-2-(naphtho[1,2-*f*]quinol-2-yl)-5-phenyl-3,4-butanophosphole (5b)

(5b): *n*BuLi (1.4 M in hexanes, 0.4 mL, 0.56 mmol) was added to a THF solution (10 mL) of diyne **4b** (96 mg, 0.23 mmol) and $[\text{Cp}_2\text{ZrCl}_2]$ (69 mg, 0.23 mmol) under argon dropwise at -78°C . The reaction mixture was warmed to room temperature and stirred overnight. Freshly distilled PhPBr_2 (53 μL , 0.26 mmol) was added to this solution at -50°C . The reaction mixture was allowed to warm to room temperature and stirred for 30 h. The mixture was then filtered over basic alumina (THF as eluent) under inert atmosphere and the volatile substances were removed in vacuo. Final purification by column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded phosphole **5b** (76 mg, 63%) as a yellow solid. Single crystals were grown by slow diffusion of pentane into a chloroform solution. M.p. 205°C ; R_f (heptane/AcOEt 8:2) = 0.3; ^{31}P NMR (81 MHz, CDCl_3): δ = 12.2 ppm; ^1H NMR (300 MHz, CDCl_3): δ = 9.23 (d, J = 8.9 Hz, 1 H), 8.92 (d, J = 8 Hz, 1 H), 8.16 (d, J = 8.7 Hz, 1 H), 8.03 (d, J = 8.7 Hz, 2 H), 7.9 (d, J = 8.7 Hz, 1 H), 7.86 (d, J = 8.7 Hz, 1 H), 7.78 (d, J = 8.7 Hz, 1 H), 7.66 (m, 2 H), 7.49 (d, J = 7.8 Hz, 2 H), 7.32–7.40 (m, 4 H), 7.08–7.22 (m, 1 H), 6.96 (m, 3 H), 3.66–3.74 (m, 1 H), 2.95–3.12 (m, 2 H), 2.79 (m, 1 H), 1.6–1.95 ppm (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3 , $J(\text{P,C})$ coupling constants not assigned): δ = 155.4 (C), 155.1 (C), 154.8 (C), 149.8 (C), 149.7 (C), 146.3 (C $\times$ 2), 144.7 (C), 144.6 (C), 137.0 (C), 135.2 (CH), 133.7 (CH), 133.5 (CH), 132.3 (C), 132.2 (C), 130.5 (CH), 130.4 (C), 130.1 (C), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH $\times$ 2), 127.6 (CH), 127.5 (CH), 127.0, 126.8 (CH), 126.4 (CH $\times$ 2), 126.1 (CH), 123.0 (C $\times$ 2), 121.1 (CH), 121.0 (CH), 29.7 (CH $_2$), 29.2 (CH $_2$), 28.2 (CH $_2$), 23.3 ppm (CH $_2$); HRMS (EI):

m/z : calcd for $\text{C}_{37}\text{H}_{28}\text{NP}$: 517.19594; found: 517.1942; UV/Vis (CH_2Cl_2): λ (ϵ) = 284 (49 000), 320 (17 000), 332 (14 300), 382 (22 800), 406 nm (28 800); elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{28}\text{NP}$: C 85.86, H 5.45, N 2.71; found: C 85.85, H 5.44, N 2.73.

2-(8-Phenylocta-1,7-diyn-1-yl)-3-[(Z,E)-2-phenylethenyl]quinoline (3d)

*n*BuLi (1.35 M in hexanes, 1.05 mL, 1.42 mmol) was added dropwise to a stirred suspension of benzylphosphonium bromide **2a** (617 mg, 1.42 mmol) in anhydrous THF (10 mL) cooled to -78°C under argon. The reaction mixture was warmed to room temperature and stirred for 30 min. Then the reaction mixture was cooled to -78°C and a solution of aldehyde **1b** (480 mg, 1.42 mmol) in anhydrous THF (5 mL) was added dropwise. After stirring under argon at room temperature for three hours, the reaction mixture was filtered over Celite. Evaporation of the solvent and column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **3d** (570 mg, 97%) as a *Z/E* isomer mixture. ^1H NMR (300 MHz, CDCl_3): δ = 8.37 (s, 1 H, H d), 8.46 (d, J = 8.7 Hz, 1 H), 7.60–7.80 (m, 5 H), 7.53 (m, 1 H), 7.39–7.42 (m, 4 H), 7.26–7.32 (m, 5 H), 6.93 (d, J = 12 Hz, 0.07 H, =CH *Z* isomer), 6.83 (d, J = 12 Hz, 0.07 H, =CH *Z* isomer), 2.7 (t, J = 6.8 Hz, 2 H, $\equiv\text{CCH}_2$), 2.52 (t, J = 6.8 Hz, 2 H, $\equiv\text{CCH}_2$), 1.85–1.98 ppm (m, 4 H, $\equiv\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3): 147.3 (C), 143.5 (C), 137.0 (C), 132.0 (CH), 131.6 (CH $\times$ 2), 130.8 (CH), 129.6 (CH), 129.0 (CH), 128.9 (CH $\times$ 2), 128.3 (CH), 128.2 (CH $\times$ 2), 127.6 (CH), 127.5 (CH $\times$ 2), 127.3 (CH), 127.2 (CH), 126.8 (CH $\times$ 2), 124.8 (CH), 123.9 (C), 95.5 and 89.6 (C $\equiv\text{CCH}_2$), 81.1 and 79.9 (C $\equiv\text{CCH}_2$), 28.0 and 27.6 (C $\equiv\text{CCH}_2$), 19.4 and 19.1 ppm (C $\equiv\text{CCH}_2\text{CH}_2$); HRMS (EI): m/z : calcd for $\text{C}_{31}\text{H}_{25}\text{N}$: 411.19870; found: 411.1983.

6-(8-Phenylocta-1,7-diyn-1-yl)benzo[*k*]phenanthridine (4d): A toluene solution (250 mL) of quinoline **3d** (150 mg, 0.36 mmol) containing catalytic amounts of iodine was irradiated overnight with a Heraeus TQ 150 mercury vapor lamp. Evaporation of the solvent followed by purification by column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **4d** (92 mg, 62%) as an orange oil. R_f (heptane/EtOAc 8:2) = 0.21; ^1H NMR (300 MHz, CDCl_3): δ = 9.09 (m, 1 H), 8.96 (d, J = 8.7 Hz, 1 H), 8.48 (d, J = 8.7 Hz, 1 H), 8.32 (dd, J = 8.3 Hz, 1.5 Hz, 1 H), 8.0 (m, 1 H), 7.94 (d, J = 8.7 Hz, 1 H), 7.68–7.78 (m, 4 H), 7.44–7.47 (m, 2 H), 7.28–7.30 (m, 3 H), 2.76 (t, J = 6.8 Hz, 2 H, $\equiv\text{CCH}_2$), 2.57 (t, J = 6.8 Hz, 2 H, $\equiv\text{CCH}_2$), 1.91–2.04 ppm (m, 4 H, $\equiv\text{CCH}_2\text{CH}_2$); ^{13}C NMR (75 MHz, CDCl_3): 146.0 (C), 144.4 (C), 135.0 (C), 131.6 (CH $\times$ 2), 131.5 (C), 129.9 (CH), 128.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH $\times$ 2), 127.9 (CH), 127.6 (CH), 127.0 (CH), 126.9 (CH $\times$ 2), 125.7 (C), 124.4 (CH), 124.0 (C), 123.9 (C), 95.5 and 89.7 (C $\equiv\text{CCH}_2$), 81.2 and 79.6 (C $\equiv\text{CCH}_2$), 28.1 and 27.6 (C $\equiv\text{CCH}_2$), 19.5 and 19.1 ppm (C $\equiv\text{CCH}_2\text{CH}_2$); HRMS (EI): m/z : calcd for $\text{C}_{31}\text{H}_{23}\text{N}$: 409.18305; found: 409.1837; UV/Vis (CH_2Cl_2): λ (ϵ) = 284 (50 000), 315 (14 500), 336 (5 000), 349 (2 500), 369 (3 600), 388 nm (3 670).

1-Phenyl-2-(benzo[*k*]phenanthrid-6-yl)-5-phenyl-3,4-butanophosphole (5d)

(5d): *n*BuLi (1.6 M in hexanes, 0.4 mL, 0.66 mmol) was added dropwise to a THF solution (10 mL) of diyne **4d** (113 mg, 0.28 mmol) and $[\text{Cp}_2\text{ZrCl}_2]$ (81 mg, 0.28 mmol) under argon at -78°C . The reaction mixture was warmed to room temperature and stirred overnight. Freshly distilled PhPBr_2 (63 μL , 0.3 mmol) was added to this solution at -50°C . The reaction mixture was allowed to warm to room temperature and stirred for 30 h. The mixture was then filtered over basic alumina (THF as eluent) under inert atmosphere and the volatile substances were removed in vacuo. Final purification by column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded phosphole **5d** (65 mg, 45%) as a yellow solid. M.p. 179°C ; R_f (heptane/EtOAc 8:2) = 0.2; ^{31}P NMR (81 MHz, CDCl_3): δ = 20.7 ppm; ^1H NMR (300 MHz, CDCl_3): δ = 9.2 (m, 1 H), 9.03 (d, J = 8 Hz, 1 H), 8.38 (d, J = 7.7 Hz, 1 H), 8.02 (m, 2 H), 7.66–7.87 (m, 5 H), 7.58 (brd, J = 8 Hz, 2 H), 7.39 (brt, J = 7.3 Hz, 2 H), 7.26 (m, 3 H), 7.02 (m, 3 H), 2.95 (m, 2 H), 2.65 (m, 1 H), 2.25 (m, 1 H), 1.85 (m, 2 H), 1.65 ppm (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3) ($J(\text{P,C})$ coupling constants not assigned): δ = 157.4 (C), 157.2 (C), 156.9, 148.6 (C), 148.4 (C), 146.2 (C), 145.0 (C), 143.6 (C), 143.5 (C), 141.9 (C), 137.3 (C), 137.1 (C), 134.7 (C), 133.2 (CH), 132.9 (CH), 132.0 (C), 131.6 (C), 131.4 (C), 130.3 (CH), 129.3 (CH), 129.2 (CH), 129.1 (C), 128.7 (CH $\times$ 2), 128.6 (CH), 128.4 (CH $\times$ 2), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 126.9 (CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 125.0 (C), 124.9 (C),

124.4 (C×2), 123.6 (C), 28.1 (CH₂×2), 23.3(CH₂), 22.3 ppm (CH₂); HRMS (EI): *m/z*: calcd for C₃₇H₂₈NP: 517.19594; found: 517.1950; UV/Vis (CH₂Cl₂): λ (ε)=278 (34200), 317 (12700), 336 (5800), 361 (5400), 379 nm (4900); elemental analysis (%) calcd for C₃₇H₂₈NP: C 85.86, H 5.45, N 2.71; found: C 85.81, H 5.41, N 2.78.

2-(8-Phenylocta-1,7-diyn-1-yl)-3-(Z,E)-[2-[(1*R*,5*S*)-6,6-dimethylbicyclo-[3.1.1]heptane-2-en-2-yl]vinyl]quinoline (3e): *n*BuLi (1.6 M in hexanes, 0.61 mL, 0.97 mmol) was added dropwise to a stirred suspension of [(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptane-2-en-2-yl]methylphosphonium bromide **2d** (425 mg, 0.9 mmol) in anhydrous THF (10 mL) cooled to −78 °C under argon. The reaction mixture was warmed to room temperature and stirred for 30 min. Then the reaction mixture was cooled to −78 °C and a solution of aldehyde **1b** (300 mg, 0.89 mmol) in anhydrous THF (5 mL) was added dropwise. After stirring under argon at room temperature for three hours, the reaction mixture was filtered over Celite. Evaporation of the solvent and column chromatography over silica gel (heptane/EtOAc 8:2 as eluent) afforded **3e** (385 mg, 95%) as a *Z/E* isomer mixture. ¹H NMR (300 MHz, CDCl₃): δ=8.24 (s, 0.9H), 8.2 (s, 0.1H), 8.08 (d, *J*=8.4 Hz, 0.1H), 8.03 (d, *J*=8.4 Hz, 0.9H), 7.74 (d, *J*=8.1 Hz, 1H), 7.61 (m, 1H), 7.48 (d, *J*=7.5 Hz, 1H), 7.42 (m, 3H), 7.27 (m, 3H), 7.04 (d, *J*=16.2 Hz, =CH *E* isomer), 6.97 (d, *J*=16.2 Hz, =CH *E* isomer), 6.61 (d, *J*=12 Hz, =CH *Z* isomer), 6.40 (d, *J*=12 Hz, =CH *Z* isomer), 5.84 (s, 0.9H), 5.77 (s, 0.1H), 2.80 (t, *J*=5.2 Hz, 1H), 2.64 (t, *J*=6.4 Hz, 2H), 2.53 (m, 4H, =CCH₂), 2.46 (m, 1H), 2.19 (m, 1H), 1.89 (m, 4H, =CCH₂CH₂), 1.86 (s, 3H), 1.23–1.19 (m, 1H), 0.98 (d, *J*=14.7 Hz, 1H), 0.88 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): 146.8 (C), 146.75 (C), 143.4 (C), 134.1 (C), 133.3 (CH), 132.5 (C), 131.6 (CH), 130.1 (CH), 129.2 (CH), 128.8 (CH), 128.6 (C), 128.4 (CH), 128.2 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.2 (C), 127.0 (CH), 123.9 (C), 120.6 (CH), 95.4 (C=CCH₂), 89.5 (C=CCH₂), 81.2 (C=CCH₂), 79.9 (C=CCH₂), 77.3 (C), 41.4 (CH), 40.9 (CH), 37.9 (C), 32.3 (CH₂), 31.2 (CH₂), 27.9 (C=CCH₂), 27.5 (C=CCH₂), 26.4 (CH₃), 20.9 (CH₃), 19.3 (C=CCH₂CH₂), 19.0 ppm (C=CCH₂CH₂); HRMS (EI): *m/z*: calcd for C₃₄H₃₄N: 456.26913; found: 456.2696.

6-(8-Phenylocta-1,7-diyn-1-yl)-[(4*S*,6*R*)-3,4,5,6-tetrahydro-5,5-dimethyl-4,6-methano]benzo[1,2-*k*]-phenanthridine (4e): A toluene (700 mL) solution of quinoline **3e** (260 mg, 0.57 mmol) containing catalytic amounts of iodine was irradiated overnight with a Heraeus TQ 150 mercury vapor lamp. Evaporation of the solvent followed by purification by column chromatography over silica gel (heptane/EtOAc 9:1 as eluent) afforded **4e** (64 mg, 25%) as a yellow oil. [*α*]_D²⁵=−42.9 (CH₂Cl₂, *c*=0.95). *R*_f (heptane/EtOAc 8:2)=0.25; ¹H NMR (500 MHz, CDCl₃): δ=8.97 (d, *J*=8.3 Hz, 1H), 8.53 (d, *J*=8.1 Hz, 1H), 8.24 (dd, *J*₁=8.1 Hz, *J*₂=1.5 Hz, 1H), 7.74 (m, 1H), 7.65 (m, 1H), 7.44 (m, 2H), 7.36 (d, *J*=8.1 Hz), 7.29 (m, 3H), 3.90 (AB system, dd, *J*₁=16.1 Hz, *J*₂=3.1 Hz, 1H), 3.70 (AB system, dd, *J*₁=16.1 Hz, *J*₂=2.6 Hz, 1H), 3.0 (t, *J*=5.8 Hz, 1H), 2.7 (t, *J*=6.8 Hz, 2H, =CCH₂), 2.69–2.75 (m, 1H), 2.56 (t, *J*=6.8 Hz, 2H, =CCH₂), 1.99 (m, 2H, =CCH₂CH₂), 1.92 (m, 2H, =CCH₂CH₂), 1.48 (s, 3H), 1.4 (d, *J*=9.2 Hz, 1H), 0.69 ppm (s, 3H); ¹³C NMR (125.8 MHz, CDCl₃): 151.7 (C), 146.3 (C), 145.5 (C), 131.7 (C), 131.6 (CH), 130.5 (CH), 128.2 (C), 127.9 (CH), 127.6 (CH), 127.4 (CH), 127.2 (C), 126.9 (C), 126.7 (CH), 126.5 (CH), 125.7 (C), 123.9 (C), 95.6 (C=CCH₂), 89.7 (C=CCH₂), 81.1 (C=CCH₂), 79.8 (C=CCH₂), 49.7 (CH), 41.1 (CH), 38.0 (C), 37.9 (CH₂), 31.1 (CH₂), 28.1 (C=CCH₂), 27.6 (C=CCH₂), 25.7 (CH₃), 21.2 (CH₃), 19.4 (C=CCH₂CH₂), 19.1 ppm (C=CCH₂CH₂); HRMS (EI): *m/z*: calcd for C₃₄H₃₁N: 453.24565; found: 453.2455; UV/Vis (CH₂Cl₂): λ (ε)=292 (3200), 350 (190), 364 (180).

1-Phenyl-2-[(4*S*,6*R*)-3,4,5,6-tetrahydro-5,5-dimethyl-4,6-methano]benzo-[1,2-*k*]phenanthrid-6-yl]-5-phenyl-3,4-butanophosphole (5e) (two diastereomers): *n*BuLi 1.5 M in hexanes (0.44 mL, 0.66 mmol) was added dropwise to a THF solution (15 mL) of diyne **4e** (126 mg, 0.28 mmol) and [Cp₂ZrCl₂] (81 mg, 0.28 mmol) under argon, at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. Freshly distilled PhPBr₂ (63 μL, 0.3 mmol) was added to this solution at −50 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 30 h. The mixture was then filtered over basic alumina (THF as eluent) under inert atmosphere and the volatile substances were removed in vacuo. Final purification by column chromatography over silica

gel (heptane/EtOAc 8:2 as eluent) afforded phosphole **5e** (42 mg, 27%) as a yellow solid. *R*_f (heptane/EtOAc 8:2)=0.23; [*α*]_D²⁵=−11 (CH₂Cl₂, *c*=0.83); ³¹P NMR (81 MHz, CDCl₃): δ=20.4 and 20.7 ppm (two diastereomers); ¹H NMR (300 MHz, CDCl₃): δ=8.96 (d, *J*=8 Hz, 1H), 8.27 (d, *J*=7 Hz, 1H), 7.73 (m, 1H), 7.62–7.80 (m, 1H), 7.53 (d, *J*=7.7 Hz, 2H), 7.37 (t, *J*=7.7 Hz, 2H), 7.28–7.22 (m, 5H), 6.98 (m, 3H), 3.5 (m, 1H), 2.99 (t, *J*=5.4 Hz, 1H), 2.88 (s, 1H), 2.68–2.62 (m, 4H), 1.88 (m, 1H), 1.68 (m, 4H), 1.61 (s, 3H, H⁷), 1.46 (s, 1H), 0.88 ppm (d, *J*=8 Hz); ¹³C NMR (75 MHz, CDCl₃): 171.1 (C), 159.2 (C), 159.1 (C), 150.8 (C), 145.6 (C), 137.4 (C), 137.2 (C), 133.1 (CH), 132.9 (CH), 131.9 (C), 130.8 (CH), 129.3 (CH), 129.2 (CH), 128.6 (CH), 128.5 (CH), 128.4 (C), 128.2 (CH), 127.6 (CH), 127.2 (CH), 126.8 (CH), 126.7 (CH), 126.3 (CH), 125.6 (CH), 125.2 (C), 77.2 (CH), 68.0 (CH₂), 65.9 (C), 60.4 (CH₂), 49.7 (CH), 77.3 (C), 41.2 (CH), 38.0 (CH₂), 31.1 (CH₂), 28.2 (CH₂), 25.8 (CH), 26.5 (CH₂), 23.3 (CH₂), 22.8 (CH), 21.3 (CH₃), 21.2 (CH₃), 21.1 ppm (CH₃); HRMS (EI): *m/z*: calcd for C₄₀H₃₆NOP: 577.25345; found: 577.2493; UV/Vis (CH₂Cl₂): λ (ε)=350 (3500); elemental analysis (%) calcd for C₄₀H₃₆NP: C 85.53, H 6.46, N 2.49; found: C 85.51, H 6.45, N 2.51.

[Pd(5b)Cl₂]: [Pd(CH₃CN)₂Cl₂] (25 mg, 96.6 μmol) was added to a solution of phosphole (50 mg, 96.6 μmol) in dry CH₂Cl₂ (5 mL) under argon. After stirring at room temperature under argon for 1 h, the solvent was stripped off and the precipitate washed with dry Et₂O, yielding [Pd(5b)Cl₂] as a dark red solid (62 mg, 92%). ³¹P NMR (81 MHz, CD₂Cl₂): δ=+60.0 ppm; ¹H NMR (300 MHz, CD₂Cl₂): δ=9.51 (d, 1H, *J*=8.3 Hz), 9.21 (d, 1H, *J*=7.9 Hz), 8.8 (d, 1H, *J*=8.3 Hz), 8.03–8.21 (m, 3H), 7.65–7.92 (m, 7H), 7.19–7.4 (m, 7H), 3.9 (m, 1H), 3.4 (m, 1H), 3.2 (m, 2H), 2.98 ppm (m, 4H). UV/Vis (CH₂Cl₂): λ (ε)=295 (30000), 352 (10600), 393 (8310), 407 (8170), 478 nm (2400); elemental analysis calcd (%) for C₃₇H₂₈Cl₂NPPd: C 63.95, H 4.06, N 2.02; found: C 63.91, H 4.10, N 1.99.

[Pd(5d)Cl₂]: [Pd(CH₃CN)₂Cl₂] (25 mg, 96.6 μmol) was added to a solution of phosphole (50 mg, 96.6 μmol) in dry CH₂Cl₂ (5 mL) under argon. After stirring at room temperature under argon for 1 h, the solvent was stripped off and the precipitate washed with dry Et₂O, yielding [Pd(5d)Cl₂] as a dark red solid (57 mg, 85%). ³¹P NMR (121.5 MHz, CD₂Cl₂): δ=+72 ppm; UV/Vis (CH₂Cl₂): λ (ε)=307 (27000), 325 (18300), 436 (5760), 482 nm (2120); elemental analysis calcd (%) for C₃₇H₂₈Cl₂NPPd: C 63.95, H 4.06, N 2.02; found: C 63.93, H 4.08, N 1.98.

[Pd(5b)₂](SbF₆)₂]: [Pd^{II}(CH₃CN)₄](SbF₆)₂ (39 mg, 0.87 mmol) was added to a solution of phosphole **5b** (90 mg, 1.74 mmol) in dry CH₂Cl₂ (5 mL) under argon. After stirring at room temperature under argon for 1 h, the solvent was stripped off and the precipitate washed with dry Et₂O, yielding [Pd(5b)₂](SbF₆)₂ (70 mg, 61%) as a dark red solid. Single crystals were grown by slow diffusion of pentane vapor into a CH₂Cl₂ solution, but they were too small for X-ray analysis. ³¹P NMR (81 MHz, CDCl₃): δ=76.7 ppm; ¹H NMR (200 MHz, CDCl₃): δ=9.11 (d, *J*=8.9 Hz, 1H), 8.3 (d, *J*=8.7 Hz, 1H), 8.03–8.14 (m, 2H), 7.9 (d, *J*=8.6 Hz, 1H), 7.79 (m, 2H), 7.28–7.65 (m, 7H), 6.83–6.97 (m, 3H), 6.66 (m, 3H), 3.95 (m, 1H), 3.30 (m, 1H), 2.63 (m, 2H), 2.41 (m, 2H), 2.04–12.12 ppm (m, 4H); HRMS (ES): *m/z*: calcd for C₇₄H₅₆N₂³⁵ClP₂¹⁰⁶ ([C⁺⁺, Cl[−]]⁺): 1175.26420; found: 1175.2674; UV/Vis (CH₂Cl₂): λ (ε)=280 (39400), 303 (32400), 320 (25800), 340 (17300), 399 (11600), 525 nm (1400).

[Pd(5d)₂](SbF₆)₂]: [Pd^{II}(CH₃CN)₄](SbF₆)₂] (12 mg, 24 μmol) was added to a solution of phosphole **5d** (25 mg, 48 μmol) in dry CH₂Cl₂ (2 mL) under argon. After stirring at room temperature under argon for 1 h, the solvent was stripped off and the precipitate washed with dry Et₂O, yielding [Pd(5d)₂](SbF₆)₂ (28 mg, 85%) as a dark red solid. Single crystals suitable for X-ray analysis were grown by slow diffusion of pentane vapor into a CH₂Cl₂ solution. ³¹P NMR (81 MHz, CD₂Cl₂): δ=81.6 ppm; HRMS (ES): *m/z*: calcd for C₇₄H₅₆N₂³⁵ClP₂¹⁰⁶ ([C⁺⁺, Cl[−]]⁺): 1175.26420; found: 1175.2710; UV/Vis (CH₂Cl₂): λ (ε)=284 (98900), 313 (57500), 402 (15400), 500 nm (3400).

[Cu(5b)₂]PF₆]: [Cu(CH₃CN)₄]⁺PF₆[−] (10 mg, 0.28 mmol) was added to a solution of phosphole **5b** (30 mg, 0.56 mmol) in dry CH₂Cl₂ (5 mL) under argon. After stirring at room temperature under argon for 1 h, the solvent was stripped off and the precipitate washed with dry Et₂O, yielding [Cu(5b)₂]PF₆ (49 mg, 77%) as a yellow solid. Single crystals

were grown by slow diffusion of pentane vapor into a CH_2Cl_2 solution. ^{31}P NMR (81 MHz, CDCl_3): δ = 5–6 ppm; UV/Vis (CH_2Cl_2): λ (ϵ) = 292 (44400), 342 (20400), 384 (16600), 403 nm (17400).

[Cu(5d)₂]Cl: CuCl (2 mg, 20 μmol) was added to a solution of phosphole 5d (20 mg, 39 μmol) in dry CH_2Cl_2 (2 mL) under argon. After stirring at room temperature under argon for 1 h, the solvent was stripped off and the precipitate was washed with dry Et_2O , yielding **[Cu(5d)₂]Cl** (18 mg, 82%) as a bright yellow solid. Single crystals suitable for X-ray analysis were grown by slow diffusion of pentane vapor into a CH_2Cl_2 solution. ^{31}P NMR (81 MHz, CDCl_3): δ = 5–6 ppm; UV/Vis (CH_2Cl_2): λ (ϵ) = 278 (71400), 322 (45200), 368 (29900), 403 nm (24800).

X-ray crystallography: Single crystals of (–)-**4c**, **5a**, and **[Pd(5c)Cl₂]** suitable for X-ray crystal analysis were obtained at room temperature by slow diffusion of pentane vapor into dichloromethane solutions. Single-crystal data collection was performed at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with $\text{MoK}\alpha$ radiation (λ = 0.71069 Å). Reflections were indexed, corrected for Lorentzian and polarization effects, and integrated by the DENZO program of the KappaCCD software package. The data merging process was performed by using the SCALEPACK program.^[17] Structure determinations were performed by direct methods with the solving program SIR97,^[18] which revealed all the non-hydrogen atoms. SHELXL program^[19] was used to refine the structures by full-matrix least-squares methods 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.

In the crystal lattice of **[Pd(5c)Cl₂]**, a dichloromethane molecule was found in addition to the neutral coordination complex. This solvent molecule was found to be disordered and modeled over two positions. Hydrogen atoms were been introduced in this model. As a result, rather high anisotropic displacement parameters for some of its atoms were obtained. In addition, the cyclohexyl ring of the phosphole ligand in **[Pd(5c)Cl₂]** was found to be disordered over two positions, whose relative occupancies were refined. As a consequence, final agreement factor (R) has modest values (Table 2). Nevertheless, anisotropic displacement parameters associated to the atoms of the neutral coordination complexes that are not involved in the disorder are satisfactory. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.^[20] CCDC-736269 ((–)-**4c**), CCDC-736270 (**5a**), and CCDC-736271 (**[Pd(5c)Cl₂]**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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