Stereoselective coordination of ditopic phospholyl-azahelicenes: a novel approach towards structural diversity in chiral π-conjugated assemblies†

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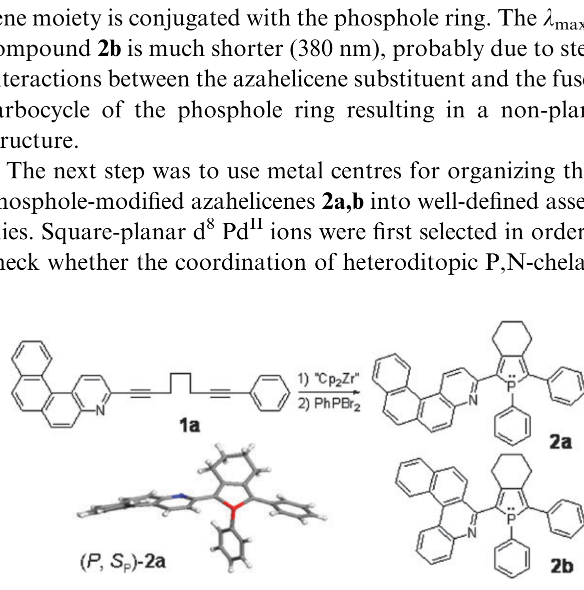
Phosphole-modified aza[4]helicenes act as heteroditopic chelates toward metal ions having different coordination geometries (Pd^{II}, Cu^{I}).

The design and synthesis of molecules endowed with helical chirality and π-conjugated backbones is of great interest due to their fascinating optical and electronic properties.[1] One challenge in expanding the potential of these derivatives is to develop short and efficient synthetic approaches allowing the generation of different frameworks with diverse properties. Quite surprisingly, coordination chemistry has rarely been used for the tailoring of helicoidal π-conjugated systems (helicenes),[2] despite metals being powerful platforms for organizing organic chromophores into well-defined supramolecular assemblies.[3] The metal ions can furthermore potentially (i) allow for the generation of structural diversity through variation in their coordination geometries, and (ii) affect the optical properties of the coordinated π-conjugated systems. Herein, we describe the unprecedented controlled self-assembly of helicenes into sophisticated chiral architectures using supramolecular coordination-driven chemistry. Helicenes designed to act as ditopic P,N-chelates toward metal ions are reported and, utilizing the power and simplicity of coordination chemistry, varied helical π-conjugated assemblies are readily obtained with high stereoselectivity. Moreover, due to intimate metal–ligand interactions, the optical properties of these P,N-helicenes are modified upon coordination.

Our strategy was to prepare phosphole-modified azahelicenes having a 1,4-P,N moiety and to generate structurally diverse assemblies through their coordination onto a metal having either a square planar (Pd^{II}) or a tetrahedral (Cu^{I}) geometry. The (phospholyl)azahelicenes **2a,b** (Scheme 1) were targeted as model compounds since they possess different structures with either a terminal (**2a**) or an inner (**2b**) chelating P,N-moiety. They were prepared *via* a "zirconocene"-promoted intramolecular coupling of 1,7-diynes[4,5] and subsequent addition of $PhPBr_2$ as illustrated by the transformation **1a** → **2a** (Scheme 1). They were isolated as air-stable solids in moderate yields (**2a**, 63%; **2b**, 45%) following purification by column chromatography. It is noteworthy that this organometallic route (Fagan–Nugent method)[6] offers straightforward access to these novel phosphole scaffolds decorated with different helicene-substituents.

The structures of derivatives **2a,b** were supported by high-resolution mass spectrometry and elemental analyses. They exhibit classical ^{1}H and ^{13}C NMR data, and their $^{31}P\{^{1}H\}$ NMR spectra showed a sharp singlet in the range expected for P-aryl phospholes[4] (**2a**, +12.2; **2b**, +20.7). It is worth noting that the two stereogenic elements of **2a,b** (P-centre, [4]azahelicene) undergo rapid inversion in solution at room temperature.[7] Derivative **2a** was further characterized by an X-ray diffraction study (Scheme 1).[8] Although the P and N atoms have a mutual "*anti*" conformation in the solid state, this structural feature should not prevent derivative **2a** from acting as a P,N-chelate since the energy barrier to rotation about the inter-ring C–C bond of (2-pyridyl)phospholes is low (12–16 kJ mol^{-1}).[9] The twist angles between the phosphole ring and the π-substituents (azahelicene, 36.5°; Ph, 37.7°) allow extended delocalization of the π-system[4,9] since the orbital overlap varies approximately with the cosine of the twist angles. As expected, the naphtho[1,2-*f*]quinoline part of **2a** displays a helical geometry with a dihedral angle of 30.1° between the two terminal aromatic rings (Scheme 1). The UV-Vis absorption maximum, assigned to π–π* transitions, of **2a** is notably red-shifted (406 nm) compared to that for 5-phenyl-2-pyridylphosphole (390 nm),[4b] clearly indicating that the [4]azahelicene moiety is conjugated with the phosphole ring. The λ_{max} of compound **2b** is much shorter (380 nm), probably due to steric interactions between the azahelicene substituent and the fused-carbocycle of the phosphole ring resulting in a non-planar structure.

The next step was to use metal centres for organizing these phosphole-modified azahelicenes **2a,b** into well-defined assemblies. Square-planar d^8 Pd^{II} ions were first selected in order to check whether the coordination of heteroditopic P,N-chelates



Scheme 1 Synthesis of phosphole-based helicenes **2a,b**.

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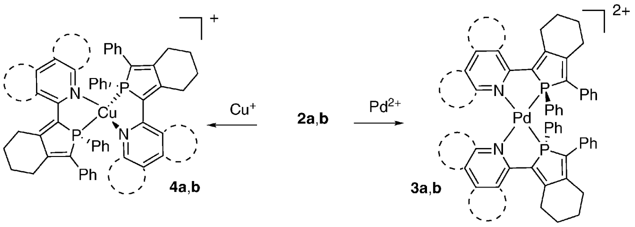

Scheme 2 Synthesis of Pd^{II}-complexes **3a,b** and Cu^{I}-complexes **4a,b**.

2a,b is stereoselective, as could be expected from the different *trans*-effects[10] of their donor sites. Derivatives **2a,b** reacted in CH_2Cl_2 solution with $[Pd(CH_3CN)_4][SbF_6]_2$ (2 : 1 molar ratio) giving rise almost quantitatively to air-stable complexes **3a,b** (Scheme 2). The simplicity of their multinuclear NMR spectra clearly shows that these complexes are obtained as single diastereoisomers. Their high frequency ^{31}P NMR chemical shifts (**3a**, +76.6 ppm; **3b**, +81.6 ppm) are typical for Pd^{II}-complexes bearing (2-pyridyl)phosphole ligands in a mutually *cis* configuration.[4a–c] The stereoselective coordination of heteroditopic P,N-helicenes **2a,b** on Pd^{II} was confirmed by an X-ray diffraction study performed on single crystals of **3b**. Due to the "*trans effect*", the square-planar metal imposes a noncentrosymmetric assembly of **2a,b** with the azahelicene fragments having a mutual *syn*-arrangement (Fig. 1). This result clearly shows that, in spite of their unusual structures and the presence of sterically demanding azahelicene substituents, the heteroditopic P,N-moieties of derivatives **2a,b** dictate their coordination behaviour. This point is very important in view of the extension of the helical backbone to configurationally more stable helicenes (aza[6]helicenes and higher derivatives).

Complex **3b** has an approximate C_2-symmetry. The Pd^{II} centre shows a highly distorted square-planar geometry with an angle between the two N–Pd–P planes of 19.5° (Fig. 1, left). This distortion, which is due to the overlapping of the two coordinated azahelicene moieties, results in a chiral helicene-type coordination sphere around the Pd^{II} centre.[10b] It is likely that the configuration at the metal is also rigid in solution due to the overlapping of the helices (Fig. 1, right) which prevents a "flopping" of the ligands. It is important to note that the structure of the [4]azahelicene moieties is not perturbed by the coordination on to the metal centre. For example, the dihedral angles between the two terminal aromatic rings in complex **3b** (30 and 35.1°) are comparable to those of **2a** (30.1°). Finally, although the rather large distance between the two helicenes (shortest inter-ring distance, 4.1 Å) indicates that no intramolecular π–π interaction takes place, the two azahelicenes moieties wind with the same helical sense (Fig. 1). Two features directly arising from the coordination of P,N-helicenes on Pd^{II} are particularly noteworthy. The first is the unique structure of complex **3b** featuring three helicoidal moieties: two organic (the azahelicenes) and one inorganic (the PdP_2N_2 core) (Fig. 1, left). This nicely illustrates that metallohelicenes can provide novel topologies in chiral π-conjugated derivative chemistry. The second is the highly stereoselective assembly of P,N-helicenes **2a,b** on to Pd^{II}. It is remarkable that amongst the numerous possible stereoisomers (2^6), only one pair of enantiomers is obtained. This highly diastereoselective assembly is due to a combination of electronic (*trans*-effect, ...) and steric (repulsion of (i) the P–Ph substituents, (ii) the azahelicenes, ...) factors in the metal coordination sphere. For example, the *anti*-configuration of the P–Ph groups (Fig. 1, right) is clearly sterically favoured over a possible *syn*-arrangement. Indeed, phosphole-modified azahelicenes appear to be well designed to self-assemble on to metal ions in a highly stereoselective way to afford quantitatively original chiral π-conjugated metallohelicenes.

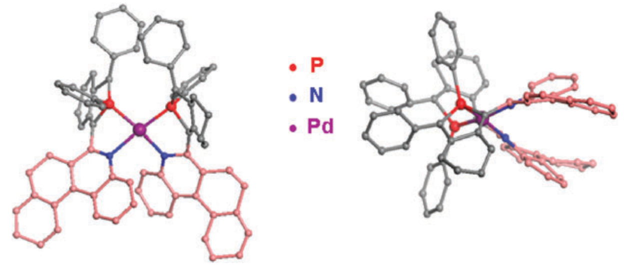

Fig. 1 Views of dicationic complex **3b** (H atoms, counteranions and solvent molecules have been omitted for clarity). One of the two symmetrically independent complexes is shown.

Having demonstrated that helicenes **2a,b** with different structures act as P,N-chelates, the next step was to illustrate the possibility of generating other topologies using metals with other coordination geometries. Cu^{I}, a tetrahedral d^{10} centre, was thus selected. The reaction of derivatives **2a,b** with a Cu^{I} source (2 : 1 molar ratio) was conducted in CH_2Cl_2 solution at room temperature. Upon exposure to pentane vapours, air-stable single crystals of complexes **4a,b** (Scheme 2) grew from the homogeneous solutions (yields >77%). Their solution state $^{31}P\{^1H\}$ NMR spectra exhibited a broad singlet at δ 5–6 ppm ($\nu_{1/2}$ = 85 Hz), a typical shift for (2-pyridyl)phosphole-Cu^{I} complexes.[4e,f] Their structures were confirmed by X-ray diffraction studies (Fig. 2), both complexes crystallise in centrosymmetric space groups. The chiral Cu^{I} centres have a distorted tetrahedral geometry with the two azahelicenes having an almost perpendicular arrangement (angle between the two N–Cu–P planes: **4a**, 83.7°; **4b**, 86.4°, Fig. 2). The novel assemblies **4a,b** have an unprecedented topology, in which two helicenes are connected by a "spiro" centre (*i.e.* the Cu^{I} atom).

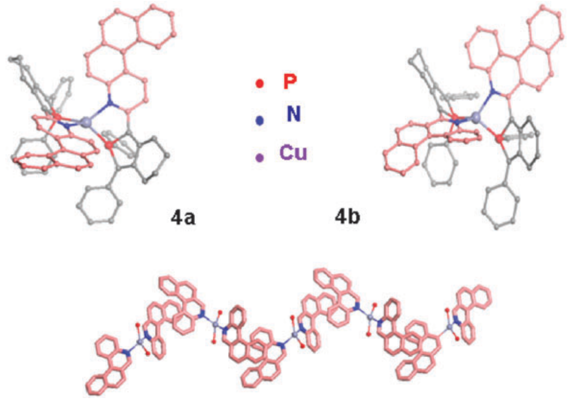

Fig. 2 Cationic complexes **4a** and **4b** (one stereoisomer, H atoms, counteranions and solvent molecules have been omitted for clarity). Simplified view showing the packing of **4b** along the *b*-axes.

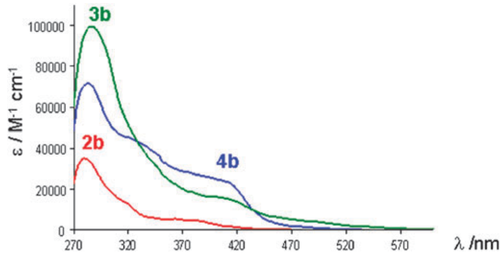

Fig. 3 UV-visible spectra of free helicene **2b**, and of its Pd^{II}- (**3b**) and Cu^{I}- (**4b**) complexes in CH_2Cl_2.

As observed for the square planar Pd^{II} complexes, (i) the coordination of heteroditopic helicenes **2a,b** on tetrahedral Cu^{I} centres does not affect their structure, and (ii) the coordination is highly stereoselective. Among the numerous theoretically possible stereoisomers, only two (complex **4a**) and one (complex **4b**) diastereoisomers were found in the solid state. Note that the diastereoisomers of **4a** differ only by the conformation of the flexible –$(CH_2)_4$– moiety grafted on to the phosphole rings. This result demonstrates the versatility of supramolecular coordination-driven chemistry in generating structural diversity in the field of helicoidal π-conjugated systems. In fact, starting from one programmed heteroditopic P,N-helicene such as **2a,b**, air-stable chiral π-conjugated assemblies can be readily obtained in an highly stereoselective way upon coordination on metal ions having different coordination geometries.

Finally, two important features are worth noting that illustrate the potential functionality of these metallohelicenes. First, the π–π* transition of phosphole-modified helicenes **2a,b** are hardly perturbed upon coordination on the metal centres, but new transitions of low intensity are observed at higher wavelength ($\lambda_{\max} > 450$ nm, Fig. 3). These low energy UV-Vis absorptions, which are due to charge transfer involving the metal and the 2-pyridylphosphole ligand,[4a–d] reveal that the coordinated π-conjugated helicenes are electronically coupled with the metal centres. It is interesting to note that these long wavelengths absorptions are more red-shifted for the Pd^{II}-complexes than for their Cu^{I}-analogues (Fig. 3), showing that the optical properties of P,N-helicenes **2a,b** can be tuned by coordination. Secondly, helicene complexes **3b** and **4b** aggregate into infinite columns in the solid state due to intermolecular π-stacking of the helicene moieties (intermolecular distances, 3.5–3.6 Å) (Fig. 2). This type of supramolecular organization, is crucial in obtaining helicene-based materials with appealing properties (NLO-phores, circularly polarized materials, . . .).[11]

In conclusion, we have described a rational and simple synthetic approach to a variety of nano-scale chiral π-conjugated molecules *via* stereoselective coordination of heteroditopic phosphole-modified azahelicenes on metal centres. The high stereoselectivity of this method, giving rise to a reduced number of enantiomeric pairs, should facilitate the isolation of enantiomerically pure substances. Extension of this versatile synthetic methodology to phosphole-modified azahelicenes with longer conjugated systems is under active investigation.

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Notes and references

1 (*a*) T. J Katz, *Angew. Chem., Int. Ed.*, 2000, **39**, 1921; (*b*) A. Urbano, *Angew. Chem., Int. Ed.*, 2003, **42**, 3986; (*c*) A. Rajca, M. Miyasaka, M. Pink, H. Wang and S. Rajca, *J. Am. Chem. Soc.*, 2004, **126**, 15211; (*d*) R. H. Martin, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 649; (*e*) M. S. Gin, T. Yokozawa, R. B. Prince and J. S. Moore, *J. Am. Chem. Soc.*, 1999, **121**, 2643; (*f*) L. Pu, *Chem. Rev.*, 2004, **104**, 1687.

2 (*a*) For metal complexes of phosphorus-containing helicenes, see: R. El-Abed, F. Aloui, J.-P. Genet, B. Ben-Hassine and A. Marinetti, *J. Organomet. Chem.*, 2007, **692**, 1156; (*b*) for other complexes containing helicenes, see: T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. P. Robben, M. Wuensch, M. D. Ward, C. Nuckolls, T. J. Katz and L. Castellanos, *J. Am. Chem. Soc.*, 1993, **115**, 3182; (*c*) Y. Dai and T. J. Katz, *J. Org. Chem.*, 1997, **62**, 1274.

3 (*a*) O. Maury and H. Le Bozec, *Acc. Chem. Res.*, 2005, **38**, 691; (*b*) N. Giuseppone, J.-L. Schmitt and J.-M. Lehn, *J. Am. Chem. Soc.*, 2006, **128**, 16748 and references therein; (*c*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*d*) C. A. Mirkin and B. J. Hollidays, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022.

4 (*a*) C. Fave, M. Hissler, K. Sénéchal, I. Ledoux, J. Zyss and R. Réau, *Chem. Commun.*, 2002, 1674; (*b*) M. Sauthier, F. Leca, L. Toupet and R. Réau, *Organometallics*, 2002, **21**, 1591; (*c*) M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J.-F. Halet and R. Réau, *Angew. Chem., Int. Ed.*, 2001, **40**, 228; (*d*) F. Leca, M. Sauthier, V. Deborde, L. Toupet and R. Réau, *Chem.–Eur. J.*, 2003, **9**, 3785; (*e*) F. Leca, C. Lescop, E. Rodriguez, K. Costuas, J.-F. Halet and R. Réau, *Angew. Chem., Int. Ed.*, 2005, **44**, 4362; (*f*) B. Nohra, S. Graule, C. Lescop and R. Réau, *J. Am. Chem. Soc.*, 2006, **128**, 3520; (*g*) T. Baumgartner and R. Réau, *Chem. Rev.*, 2006, **106**, 4681.

5 (*a*) See ESI.† For the synthesis of azahelicenes, see: D. C. Harrowven, I. L. Guy and L. Nanson, *Angew. Chem., Int. Ed.*, 2006, **45**, 2242; (*b*) K. Schmidt, S. Brovelli, V. Coropceanu, J.-L. Brédas, C. Bazzini, T. Caronna, R. Tubino and F. J. Meinardi, *J. Phys. Chem. A*, 2006, **110**, 11018.

6 (*a*) P. J. Fagan, W. A. Nugent and J. C. Calabrese, *J. Am. Chem. Soc.*, 1994, **116**, 1880; (*b*) P. J. Fagan and W. A. Nugent, *J. Am. Chem. Soc.*, 1988, **110**, 2310.

7 The inversion barrier of phospholes is *ca.* 15 kcal mol^{-1}, see: L. D. Quin and G. S. Quin, in *Phosphorus–Carbon Heterocyclic Chemistry: The Rise of a New Domain*, ed. F. Mathey, Elsevier Science Ltd, Oxford, 2001.

8 CCDC 651119–651122 for **2a**, **4b**, **4a** and **3b**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714340k.

9 (*a*) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi and R. Réau, *Chem.–Eur. J.*, 2001, **7**, 4222; (*b*) H.-C. Su, O. Fadhel, C.-J. Yang, T.-Y. Cho, C. Fave, M. Hissler, C.-C. Wu and R. Réau, *J. Am. Chem. Soc.*, 2006, **128**, 983.

10 (*a*) R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712; (*b*) O. Mamula and A. von Zelewsky, *J. Chem. Soc., Dalton Trans.*, 2001, 219; (*c*) J. N. Harvey, K. M. Heslop, A. G. Orpen and P. G. Pringle, *Chem. Commun.*, 2003, 278.

11 (*a*) L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071; (*b*) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039; (*c*) C. Nuckolls, T. J. Katz, G. Katz, P. J. Collings and L. Castellanos, *J. Am. Chem. Soc.*, 1999, **121**, 79; (*d*) A. J. Lovinger, C. Nuckolls and T. J. Katz, *J. Am. Chem. Soc.*, 1998, **120**, 264; (*e*) C. Nuckolls, T. J. Katz and L. Castellanos, *J. Am. Chem. Soc.*, 1996, **118**, 3767.