



**HAL**  
open science

## **Rhenium complexes bearing phosphole-pyridine chelates: simple molecules with large chiroptical properties.**

Eszter Takacs, Aude Escande, Nicolas Vanthuyne, Christian Roussel,  
Christophe Lescop, Elisabeth Guinard, Camille Latouche, Abdou Boucekkine,  
Jeanne Crassous, Regis Réau, et al.

### ► To cite this version:

Eszter Takacs, Aude Escande, Nicolas Vanthuyne, Christian Roussel, Christophe Lescop, et al.. Rhenium complexes bearing phosphole-pyridine chelates: simple molecules with large chiroptical properties.. *Chemical Communications*, 2012, 48, pp.6705-6707. 10.1039/c2cc32542j . hal-01070115

**HAL Id: hal-01070115**

**<https://hal.science/hal-01070115>**

Submitted on 2 Jun 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Rhenium Complexes Bearing Phosphole-Pyridine Chelates: Simple Molecules with Large Chiroptical Properties

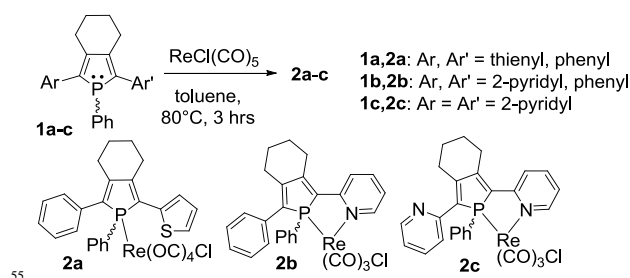
Esther Tazacs,<sup>a</sup> Aude Escande,<sup>a</sup> Nicolas Vanthuyne,<sup>b</sup> Christian Roussel,<sup>b</sup> Christophe Lescop,<sup>a</sup> Elisabeth Guinard,<sup>a</sup> Camille Latouche,<sup>a</sup> Abdou Boucekkine,<sup>a</sup> Jeanne Crassous,<sup>a</sup> Régis Réau,<sup>a</sup> M. Hissler<sup>\*a</sup>

The synthesis and chiroptical properties of chiral rhenium complexes bearing mono- or di-topic phosphole ligands are described.

There is an increasing demand in developing chiral molecular materials<sup>1a,b</sup> in diverse domains such as molecular switches,<sup>1c</sup> circular polarized light (CPL) emitters,<sup>1d</sup> chiral metallogels and nanofibers,<sup>1a</sup> ... Further developments in these important domains require molecular engineering for developing easily accessible enantiopure molecules displaying large chiroptical properties, a task that is difficult to achieve using classical synthetic chemistry.<sup>1,2</sup> Coordination chemistry has been rarely used for this purpose although it offers a straightforward access to derivatives exhibiting appealing properties due to the presence of the metal atom.<sup>1b</sup> For example, it has been shown that the intrinsic nature of the rhenium ion (diverse coordination modes, large spin-orbit coupling, relativistic effects...) impacts the redox and optical properties of the corresponding Re<sup>I</sup>(carbonyl)(diimine) complexes leading to numerous applications in solar chemistry, optoelectronics and photocatalysis.<sup>3</sup> However, up to now, few chiral Re<sup>I</sup> complexes have been prepared,<sup>4</sup> and little attention has been paid on their chiroptical properties.<sup>4d-1</sup> In this paper, the synthesis, enantioresolution and optical properties of chiral rhenium complexes (**2a-c**, Scheme 1) bearing phosphole-based  $\pi$ -conjugated ligands behaving either as monotopic P-donors (**1a**, Scheme 1) or as ditopic 1,4-P,N chelates (**1b,c**) are described.<sup>5,6</sup> The chiroptical properties, namely circular dichroism (CD) and optical rotation (OR), of these complexes are unexpectedly very large. This unprecedented coordination-driven molecular engineering offers a straightforward access to very simple molecules exhibiting large chiroptical properties.

The target Re<sup>I</sup>-complexes **2a-c** (Scheme 1) were prepared by reacting  $\pi$ -conjugated phospholes **1a-c**<sup>5a,d</sup> with ReCl(CO)<sub>5</sub> in toluene at 80°C under argon.<sup>3</sup> These air-stable compounds were purified by column chromatography over silica gel and isolated with moderate yields (55-60%). Their multinuclear NMR spectroscopy and mass spectrometry data support the proposed structures (see SI). For example, the formation of the five-membered metallacycles in **2a,c** upon coordination of the (2-pyridyl)phosphole moiety of **1a,c** results in a downfield

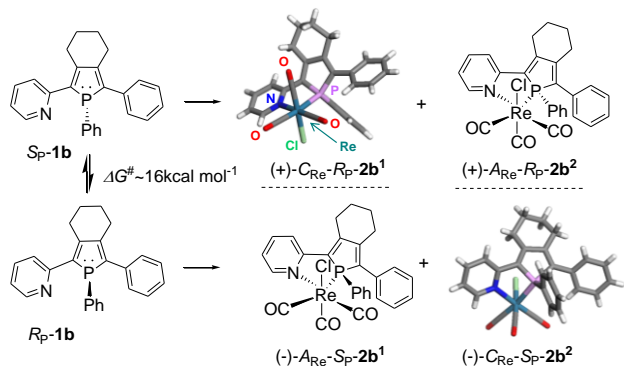
<sup>31</sup>P NMR coordination chemical shifts (**2a**, +21.3 ppm; **2b,c**: +45.7/+50.7 ppm).<sup>5d</sup> The proposed structures were confirmed by an X-ray diffraction study on complex **2b** (*vide infra*).



Scheme 1. Synthesis of rhenium complexes **2a-c**.

It is worth noting that, although phospholes **1a-b** feature a P-chirogenic center, they cannot be isolated as single enantiomers due to the rapid P-inversion in solution (inversion barrier, ca. 16 kcal mol<sup>-1</sup>).<sup>6</sup> Furthermore, symmetrical phosphole **1c** becomes chiral only upon coordination on the Re<sup>I</sup>-center (Scheme 1). As a consequence, the isolation of enantiomerically pure derivatives was undertaken on complexes **2a-c**. Complex **2a** consists of a *R<sub>p</sub>/S<sub>p</sub>* enantiomeric mixture, which was resolved with *ee*'s higher than 98% by HPLC separations over a Chiralpak IA stationary phase (see SI). Complexes **2b,c** exist as four configurationally stable stereoisomers, observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (**2b**, +47.7, +50.7; **2c**, +48.2, +45.7), due to the presence of two stereogenic centers (*R<sub>p</sub>/S<sub>p</sub>*, *A<sub>Re</sub>/C<sub>Re</sub>*). The four stereoisomers of complex **2b** were obtained with *ee*'s higher than 97% by chiral HPLC (Scheme 2). The two epimers of complex **2b** *C<sub>Re</sub>-R<sub>p</sub>-2b<sup>1</sup>* and *C<sub>Re</sub>-S<sub>p</sub>-2b<sup>2</sup>* were characterized by an X-ray diffraction study (Scheme 2). The Re<sup>I</sup>-ions display a classic distorted octahedral geometry with the Cl-ligand occupying apical positions. The epimerization barrier of complex **2b** is high enough (ca. 27 kcal.mol<sup>-1</sup> at 50°C, see SI) to prevent racemization to take place at room temperature. The enantiomers of complex **2c** were also obtained in high *ee*'s (> 98 %) by chiral HPLC, however the two epimers appear to have different configurational stability. The epimerization barrier of **2c<sup>2</sup>** is rather low (~23 kcal mol<sup>-1</sup> at 22°C), preventing its chiroptical properties to be examined, while

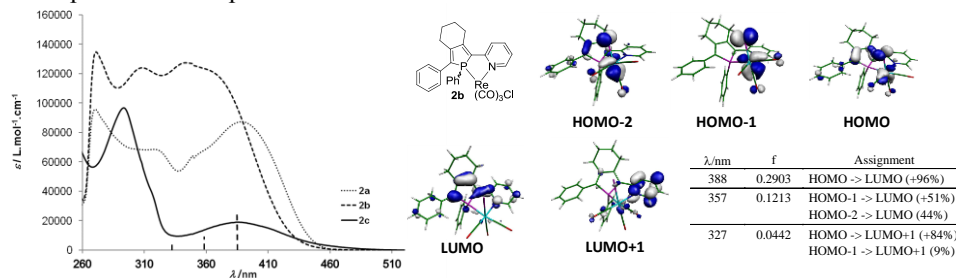
enantiomers **2c**<sup>1</sup> are stable enough to be investigated by CD spectroscopy. Indeed, a family of configurationally stable chiral (phosphole-pyridine)Re<sup>I</sup>-complexes **2b**<sup>1,2</sup>-**2c**<sup>1</sup> (Figure 1) with various  $\pi$ -conjugated framework have been synthesized.



**Scheme 2.** Stereochemical aspects of complex **2b**. Molecular structures of **2b**<sup>1,2</sup> determined by X-ray crystallography. For *A/C* stereochemical assignments see reference 1b.

The UV-vis spectra of rhenium complexes **2a-c** display a large absorption band tailing down to 500 nm (Figure 1). Note that, according to the X-Ray diffraction study performed on **2b**<sup>1,2</sup>, the twist angle between the coordinated pyridine and phosphole ring (CCCC dihedral angle,  $+51.0^\circ \pm 2^\circ$ ) is within classical range<sup>2b,5d</sup> and allow efficient  $\pi$ -conjugation along the sp<sup>2</sup>-carbon backbone. According to PBE0 DFT and TD-DFT calculations using a polarized LanL2DZ basis set, the lowest energy transition of complex **2b**<sup>2</sup> is essentially (>96%) an HOMO  $\rightarrow$  LUMO transition. The HOMO spans from the Cl-Re-CO fragment to the phosphole ring and the LUMO is essentially spread over the pyridyl-phosphole moiety (Figure 1), showing that this transition is a metal-ligand to ligand charge transfer (MLLCT).

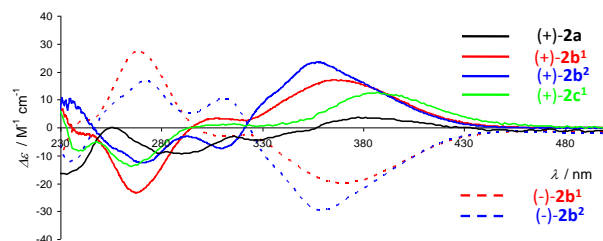
The complex **2a** is fluorescent at room temperature ( $\lambda_{em} = 518$  nm), which is ligand-centered according to theoretical calculation, whereas **2b,c** displayed no luminescence properties. The experimental CD spectra of complexes **2a-c** were recorded in CH<sub>2</sub>Cl<sub>2</sub> ( $5 \times 10^{-5}$  M). The CD spectrum of (+)-**2a** shows several bands with small  $\Delta\epsilon$  values (Figure 2). The CD spectra of complexes **2b**<sup>1,2</sup> and **2c**<sup>1</sup>



**Figure 1.** Absorption spectra of **2a-c** in CH<sub>2</sub>Cl<sub>2</sub>, TD-DFT simulated spectrum and molecular orbitals for diastereoisomer **2b**<sup>2</sup> (vertical dashed lines).

Indeed, the HOMO-LUMO transition in **2a** involves the  $\pi$ -conjugated system centered on the phosphole ligand *only*, with a marginal participation of the rhenium atom (see SI).

display a similar general shape with a broad positive CD band between 330 and 430 nm ( $\Delta\epsilon \sim 15$ -22 M<sup>-1</sup> cm<sup>-1</sup>) and a negative one around 280 nm ( $\Delta\epsilon \sim -40$  to -20 M<sup>-1</sup> cm<sup>-1</sup>) for the (+) enantiomers (Figure 2). The only noticeable difference is observed at ca. 310 nm, the smaller CD band have opposite sign for (+)-**2b**<sup>1</sup> and (+)-**2b**<sup>2</sup>, while for (+)-**2c**<sup>1</sup> this band is almost vanishing. It is noteworthy that the CD bands complexes **2b**<sup>1,2</sup> and **2c**<sup>1</sup> featuring  $\pi$ -conjugated (2-pyridine)phosphole chelates are relatively intense for small molecules, and especially compared to complex **2a** bearing a monodentate phosphole ligand (Figure 2). Indeed, complex **2a** displays optical rotations equal to zero. In marked contrast, Re<sup>I</sup>-complexes **2b**<sup>1,2</sup> and **2c**<sup>1</sup> exhibit specific rotations  $[\alpha]_D^{23}$  between 520-625 and molar rotations  $[\phi]_D^{23}$  between 3200-4240 (Table 1). These values are surprisingly large, almost the same order of magnitude as helicenes molar rotations,<sup>2</sup> and deserve to be examined in more details.



**Figure 2.** Circular dichroism spectra of complexes (+)-**2a**, (+)/(-)-**2b**<sup>1</sup>, (+)/(-)-**2b**<sup>2</sup> and (+)-**2c**<sup>1</sup>.

PBE0 TD-DFT calculations using an extended basis set well-reproduce the CD shape of diastereomeric complexes **2b**<sup>1,2</sup> and **2c**<sup>1</sup> and enabled to assign their absolute configurations ((+)-C<sub>Re</sub>-R<sub>P</sub>-**2b**<sup>1</sup>; (+)-A<sub>Re</sub>-R<sub>P</sub>-**2b**<sup>2</sup>, Scheme 2, (+)-C<sub>Re</sub>-R<sub>P</sub>-**2c**<sup>1</sup>) (see SI). These absolute configuration assignments were further confirmed by X-ray crystallography of (+)-C<sub>Re</sub>-R<sub>P</sub>-**2b**<sup>1</sup> and (-)-C<sub>Re</sub>-S<sub>P</sub>-**2b**<sup>2</sup> (Scheme 2). The fact that complexes **2b**<sup>1,2</sup> and **2c**<sup>1</sup> show large chiroptical properties may be explained by analyzing the MO's involved in the low energy CD-active electronic transitions that significantly contribute to the molar rotations.

Such transition has a small rotational strength and may account for the zero optical rotation value for **2a**. On the contrary, the positive CD-active band at 380-400 nm in

(+)-**2b**<sup>1</sup> is a HOMO-LUMO transition with a high charge transfer character (MLLCT, Figure 1) and a substantial rotational strength since it involves a highly dissymmetric environment around the rhenium atom and the 1,4-P,N chelate. Relativistic effects may also affect the optical rotation, because 5d/6s orbitals in 5d metals hybridize better than 4d/5s orbitals in 4d metals. Note that the sign of the optical rotation is determined by the stereochemistry at the phosphorus center (*R*<sub>P</sub>(+) and *S*<sub>P</sub>(-)). The same conclusions can be drawn for complex **2c**<sup>1</sup>, for which the CD active band at ~380 nm involves the HOMO-2 to LUMO+1 orbitals, that are respectively metal-ligand centered and ligand centered (see SI). These last results highlight the fact that large molar rotations and CD values can be obtained upon complexation of the N,P-moiety of a symmetrical molecule such as the bis(2-pyridyl)phosphole **1c** (Scheme 1).<sup>5c,d</sup>

**Table 1.** Experimental specific and molar rotations of enantio-enriched compounds **2b**<sup>1,2</sup> and **2c**<sup>1</sup> enantiomers.

	(-)- <b>2b</b> <sup>1</sup>	(+)- <b>2b</b> <sup>1</sup>	(-)- <b>2b</b> <sup>2</sup>	(+)- <b>2b</b> <sup>2</sup>	(-)- <b>2c</b> <sup>1</sup>	(+)- <b>2c</b> <sup>1</sup>
$[\alpha]_D^{23}$ [a,b]	-625	+570	-520	+480	-555	+500
$[\phi]_D^{23}$ [a,d]	-4240	+3860	-3510	+3205	-3740	+3370

<sup>a</sup> 0.01 g/100mL in CH<sub>2</sub>Cl<sub>2</sub>. Measured. <sup>b</sup> In deg cm<sup>2</sup> dmol<sup>-1</sup> and within an error of ±10%.

In conclusion, we have shown that optically active Re<sup>I</sup> complexes bearing 2-pyridyl-phosphole P,N exhibit surprisingly large chiroptical properties originating from *i*) the presence of the heavy metal, *ii*) the large dissymmetric environment about the metal center, and *iii*) the π-conjugated nature of the (2-pyridyl)phosphole ligands. This molecular engineering based on coordination of π-conjugated phosphole-pyridine ligands on heavy metal atoms opens a new route for the easy synthesis of simple molecules with appealing chiroptical behavior.

## Notes and references

<sup>a</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, Franc). Fax: (+33) 2-23-23-69-39; Tel: (+33) 2-23-23-57-83; E-mail: [marie.hissler@univ-rennes1.fr](mailto:marie.hissler@univ-rennes1.fr); [jeanne.crassous@univ-rennes1.fr](mailto:jeanne.crassous@univ-rennes1.fr); [regis.reau@univ-rennes1.fr](mailto:regis.reau@univ-rennes1.fr)

<sup>b</sup> Chirosciences, UMR 7313, Stéréochimie Dynamique et Chiralité, Aix-Marseille University, 13397 Marseille Cedex 20, France

<sup>†</sup> Electronic Supplementary Information (ESI) available: [Experimental section, theoretical calculations, spectroscopic data, X-ray crystallographic data and a CIF files]. See DOI: 10.1039/b000000x/

1 (a) *Chirality at the Nanoscale Nanoparticles, Surfaces, Materials and more*, D. Amabilino (ed.), Wiley-VCH, 2009. (b) A. Amouri, M. Gruselle, *Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials*, Wiley-VCH, 2009. (c) B. L. Feringa, W.R. Browne, *Molecular Switches*, Wiley-VCH, 2001. (d) G. Muller, *Dalton Trans.*, 2009, 9692.

2 (a) S. Graule, M. Rudolph, N. Vanthuyne, J. Autschbach, C. Roussel, J. Crassous, R. Réau, *J. Am. Chem. Soc.*, 2009, **131**, 3183; (b) L. Norel, M. Rudolph, N. Vanthuyne, J. A. G. Williams, C. Lescop, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Angew. Chem. Int. Ed.* 2010, **49**, 99. (c) E. Anger, M. Rudolph, L. Norel, S. Zrig, C. Shen, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Chem. Eur. J.*, 2011, **17**, 14178.

3 (a) M. Wrighton, D. L. Morse, *J. Am. Chem. Soc.* 1974, **96**, 998. (b) J. V. Caspar, T. J. Meyer, *J. Phys. Chem.* 1983, **87**, 952. (c) M. M. Richter *Chem Rev.* 2004, **101**, 3003. (d) H. Tsubaki, A. Sekine, Y. Ohashi, K. Koike, H. Takeda, O. Ishitani, *J. Am. Chem. Soc.* 2005, **127**, 15544. (e) D. Beck, J. Brewer, J. Lee, D. McGraw, B. A. DeGraff, J. N. Demas, *Coord. Chem. Rev.* 2007, **251**, 546. (f) M. Mauro, E. Q. Procopio, Y. Sun, C.-H. Chien, D. Donghi, M. Panigati, P. Mercandelli, P. Mussini, G. D'Alfonso, L. De Cola, *Adv. Funct. Mater.* 2009, **19**, 2607. (g) D. M. Cleland, G. Irwin, P. Wagner, D. L. Officer, K. C. Gordon, *Chem Eur. J.* 2009, **15**, 3682. (h) V. W.-W. Yam, K. M. -C. Wong, *Chem. Commun.*, 2011, **47**, 11579. (i) J. E. Yarnell, J. C. Deaton, C. E. McCusker, F. N. Castellano, *Inorg. Chem.* 2011, **50**, 7820. (j) C. Wang, Z. Xie, K. E. deKrafft, W. Bin, *J. Am. Chem. Soc.* 2011, **133**, 13445.

4 Selected examples: (a) S. J. Lee, W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 4554. (b) F. Bock, F. Fischer, W. A. Schenk, *J. Am. Chem. Soc.*, 2006, **128**, 68. (c) J. -D. Chen, F. A. Cotton, *J. Am. Chem. Soc.*, 1991, 113, 2509. (d) J. H. Merrifield, C. E. Strouse, J. A. Gladysz, *Organometallics*, 1982, **1**, 1204. (e) W. E. Buhro, A. Wong, J. H. Merrifield, G. -Y. Lin, A. C. Constable, J. A. Gladysz, *Organometallics*, 1983, **2**, 1852. (f) P. R. Lassen, L. Guy, I. Karame, T. Roisnel, N. Vanthuyne, C. Roussel, X. Cao, R. Lombardi, J. Crassous, T. B. Freedman, L. A. Nafie, *Inorg. Chem.*, 2006, **45**, 10230. (g) F. De Montigny, L. Guy, G. Pilet, N. Vanthuyne, C. Roussel, R. Lombardi, T. B. Freedman, L. A. Nafie, J. Crassous, *Chem. Commun.*, 2009, 4841. (h) J. W. Faller, A. R. Iavoie, *Organometallics*, 2000, **19**, 3957. (i) W. K. Rybak, A. Skarzynska, T. Glowiak, *Angew. Chem. Int. Ed.*, 2003, **42**, 1725. (j) C. M. Alvarez, R. Carrillo, R. Garcia-Rodriguez, D. Miguel, *Chem. Commun.*, 2011, 12765.

5 (a) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi, R. Réau, *Chem. Eur. J.* 2001, **7**, 4222. (b) F. Leca, C. Lescop, E. Rodriguez, K. Costuas, J.-F. Halet, R. Réau, *Angew. Chem. Int. Ed.*, 2005, **44**, 4362; (c) M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J.-F. Halet, R. Réau, *Angew. Chem. Int. Ed.*, 2001, **40**, 228; (d) F. Leca, C. Lescop, L. Toupet, R. Réau, *Organometallics*, 2004, **23**, 6191; (e) C. Fave, M. Hissler, K. Sénéchal, I. Ledoux, J. Zyss, R. Réau, *Chem. Commun.*, 2002, 1674; (f) H. -C. Su, O. Fadhel, C.-J. Yang, T.-Y. Cho, C. Fave, M. Hissler, C. -C. Wu, R. Réau, *J. Am. Chem. Soc.*, 2006, **128**, 983. (g) B. Nohra, E. Rodriguez-Sanz, C. Lescop, R. Réau, *Chem. Eur. J.*, 2008, **14**, 3391; (h) H. Chen, W. Delaunay, L. Yu, D. Joly, Z. Wang, J. Li, Z. Wang, C. Lescop, D. Tondelier, B. Geffroy, Z. Duan, M. Hissler, F. Mathey, R. Réau, *Angew. Chem. Int. Ed.*, 2012, **51**, 214.

6 (a) R. Réau, P. Dyer, *Comprehensive Heterocyclic Chemistry*, Elsevier, Oxford, 2008; (b) F. Mathey, *Phosphorus-carbon Heterocyclic Chemistry: The Rise of a New Domain*. Elsevier Science Ltd, Oxford, 2001.