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

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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^{1a,b} in diverse domains such as molecular switches,^{1c} circular polarized light (CPL) emitters,^{1d} chiral metallogels and nanofibers,^{1a} ... 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.^{1,2} 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.^{1b} 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^I(carbonyl)(diimine) complexes leading to numerous applications in solar chemistry, optoelectronics and photocatalysis.³ However, up to now, few chiral Re^I complexes have been prepared,⁴ and little attention has been paid on their chiroptical properties.^{4d-i} In this paper, the synthesis, enantioresolution and optical properties of chiral rhenium complexes (**2a-c**, Scheme 1) bearing phosphole-based π -conjugated ligands behaving either as monotopic P-donors (**1a**, Scheme 1) or as ditopic 1,4-P,N chelates (**1b,c**) are described.^{5,6} 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^I-complexes **2a-c** (Scheme 1) were prepared by reacting π -conjugated phospholes **1a-c**^{5a,d} with ReCl(CO)₅ in toluene at 80°C under argon.³ 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

³¹P NMR coordination chemical shifts (**2a**, +21.3 ppm; **2b,c**: +45.7/+50.7 ppm).^{5d} 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⁻¹).⁶ Furthermore, symmetrical phosphole **1c** becomes chiral only upon coordination on the Re^I-center (Scheme 1). As a consequence, the isolation of enantiomerically pure derivatives was undertaken on complexes **2a-c**. Complex **2a** consists of a *R_P/S_P* 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 ³¹P{¹H} NMR spectroscopy (**2b**, +47.7, +50.7; **2c**, +48.2, +45.7), due to the presence of two stereogenic centers (*R_P/S_P*, *A_{Re}/C_{Re}*). 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_{Re}-R_P-2b¹* and *C_{Re}-S_P-2b²* were characterized by an X-ray diffraction study (Scheme 2). The Re^I-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⁻¹ 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 **2c²** is rather low (~23 kcal mol⁻¹ at 22°C), preventing its chiroptical properties to be examined, while

enantiomers **2c**¹ are stable enough to be investigated by CD spectroscopy. Indeed, a family of configurationally stable chiral (phosphole-pyridine)Re^I-complexes **2b**^{1,2}-**2c**¹ (Figure 1) with various π -conjugated framework have been synthesized.

Scheme 2. Stereochemical aspects of complex **2b**. Molecular structures of **2b**^{1,2} 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**^{1,2}, the twist angle between the coordinated pyridine and phosphole ring (CCCC dihedral angle, $+51.0^\circ \pm 2^\circ$) is within classical range^{2b,5d} and allow efficient π -conjugation along the sp²-carbon backbone. According to PBE0 DFT and TD-DFT calculations using a polarized LanL2DZ basis set, the lowest energy transition of complex **2b**² 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 (MLCT).

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 CH₂Cl₂ (5×10^{-5} M). The CD spectrum of (+)-**2a** shows several bands with small $\Delta\epsilon$ values (Figure 2). The CD spectra of complexes **2b**^{1,2} and **2c**¹

Figure 1. Absorption spectra of **2a-c** in CH₂Cl₂, TD-DFT simulated spectrum and molecular orbitals for diastereoisomer **2b**² (vertical dashed lines).

Indeed, the HOMO-LUMO transition in **2a** involves the π -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⁻¹ cm⁻¹) and a negative one around 280 nm ($\Delta\epsilon \sim -40$ to -20 M⁻¹ cm⁻¹) for the (+) enantiomers (Figure 2). The only noticeable difference is observed at ca. 310 nm, the smaller CD band have opposite sign for (+)-**2b**¹ and (+)-**2b**², while for (+)-**2c**¹ this band is almost vanishing. It is noteworthy that the CD bands complexes **2b**^{1,2} and **2c**¹ featuring π -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^I-complexes **2b**^{1,2} and **2c**¹ 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,² and deserve to be examined in more details.

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

PBE0 TD-DFT calculations using an extended basis set well-reproduce the CD shape of diastereomeric complexes **2b**^{1,2} and **2c**¹ and enabled to assign their absolute configurations ((+)-C_{Re}-R_P-**2b**¹; (+)-A_{Re}-R_P-**2b**², Scheme 2, (+)-C_{Re}-R_P-**2c**¹) (see SI). These absolute configuration assignments were further confirmed by X-ray crystallography of (+)-C_{Re}-R_P-**2b**¹ and (-)-C_{Re}-S_P-**2b**² (Scheme 2). The fact that complexes **2b**^{1,2} and **2c**¹ 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**¹ 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*_P(+) and *S*_P(-)). The same conclusions can be drawn for complex **2c**¹, 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).^{5c,d}

Table 1. Experimental specific and molar rotations of enantio-enriched compounds **2b**^{1,2} and **2c**¹ enantiomers.

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

^a 0.01 g/100mL in CH₂Cl₂. Measured. ^b In deg cm² dmol⁻¹ and within an error of ±10%.

In conclusion, we have shown that optically active Re^I 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

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