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Tetrathiafulvalene based phosphino-oxazolines: a new family of redox active chiral ligands

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Received (in Cambridge, UK) 20th February 2004, Accepted 14th April 2004
First published as an Advance Article on the web 12th May 2004

Reaction of the lithium salt of EDT-TTF-2-(4-methyl)oxazoline with chloro-diphenylphosphine afforded the novel redox active chiral chelating ligands, EDT-TTF-phosphino-oxazolines, for which a palladium (II) dichloride complex was synthesized and structurally characterized.

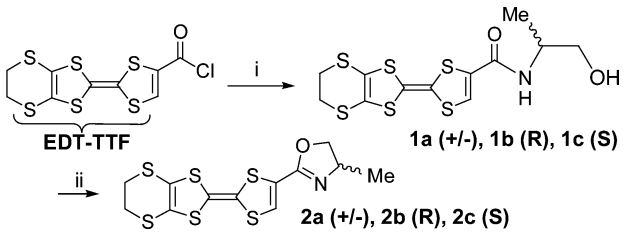
Since the original reports by the groups of A. Pfaltz,[1] G. Helmchen[2] and J. M. J. Williams,[3] the phosphinooxazolines (PHOX) have been widely used in a variety of asymmetric catalytic reactions such as allylic substitution, Heck type reactions, enantioselective hydrogenation, Diels–Alder reactions.[4] Within this type of ligand, the connectivity between the oxazoline ring and the phosphine is ensured by a backbone which is very often an aryl group. Of special interest is the case when the backbone is a ferrocenyl group,[5] because of its planar chirality on the one hand, and its redox-active character on the other hand. This last feature is very interesting from a material point of view, since ferrocene derivatives can be generally reversibly oxidized to the corresponding ferricinium radical cations. Nevertheless, ferrocene based PHOX have not been exploited so far in the synthesis of magnetic molecular materials.[6] Another prominent redox-active class of compounds is represented by the tetrathiafulvalene (TTF) derivatives which have been extensively studied in the search for molecular conductors and superconductors.[7] In this context, the incorporation of TTF as backbone for the phosphinooxazoline ligands opens the way to a new class of redox-active chiral ligands which would eventually allow an electrochemical modulation of the catalytic processes thanks to the electroactive TTF core.[8] In addition, these functional chiral redox ligands or their transition metal complexes may be activated by electrocrystallization into stable radical cation salts, thus having a powerful access to chiral molecular materials with conducting and/or magnetic properties. The coexistence and, more interesting, but also more challenging, the interplay of conducting, magnetic and optical properties hold much promise for the development of multifunctional molecular materials, a field of much current activity.[9] Indeed, cooperative properties may lead to interesting phenomena, such as the magnetoresistance.[9b]

There are several reports in the literature of enantiopure TTF derivatives, the chirality being provided either by the appropriate functionalization of the aliphatic backbone of BEDT-TTF and its related compounds,[10] or by a chiral binaphthyl block.[11] A most notable example consists in a series of TTF-oxazolines,[8] the catalytic activity of which proved to be rather modest. No example of transition metal complexes with chiral TTFs has been described so far. The PHOX ligands which we targeted possess a EDT-TTF backbone since functional derivatives of the latter proved to be appropriate precursors for interesting molecular materials.[12] Indeed, it is worthwhile to preserve an ethylenedithio bridge on one side of the TTF core, because of its ability to establish more lateral S–S intermolecular interactions, with the aim of increasing the dimensionality of the material. The synthesis of the TTF-PHOX ligands required three steps, the first two being achieved by the reaction of EDT-TTF-COCl[12a] with racemic or enantiopure alaninol, isolation and purification of the intermediary hydroxyamides **1a–c**, followed by cyclization in the presence of methanesulfonyl chloride (MsCl)[13] to give the chiral EDT-TTF-oxazolines **2a–c** (Scheme 1).†

An ultimate proof for their formation was provided by a single crystal X-ray study of (*R*)-EDT-TTF-OX **2b**, for which thin single crystalline platelets could be grown by slow evaporation of an AcOEt solution of donor. The compound crystallizes in the chiral monoclinic group space $P2_1$.‡ The overall geometry of the donor is nearly planar, only the methyl group C(12) at the asymmetric carbon C(11), going out of the mean plane of the molecule (Fig. 1).

Furthermore, lithiation of the EDT-TTF-OX has been performed with LDA; the reaction of the corresponding lithium salts with Ph_2PCl yielded the targeted phosphinooxazolines **3a–c** (Scheme 2).

Note that the hydrogen abstraction and generation of the intermediary carbanion is very likely facilitated by the presence of the oxazoline ring.[5] The ^{31}P NMR spectroscopy demonstrates unambiguously the formation of the PHOX ligands (δ = −15.6 ppm), by comparison with chemical shifts of other TTF-phosphines.[14] All the other analytical data and elemental analysis confirm the successful preparation of the new redox-active chelating ligands.† In order to test the coordination properties of the EDT-TTF-PHOX thus obtained, and also to check the influence on their electrochemical behaviour, we reacted the racemic donor **3a** with $PdCl_2$, keeping in mind that many of the asymmetric catalytic



Scheme 1 *Reagents and conditions*: i) 2-amino-1-propanol (± or *R* or *S*), NEt_3, THF, 12 h, RT; ii) NEt_3, THF, MsCl at 0 °C, then 20 h at 50 °C.

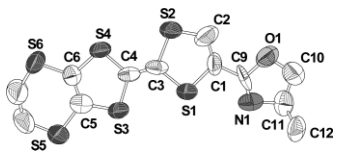
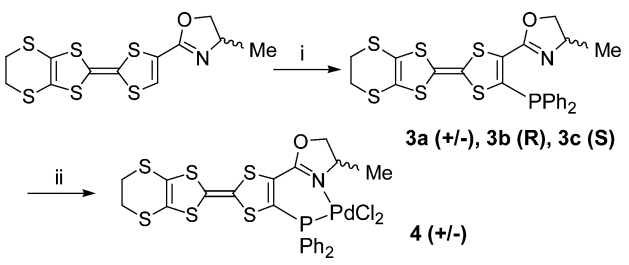


Fig. 1 ORTEP view of the enantiopure EDT-TTF-OX **2b** (thermal ellipsoids set at 50% probability, H atoms omitted). Selected bond lengths (Å): C(1)–C(2) 1.34(3), C(1)–S(1) 1.75(2), C(2)–S(2) 1.66(3), C(9)–N(1) 1.20(3), C(3)–C(4) 1.28(2).



Scheme 2 *Reagents and conditions*: i) LDA, THF, −78 °C, Ph_2PCl; ii) $PdCl_2$, reflux in $CHCl_3$ overnight.

DOI: 10.1039/b402877e

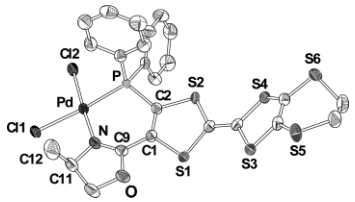


Fig. 2 ORTEP view of the (EDT-TTF-PHOX)$PdCl_2$ complex **4** (thermal ellipsoids set at 50% probability, H atoms omitted). Selected bond lengths (Å) and angles (°): Pd–P 2.2194(8), Pd–N 2.054(3), Pd–Cl(1) 2.3742(8), Pd–Cl(2) 2.2927(9), C(1)–C(2) 1.349(5); Cl(1)–Pd–Cl(2) 90.43(3), Cl(1)–Pd–N 92.30(8), Cl(2)–Pd–P 85.08(3), P–Pd–N 92.15(8).

reactions involve PHOX-palladium complexes (Scheme 2). The complexation was monitored by ^{31}P NMR spectroscopy, the chemical shift of the complex (δ = 14.8 ppm) being in the usual range. The structure of the square planar complex **4** has been determined by X-ray diffraction analysis. Suitable single crystals have been grown by slow diffusion of pentane into a CH_2Cl_2 solution of **4**. The complex crystallized in the triclinic centrosymmetric group space $P\bar{1}$, with one enantiomer molecule in general position,‡ the other enantiomer being generated through the inversion center. As expected, the palladium atom lies in a square planar environment formed by two chlorine atoms, the N atom of the oxazoline and the P atom of the phosphine (Fig. 2). Bond lengths and angles are in the usual range.

The TTF framework is twisted along the three S–S hinges, which is not surprising for a neutral TTF derivative. Cyclic voltammetry measurements on the series of EDT-TTF-OX **2a–c**, EDT-TTF-PHOX **3a–c** and on the palladium complex **4** show for all the compounds the two reversible single electron oxidation waves, corresponding to the formation of the $TTF^{+\cdot}$ radical cations, then TTF^{2+}, with values for $E^{1/2}$ (V) as follows (ref. Ag/AgCl, 0.1 M $TBAPF_6$ in CH_2Cl_2, 0.1 V s^{-1}): **2** 0.65 and 1.13, **3** 0.63 and 1.09, **4** 0.87 and 1.25. The anodic shift of about 0.24 V when comparing **3** and **4** is in the same range as that observed for a chelating TTF-diphosphine coordinated to various transition metal fragments.[15] This difference shows a significant electronic communication between the TTF core and the coordinated metallic centre, an important feature in the view of electrochemical controlled catalytic processes based on TTF-PHOX ligands.

The synthesis of the new electroactive ligands EDT-TTF-OX and EDT-TTF-PHOX offers further interesting developments such as: (i) preparation of TTF based chiral molecular materials, with the eventuality of chiral resolution of racemic anions by electrocrystallization; (ii) utilization in asymmetric catalytic reactions. Also, the synthetic path to access the EDT-TTF-PHOX opens up the possibility to prepare bis(oxazoline) ligands in a modular way.[16]

Financial support from the CNRS, the Ministère de l'Education et de la Recherche (grant for C.R.) and University of Angers.

Notes and references

† Compounds **1a–c** were prepared by stirring 2-amino-1-propanol (9.84 mmol) with dry NEt_3 (16 mmol) and EDT-TTF-COCl (8 mmol) in THF, then purified by column chromatography on silica gel eluted with THF. Then, to solutions of **1a–c** (5.06 mmol) and NEt_3 (10.8 mmol) in THF, methanesulfonyl chloride (MsCl) (10.34 mmol) was added and, after 0.5 h of stirring at 0 °C, NEt_3 (45.2 mmol) was further added and the reaction mixture thus obtained was heated at 50 °C for 20 h. After purification by column chromatography on silica gel (AcOEt/cyclohexane 2 : 1) and recrystallization in MeCN, **2a–c** were recovered as orange crystalline solids (60% yield). Reaction of **2a–c** (1.32 mmol) with LDA (1.45 mmol) in THF at −78 °C, 4 h, then addition of Ph_2PCl (1.45 mmol), followed by stirring the solution overnight at RT and a rapid column chromatography (CH_2Cl_2/cyclohexane 4 : 1) provided the compounds **3a–c** as red solids after evaporation of solvent (27% yield).

Selected spectroscopic and analytical data: for **2a–c**: ^1H NMR (500.04 MHz, $CDCl_3$) δ 1.31 (d, ^3J = 6.6 Hz, 3H, Me), 3.29 (s, 4H, $S(CH_2)_2S$), 3.88 (t, ^3J = ^2J = 7.9 Hz, 1H, OCH_2), 4.31 (m, 1H, NCH), 4.45 (dd, ^3J = 6.6 Hz, ^2J = 7.9 Hz, 1H, OCH_2), 6.97 (s, 1H, =CH); Anal. Calc. for $C_{12}H_{11}NOS_6$: C 38.17, H 2.94, N 3.71; found: C 38.05, H 2.97, N 3.52%.

For **3a–c**: ^1H NMR (500.04 MHz, $CDCl_3$) δ 1.14 (d, ^3J = 6.4 Hz, 3H, Me), 3.25 (s, 4H, $S(CH_2)_2S$), 3.67 (t, ^3J = ^2J = 7.6 Hz, 1H, OCH_2), 4.18 (m, 1H, NCH), 4.25 (dd, ^3J = 6.4 Hz, ^2J = 7.6 Hz, 1H, OCH_2), 7.36–7.45 (m, 10H, Ph); ^{31}P NMR (202.39 MHz, $CDCl_3$) δ −15.6 (s); Anal. Calc. for $C_{24}H_{20}NOPS_6$: C 51.31, H 3.59, N 2.49; found: C 51.66, H 3.73, N 2.55%.

For **4**: ^{31}P NMR (202.39 MHz, $CDCl_3$) δ 14.9 (s); MALDI-MS *m*/*z*: 666.9 $[M]^+$; Anal. Calc. for $C_{24}H_{20}NOPPdS_6{\cdot}CH_2Cl_2$: C 36.44, H 2.69, N 1.70; found: C 36.28, H 2.59, N 1.74%.

‡ Crystal data for **2b**: $C_{12}H_{11}NOS_6$, M = 377.58, monoclinic, space group $P2_1$, a = 6.3686(10), b = 7.667(2), c = 16.419(3) Å, β = 99.60(2), U = 790.4(3) $Å^3$, Z = 2, T = 293(2) K, μ = 0.858 mm^{-1}, D_c = 1.586 g cm^{-3}, 6434 refl. measured, 682 refl. with $I > 2\sigma(I)$, R = 0.078, R_W = 0.250.

For **4**: $C_{24}H_{20}Cl_2NOPPdS_6{\cdot}CH_2Cl_2{\cdot}H_2O$, M = 839.97, triclinic, space group $P\bar{1}$, a = 11.3583(3), b = 12.6818(4), c = 12.9393(2) Å, α = 69.912(2), β = 85.895(2), γ = 70.706(2), U = 1650.28(7) $Å^3$, Z = 2, T = 293(2) K, μ = 1.340 mm^{-1}, D_c = 1.690 g cm^{-3}, 31866 refl. measured, 5499 refl. with $I > 2\sigma(I)$, R = 0.041, R_W = 0.098. CCDC 232992 (**2b**) and CCDC 232993 (**4**). See http://www.rsc.org/suppdata/cc/b4/b402877e/ for crystallographic data in .cif or other electronic format.

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