# Efficient resolution of the *cis*-$[Ru(phen)_2(MeCN)_2]^{2+}$ complex (phen = 1,10-phenanthroline) using Δ-[tris(tetrachlorobenzenediolato)-phosphate(V)] as a chiral counter-ion

**Michel Gruselle,*[a] René Thouvenot,[a] Régis Caspar,[a] Kamal Boubekeur,[a] Hani Amouri,[a] Mikhael Ivanov[b] and Kaia Tõnsuaadu[c]**

[a] *Laboratoire de Chimie Inorganique et Matériaux Moléculaires, CNRS, Université Pierre et Marie Curie, 75252 Paris cedex 05, France. Fax: + 33 14 427 3841; e-mail: gruselle@ccr.jussieu.fr*
[b] *Department of Chemistry, Russian State Pedagogical University, 191186 St. Petersburg, Russian Federation*
[c] *Institute of Chemical Engineering, Tallinn Technical University, 19086 Tallinn, Estonia*

DOI: 10.1070/MC2004v014n06ABEH002034

**The synthesis of *cis*-$[Ru(phen)_2(MeCN)_2][(\Delta)$-tris(tetrachlorobenzenediolato)phosphate(V)$]_2$ abbreviated as [1]-[Δ-TRISPHAT]$_2$ and the separation of a mixture of the diastereomeric ion pairs by column chromatography are considered. The X-ray structure of [Δ-1][Δ-TRISPHAT]$_2$ is briefly described, as well as the CD curves of [Δ-1][Δ-TRISPHAT]$_2$ and [Λ-1][Δ-TRISPHAT]$_2$ fractions.**

The chemistry of octahedral *cis*-$[Ru(diimine)_2X_2]$ complexes of ruthenium(II) has been extensively investigated but a few of these studies have involved optically active systems. Bosnich and Dwyer[1] reported such *cis*-$[Ru(phen)_2(py)_2]^{2+}$ chiral complexes (phen = 1,10-phenanthroline) and their use as precursors of octahedral ruthenium derivatives.[1] Other complexes were obtained in enantiomerically enriched or pure forms: X = CO,[2] pyridine,[3] Cl, OSR$^1$R$^2$,[4] substituted bipyridine.[5] Kane-Maguire and co-workers[6] achieved the resolution of dicationic *cis*-$[Ru(phen)_2(MeCN)_2]^{2+}$ **1** using antimonyl *d*-tartrate as a chiral counter-ion.

Taking into account the importance of the *cis*-$[Ru(phen)_2(MeCN)_2]^{2+}$ cationic complex in pure Δ and Λ enantiomeric forms as chiral building blocks for the synthesis of related species, we have reinvestigated the resolution of this cation using Δ-[tris(tetrachlorobenzenediolato)phosphate(V)] = Δ-TRISPHAT as a chiral counter-ion.

Since the discovery of Δ-TRISPHAT by Lacour *et al.*[7] as an NMR chiral diamagnetic shift reagent, quite a few articles were published highlighting the power of such a lipophilic anion in chiral NMR enantiodifferentiation studies of chiral cations, as well as in their resolution.[8]

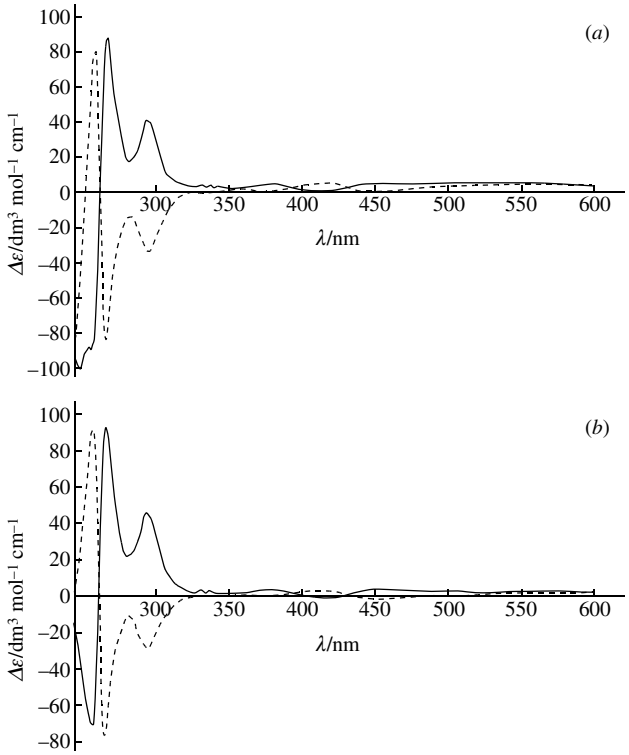


**Figure 1** CD Curves of [Δ-$Ru(phen)_2(MeCN)_2$][Δ-TRISPHAT]$_2$ (dashed line) and [Λ-$Ru(phen)_2(MeCN)_2$][Δ-TRISPHAT]$_2$ (solid line): (*a*) experimental curves, including Δ-TRISPHAT contribution; (*b*) the curves after subtraction of the Δ-TRISPHAT contribution.

Racemic complex [**1**][$CF_3SO_3$]$_2$ was synthesised from *cis*-$[Ru(phen)_2Cl_2]$ by treatment with two equivalents of $AgCF_3SO_3$ in $CH_2Cl_2$. After evaporation of $CH_2Cl_2$, MeCN was added to the solid residue. After mixing for 12 h at room temperature, the mixture was filtered, the filtrate was concentrated and [**1**][$CF_3SO_3$]$_2$ was obtained in 90% yield by precipitation with diethyl ether. Thermal analysis (TGA, DTA) showed that [**1**][$CF_3SO_3$]$_2$ starts to decompose at about 190 °C with a maximum at 244 °C. This is accompanied by an exothermic effect at 250 °C. The ruthenium salt was identified by elemental analysis, $^1$H, $^{13}$C NMR and IR spectroscopy. The [cinchonidinium][Δ-TRISPHAT] {$[\alpha]_D^{20}$ = = −468° (0.1, ethanol)} was obtained as described previously.[7]

Here we report an efficient and convenient procedure for the resolution of ruthenium bis(diimine) complexes on neutral alumina using [cinchonidinium][Δ-TRISPHAT] as a resolving agent.† Three fractions were collected: (i) pure sample of [Δ-**1**]-[Δ-TRISPHAT]$_2$, (ii) mixture of two diastereomers and (iii) pure [Λ-**1**][Δ-TRISPHAT]$_2$. These compounds were completely identified by elemental analysis, $^1$H and $^{31}$P NMR and IR spectroscopy.† The compounds are soluble in many organic solvents

† Anion metathesis was achieved by dissolving one equivalent of [**1**][$CF_3SO_3$]$_2$ (100 mg, 1.19 mmol) with two equivalents of [cinchonidinium][Δ-TRISPHAT] (274 mg, 2.6 mmol) in MeCN; this mixture was impregnated on neutral alumina, and the solvent was then evaporated under reduced pressure. The chromatography was performed on neutral alumina ($L$ = 17 cm, $\Phi$ = 2 cm) using $CH_2Cl_2$ as an eluent. Three fractions containing [**1**](Δ-TRISPHAT)$_2$ salts were recovered. The first fraction is pure [Δ-**1**][Δ-TRISPHAT]$_2$ (92.5 mg, 37% yield) obtained as an orange yellow microcrystalline compound; the second is a mixture of the two diastereomers (40/60 [Δ,Δ/Λ,Δ]; 77 mg, 31% yield), and the third is pure [Λ-**1**][Δ-TRISPHAT]$_2$ (61.5 mg, 25% yield) obtained as an orange yellow solid. A fourth fraction containing an unidentified ruthenium complex was also recovered.

*Spectroscopic data for* [Δ-**1**][Δ-TRISPHAT]$_2$: $^1$H NMR (300 MHz, $CD_2Cl_2$) δ: 9.88 (dd, 2H, *J* 5.2 Hz, *J* 1.3 Hz), 8.59 (dd, 2H, *J* 8.3 Hz, *J* 1.2 Hz), 8.18 (dd, 2H, *J* 8.3 Hz, *J* 1.2 Hz), 8.16–8.04 (AB system, 4H, $J_{AB}$ 11.2 Hz), 7.99 (dd, 2H, *J* 8.3 Hz, *J* 1.5 Hz), 7.94 (dd, 2H, *J* 5.3 Hz, *J* 1.2 Hz), 7.18 (dd, 2H, *J* 8.1 Hz, *J* 1.4 Hz), 2.21 (s, 6H). $^{31}$P NMR (121.5 MHz, $CD_2Cl_2$) δ: –80.5. IR (KBr pellet, $\nu$/cm$^{-1}$): 2929, 1633, 1597, 1452, 1428, 1390, 1301, 1249, 1236, 1148, 992, 825, 721, 674. Found (%): C, 36.72; H, 1.09; N, 4.03. Calc. for $C_{64}H_{22}N_6O_{12}P_2Cl_{24}Ru$ (%): C, 36.94; H, 1.07; N, 4.04.

*Spectroscopic data for* [Λ-**1**][Δ-TRISPHAT]$_2$: $^1$H NMR (300 MHz, $CD_2Cl_2$) δ: 9.72 (dd, 2H, *J* 5.2 Hz, *J* 1.3 Hz), 8.72 (dd, 2H, *J* 8.3 Hz, *J* 1.2 Hz), 8.35 (dd, 2H, *J* 8.3 Hz, *J* 1.2 Hz), 8.19–8.05 (AB system, 4H, $J_{AB}$ 11.2 Hz), 8.09 (dd, 2H, *J* 8.3 Hz, *J* 7.0 Hz), 7.62 (dd, 2H, *J* 5.3 Hz, *J* 1.2 Hz), 7.42 (dd, 2H, *J* 8.3 Hz, *J* 1.5 Hz), 2.24 (s, 6H). $^{31}$P NMR (121.5 MHz, $CD_2Cl_2$) δ: –80.5. IR (KBr pellet, $\nu$/cm$^{-1}$): 2929, 1635, 1597, 1452, 1428, 1390, 1302, 1236, 1249, 1009, 992, 825, 721, 674. Found (%): C, 36.53; H, 1.12; N, 4.09. Calc. for $C_{64}H_{22}N_6O_{12}P_2Cl_{24}Ru$ (%): C, 36.94; H, 1.07; N, 4.04.

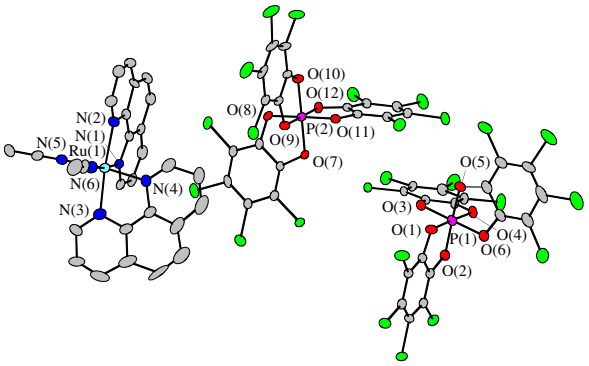


**Figure 2** Structure of (Δ)-*cis*-[Ru(phen)$_2$(MeCN)$_2$](Δ-TRISPHAT)$_2$·(MeCN) showing the all Δ configuration of the ions. The hydrogen atoms and the acetonitrile crystallisation molecule have been omitted for clarity.

such as acetone, methanol, acetonitrile and methylene chloride. The higher solubility of TRISPHAT-containing ruthenium salts over hexafluorophosphate derivatives is a potential advantage,[9] particularly to perform further substitution reactions of the MeCN ligands.

The CD curves recorded in a $CH_2Cl_2$ solution ($3\times10^{-4}$ mol dm$^{-3}$) allowed us, based on the exciton theory,[10] to establish the absolute configuration of the two isomers obtained. These curves [Figure 1(*a*)] are characteristic of enantiopure diastereomeric compounds.

The Cotton effect observed at 253 nm is related to the Δ-TRISPHAT counter-ion. The positive Cotton effect at 258 nm and the negative ones at 264 and 295 nm characterise the cation Δ-**1**, the reverse effects respectively negative and positive being related to the cation Λ-**1**. Subtraction of the Δ-TRISPHAT contribution leads to symmetrical curves [Figure 1(*b*)] highlighting the enantiomeric relationship between [Λ-**1**]$^{2+}$ and [Δ-**1**]$^{2+}$.

The absolute rotations were found to be $[\alpha]_D^{20} = -575°$ (0.04, $CH_2Cl_2$) for [Δ-**1**][Δ-TRISPHAT]$_2$ and $[\alpha]_D^{20} = -150°$ (0.04, $CH_2Cl_2$) for [Λ-**1**][Δ-TRISPHAT]$_2$.

$^1$H NMR spectra recorded in $CD_2Cl_2$ solutions allow us to determine the purity of each isomer since the two well resolved spectra are significantly different in the presence of the diamagnetic Δ-TRISPHAT counter-ion.† For example, the proton $H_{10}$ adjacent to the nitrogen atom in the phenanthroline ligand gives rise to a doublet of doublets ($J$ 5.20 Hz, 1.28 Hz) centred at 9.884 or 9.721 ppm for [Δ-**1**][Δ-TRISPHAT]$_2$ or [Λ-**1**]-[Δ-TRISPHAT]$_2$ diastereomer, respectively ($\Delta\delta$ = 163 ppb, *i.e.*, 49 Hz at 300 MHz). The $^1$H signal from coordinated acetonitrile may also be taken into consideration for the measurements of the diastereomeric excesses (de): actually, it appears as a very intense singlet (6H) located at 2.21 and 2.24 ppm ($\Delta\delta$ = 30 ppb, *i.e.,* 9 Hz at 300 MHz) for [Δ-**1**][Δ-TRISPHAT]$_2$ and [Λ-**1**][Δ-TRISPHAT]$_2$, respectively.

According to the relative integration, we can assume that the de for the two diastereomers are up to 95%. Taking into consideration the optical purity of the [cinchonidinium][Δ-TRISPHAT], which is 100%, we can conclude that the enantiomeric excesses (ee) of the Δ and Λ cationic parts are 95%.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether in a $CH_2Cl_2$ solution of the Δ-*cis*-[Ru(phen)$_2$(MeCN)$_2$](Δ-TRISPHAT)$_2$] complex.‡ The structure (Figure 2) confirms the presence of two Δ-TRISPHAT counter-anions, the *cis* orientation of the two MeCN ligands, as well as the Δ configuration of the octahedral ruthenium complex.

This work was supported by the CNRS and the University Pierre et Marie Curie (France). We are grateful to Professor J. Lacour (Geneva, Switzerland) for helpful discussions. M. Ivanov greatly acknowledges the Ministère des affaires étrangères français for the funding of his stay at the UPMC.

## References

1 (*a*) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, 1996, **19**, 2229; (*b*) B. Bosnich, *Inorg. Chem.*, 1968, **7**, 178.
2 (*a*) T. J. Rutherford, M. G. Quagliotto and F. R. Keene, *Inorg. Chem.*, 1995, **34**, 3857; (*b*) H. A. Goodwin, E. C. Gyarfas and D. P. Mellor, *Aust. J. Chem.*, 1958, **11**, 428.
3 (*a*) X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1991, **30**, 3796; (*b*) X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1995, **34**, 5791.
4 (*a*) D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda and M. G. B. Drew, *Inorg. Chem.*, 2000, **39**, 317; (*b*) F. Pezet, J.-C. Daran, I. Sasaki, H. Aït-Haddou and G. Balavoine, *Organometallics*, 2000, **19**, 4008.
5 (*a*) M. Brissard, O. Convert, M. Gruselle, C. Guyard-Duhayon and R. Thouvenot, *Inorg. Chem.*, 2003, **42**, 1378; (*b*) R. Caspar, H. Amouri, M. Gruselle, C. Cordier, B. Malézieux, R. Duval and H. Lévêque, *Eur. J. Inorg. Chem.*, 2003, 499.
6 R. T. Watson, J. L. Jackson, Jr., J. D. Harper, K. A. Kane-Maguire, L. A. P. Kane-Maguire and N. A. P. Kane-Maguire, *Inorg. Chim. Acta*, 1996, **249**, 5.
7 J. Lacour, C. Ginglinger, C. Grivet and G. Bernardinelli, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 608 (*Angew. Chem.*, 1997, **109**, 660).
8 (*a*) J. Lacour and V. Hebbe-Viton, *Chem. Soc. Rev.*, 2003, **32**, 373; (*b*) J. Lacour, S. Torche-Haldimann, J. J. Jodry, C. Ginglinger and F. Favarger, *Chem. Commun.*, 1998, 1733; (*c*) J. Lacour, C. Ginglinger, F. Favarger and S. Torche-Haldimann, *Chem. Commun.*, 1997, 2285; (*d*) M. Brissard, H. Amouri, M. Gruselle and R. Thouvenot, *C. R. Chimie*, 2002, **5**, 53; (*e*) M. Brissard, M. Gruselle, B. Malézieux, R. Thouvenot, C. Guyard-Duhayon and O. Convert, *Eur. J. Inorg. Chem.*, 2001, 1745; (*f*) H. Amouri, R. Thouvenot and M. Gruselle, *C. R. Chimie*, 2002, **5**, 257; (*g*) H. Amouri, R. Thouvenot, M. Gruselle, B. Malézieux and J. Vaissermann, *Organometallics*, 2001, **20**, 1904; (*h*) M. Chavarot, S. Ménage, O. Hamelin, F. Charnay, J. Pécaut and M. Fontecave, *Inorg. Chem.*, 2003, **42**, 4810; (*i*) G. Brutlants, C. Bresson, A. Boisdenghien, F. Pieirard, A. Kirsch-De Mesmaeker, J. Lacour and K. Bartik, *New J. Chem.*, 2003, **27**, 748.
9 O. Maury, J. Lacour and H. Le Bozec, *Eur. J. Inorg. Chem.*, 2001, 201.
10 B. Bosnich, *Acc. Chem. Res.*, 1969, **2**, 266.

*Received: 14th September 2004; Com. 04/2359*

‡ *Crystal data.* [Δ-**1**][Δ-TRISPHAT]$_2$·MeCN crystallises in the triclinic chiral $P_1$ space group with $a$ = 11.927(1), $b$ = 12.630(1) and $c$ = 15.073(1) Å, $\alpha$ = 81.75(1)°, $\beta$ = 85.74(1)°, $\gamma$ = 88.04(1)°, $V$ = 2240.2(4) Å$^3$, $T$ = 250 K, $Z$ = 1, $\mu$ = 0.98 mm$^{-1}$, $R$ = 0.0696 [for 11907 $F_0 > 4\sigma(F_0)$], $wR_2$ = = 0.1933 (for all 23810 data), Flack parameter $x$ = 0.02(3). Monoclinic crystals of [Λ-**1**][Δ-TRISPHAT]$_2$ were also obtained by slow evaporation of a $CH_2Cl_2$ solution ($a$ = 23.24, $b$ = 15.74 and $c$ = 25.36 Å; $\beta$ = 109.19°); unfortunately, the poor quality of the crystals did not allow the complete resolution of the structure.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 257770. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.