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Generation of an optically active rhodium(III) complex by crystallization-induced spontaneous resolution of a racemic mixture

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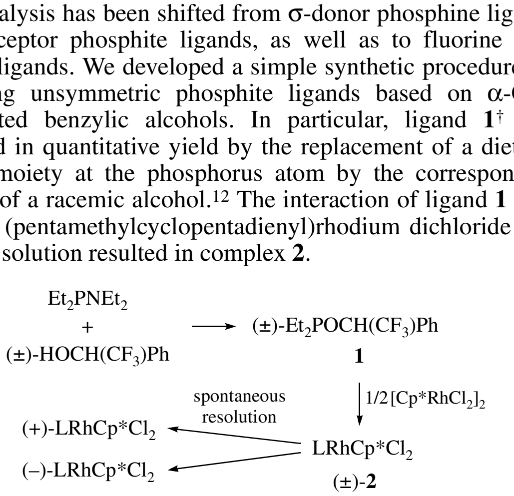
Racemic (π-pentamethylcyclopentadienyl)(2,2,2-trifluoro-1-phenylethyl diethylphosphinite)rhodium dichloride **2** was found to be a conglomerate, which undergoes spontaneous resolution during crystallization.

In principle, provided that a compound crystallises as a conglomerate (racemic mixture of homochiral crystals), the best way to obtain a pure enantiomer is spontaneous resolution in a controlled manner.[1–3] This resolution can be carried out by direct crystallization followed by the mechanical separation of crystals, or a mixture can be resolved by entrainment depending on differences in the rates of crystallization of the enantiomers in a near-racemic supersaturated solution.[1] Chromatography or manual sorting can be used to collect the first quantities of an enantiomer required to apply resolution by entrainment. Many conglomerates have been described for a variety of organic compounds,[1,3] but only a few organophosphorus compounds[4–8] are among them. Thus, the spontaneous resolution by crystallization of a BIPHOS (1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-biphosphole) ligand was used for the further synthesis of the enantiomerically pure palladium complex [$PdCl_2$–(biphos)].[8]

As for coordination compounds, there are a series of conglomerates of Werner salt type anionic complexes, in which a metal ion is coordinated by three bidentate ligands in an octahedral environment,[1,3,9] {[(η^6-*p*-cymene)RuCl(PN)][SbF_6] [PN = (3a*S*,8a*R*)-2-(2-diphenylphosphinophenyl)-3a,8a-dihydroindane[1,2-*d*]oxazole]},[10] and two neutral molybdenum complexes containing trimethylphosphite as one of the ligands {molybdenum [π-cyclopentadienyl-*trans*-iododicarbonyl(trimethylphosphite)] and its methylcyclopentadienyl analogue}.[11]

Recently, interest in the field of homogeneous metallocomplex catalysis has been shifted from σ-donor phosphine ligands to π-acceptor phosphite ligands, as well as to fluorine containing ligands. We developed a simple synthetic procedure for preparing unsymmetric phosphite ligands based on α-CF_3-substituted benzylic alcohols. In particular, ligand **1**[†] was obtained in quantitative yield by the replacement of a diethylamino moiety at the phosphorus atom by the corresponding residue of a racemic alcohol.[12] The interaction of ligand **1** with dimeric (pentamethylcyclopentadienyl)rhodium dichloride in a CH_2Cl_2 solution resulted in complex **2**.



We found using X-ray diffraction analysis that **2**[‡] crystallises in the chiral space group ($P2_12_12_1$) with two independent molecules ($Z = 8$) (Figure 1). Taking into account that both molecules are characterised by the same (*R*)-configuration [the Flack parameter is 0.00(3)], we can conclude that the crystallization of the complex leads to the spontaneous resolution of enantiomers. The higher melting point (Δ ~ 6°, without decomposition) of a single crystal in comparison with the fine mixture of a few arbitrary crystals (apparently enriched sample) confirms this fact. To determine the absolute configuration, we repeatedly performed the X-ray analysis of another arbitrary crystal of **2**, which was similar to the former by visual evaluation. We found that C(15) and C(15′) atoms of the above crystal possess the opposite (*S*)-configuration to the former sample [the Flack parameter is 0.01(2)]. Its approximate angle of rotation was $[\alpha]^{D}_{20}$ ~ +900° (*c* 1, $CHCl_3$, the low precision of the absolute rotating value was due to a low weight of the single crystal, *m* = 0.02 mg). Therefore, the absolute configuration of complex (*S*)-(+)-**2** was unambiguously determined using the combination of X-ray diffraction analysis and polarimetry.

The principal bond lengths and angles in complex **2** are close to the expected values for complexes of this type. The main difference between two independent molecules is the orientation of the phosphorus ligand with respect to the Cp* ring. This difference can be illustrated by the Cl(1)Rh(1)P(1)O(1) torsion angles (72.8 and 178.7), as well as in the variation of the torsion angle Rh(1)P(1)O(1)C(15) (35.8 and 167.3) for two independent molecules, respectively. Thus, two independent molecules may be considered as two rotamers around Rh–P and P–O bonds [Figure 1, **A** and **B**]. In addition, the mutual disposition of Cl_2P and Cp* in independent molecules is also slightly different. This, in combination with different systems

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[†] NMR spectra were recorded on Bruker WP-200SY and AMX-400 spectrometers in C_6D_6 and $CDCl_3$ solutions using residual proton signals of deuterated solvents (^1H) and 85% H_3PO_4 or CF_3COOH (^{31}P or ^{19}F, respectively) as an external standard. The angle of rotation was determined on a Perkin-Elmer Model 341 polarimeter using a 1.3 ml cell.

The starting 2,2,2-trifluoro-1-phenylethan-1-ol was obtained according to a published procedure.[13] All reactions were carried out in an argon stream using absolute solvents.

Synthesis of 2,2,2-trifluoro-1-phenylethyl diethylphosphinite **1**. An equimolar mixture of diethyl-(*N*,*N*-diethylamino)phosphonite (1.22 g, 6.926 mmol) and (±)-2,2,2-trifluoro-1-phenylethanol (1.11 g, 6.926 mmol) was placed in a distillation flask, which was heated up to 155 °C and maintained under these conditions for 45 min. During that time the distillation of diethylamine was observed. The residue was vacuum distilled to yield 1.65 g (90%) of the target compound, bp 75 °C/0.5 Torr. ^{31}P {^1H} NMR (C_6D_6) δ: 157.94. ^{19}F NMR (C_6D_6) δ: 0.83 (d, $^4J_{PF}$ 5.25 Hz). ^1H NMR (C_6D_6) δ: 0.75 (apparent quintet, 3H, Me, $^3J_{HH}$ = = $^3J_{PH}$ = 7.6 Hz), 1.12 (apparent quintet, 3H, Me, $^3J_{HH}$ = $^3J_{PH}$ = 7.6 Hz), 1.13–1.22, 1.34–1.48, 1.60–1.69 (3m, 1H + 2H + 1H, PCH_2, in each $^2J_{PH}$ 14.8 Hz), 4.92–5.01 (m, 1H, OCH), 7.05–7.14 (m, 3H, *m*- and *p*-Ph), 7.34 (d, 2H, *o*-Ph, $^3J_{HH}$ 6.0 Hz). Found (%): C, 53.86; H, 6.09. Calc. for $C_{12}H_{16}F_3OP$ (%): C, 54.55; H, 6.10.

Synthesis of (π-pentamethylcyclopentadienyl)(2,2,2-trifluoro-1-phenylethyl diethylphosphinite)rhodium dichloride **2**. A solution of $[RhCp^*Cl_2]_2$ (81.8 mg, 0.132 mmol) in 2 ml of CH_2Cl_2 was added to a solution of phosphinite **1** (70 mg, 0.265 mmol) in 5 ml of CH_2Cl_2. After stirring the red solution for 3 h at room temperature, the solvent was evaporated in a vacuum to a volume of ~0.5 ml and then about 4 ml of pentane was added. The crystal precipitate (dark red prisms) was filtered off and dried in vacuum at ambient temperature (107 mg, 78%). Mp 173 °C (fine mixture of a few arbitrary crystals, apparently enriched sample), 179 °C (single crystal). ^{31}P {^1H} NMR ($CDCl_3$) δ: 153.50 (d, $^1J_{PRh}$ 156.5 Hz). ^{19}F NMR ($CDCl_3$) δ: 2.60. ^1H NMR ($CDCl_3$) δ: 0.92 (dt, 3H, *Me*CH_2, $^3J_{HH}$ 7.6 Hz, $^3J_{PH}$ 16.8 Hz), 1.26 (dt, 3H, *Me*CH_2, $^3J_{HH}$ 7.6 Hz, $^3J_{PH}$ 16.8 Hz), 1.62 (d, 15H, MeC^*_P, J_{PH} 3.6 Hz), 2.12–2.25, 2.28–2.51 (2m, 1H + 3H, PCH_2), 5.72–5.78 (m, 1H, OCH), 7.36–7.39 (m, 3H, *m*- and *p*-Ph), 7.55–7.57 (m, 2H, *o*-Ph). Found (%): C, 45.59; H, 5.59. Calc. for $C_{22}H_{36}F_3Cl_2OPRh$ (%): C, 45.59; H, 6.27.

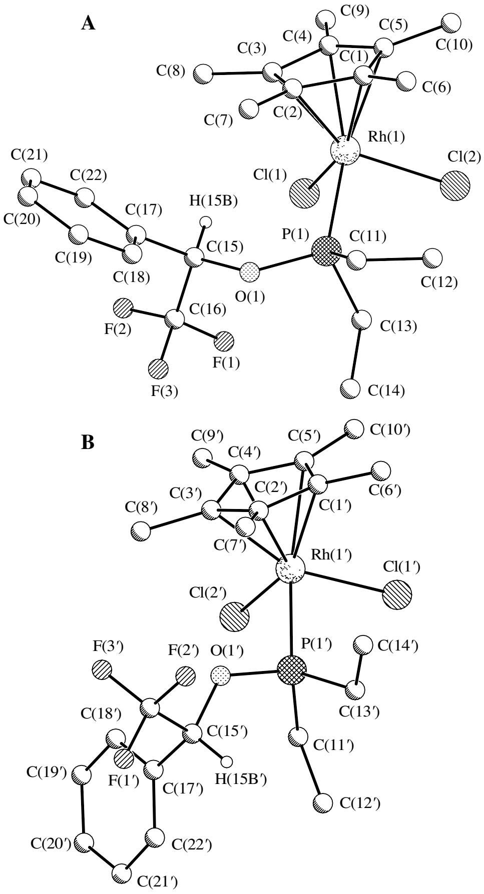

Figure 1 The general view of two independent molecules in complex **2**. The main bond lengths (Å): Rh(1)–P(1) 2.285(1), Rh(1)–Cl(1) 2.405(1), Rh(1)–Cl(2) 2.376(1), P(1)–O(1) 1.632(3), P(1)–C(11) 1.815(5), P(1)–C(13) 1.803(5) (**A**); Rh(1′)–P(1′) 2.282(1), Rh(1′)–Cl(1′) 2.405(1), Rh(1′)–Cl(2′) 2.404(1), P(1′)–O(1′) 1.645(3), P(1′)–C(11′) 1.822(5), P(1′)–C(13′) 1.806(5) (**B**); bond angles (°): P(1)–Rh(1)–Cl(1) 89.08(4), P(1)–Rh(1)–Cl(2) 88.33(4), Cl(2)–Rh(1)–Cl(1) 92.08(4), O(1)–P(1)–Rh(1) 117.8(1), O(1)–P(1)–C(11) 97.2(2), O(1)–P(1)–C(13) 105.1(2), C(11)–P(1)–Rh(1) 115.4(2), C(11)–P(1)–C(13) 104.9(2), C(13)–P(1)–Rh(1) 114.4(2) (**A**); P(1′)–Rh(1′)–Cl(1′) 86.33(4), P(1′)–Rh(1′)–Cl(2′) 87.31(4), Cl(1′)–Rh(1′)–Cl(2′) 93.69(4), O(1′)–P(1′)–Rh(1′) 104.0(1), O(1′)–P(1′)–C(11′) 108.3(2), O(1′)–P(1′)–C(13′) 108.6(2), C(11′)–P(1′)–Rh(1′) 114.3(2), C(13′)–P(1′)–Rh(1′) 119.0(2), C(11′)–P(1′)–C(13′) 102.3(2) (**B**).

of intermolecular Cl···H contacts (H···Cl 2.54–3.13 Å, C···Cl 3.44–4.15 Å, CHCl 130–164°), leads to a variation in the Rh–Cl bond lengths.

In conclusion, the spontaneous resolution of **2** by crystallization gives enantiopure crystals. Therefore, enantiopure chiral catalyst **2** can be obtained directly from a racemic solution using resolution by entrainment.

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‡ *Crystallographic data for* **2**: at 120 K, the crystals are orthorhombic, space group $P2_12_12_1$, a = 8.892(2) Å, b = 14.394(4) Å, c = 37.954(1) Å, V = 4857.8(17) Å^3, Z = 8 (Z' = 2), d_{calc} = 1.568 g cm^{-3}, μ(MoKα) = = 10.24 cm^{-1}, F(000) = 2336. Intensities of 52447 reflections were measured with a SMART 1000 CCD diffractometer at 110 K [λ(MoKα) = = 0.71072 Å, ω-scans with a 0.3 step in ω and 10 s per frame exposure, $2\theta < 60°$], and 14154 independent reflections (R_{int} = 0.0574) were used in a further refinement. The absorption correction was applied semi-empirically from equivalents. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The positions of hydrogen atoms were calculated from the geometrical point of view. The absolute configuration was determined using the Flack parameter, which, in the case of the R-configuration C(15) and C(15′) atoms, was equal to 0.00(3). The refinement converged to wR_2 = 0.0967 and GOF = 1.034 for all independent reflections [R_1 = 0.0459 was calculated against F for 12201 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT.

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 212045. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2003.