Easy Synthesis of New Chiral Tetradentate N_4 Schiff Bases and Their Use as Ligands for Metal Complexes

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The chiral N_4 Schiff bases (1*R*,2*R*)-*N*,*N*′-bis(2-*p*-tosylaminobenzylidene)-1,2-diaminocyclohexane (H_2CyTs, **1**), (1*R*,2*R*)-*N*,*N*′-bis(2-trifluoromethylsulfonaminobenzylidene)-1,2-diaminocyclohexane (H_2CyTf, **2**), (1*R*,2*R*)-*N*,*N*′-bis(2-aminobenzylidene)-1,2-diaminocyclohexane (**3**) and (1*R*,2*R*)-*N*,*N*′-bis(2-nitrobenzylidene)-1,2-diaminocyclohexane (**4**) were synthesized by a new and easy method in high purity and good yields. All the organic compounds were characterized by elemental analysis, mass spectrometry, IR and ^{1}H and ^{13}C NMR spectroscopy. Divalent Co, Cu and Ni complexes **5**–**8**, containing the sulfonamide ligands **1** or **2**, have been prepared and characterized. The X-ray crystal structures of complexes [Co(1*R*,2*R*)-CyTs] (**6**) and [Ni(1*R*,2*R*)-CyTf] (**8**) have been solved. These complexes are potential precursors for homogeneous asymmetric catalysis of a variety of reactions.

Introduction

The development of efficient catalytic asymmetric reactions is one of the most challenging tasks in current synthetic chemistry, much effort having been devoted to the creation of new chiral N-ligands and their metal complexes for evaluation in advanced asymmetric catalysis.[1−2] Condensation between an amine and an aldehyde, forming what is called a Schiff base, was one of the earliest reported reactions in chemistry.[3] Jacobsen and Katsuki developed tetradentate salen ligands, now one of the most intensely studied classes of chiral Schiff bases, able to coordinate easily to a wide variety of metals. The interest in such bases has increased since the discovery of manganese(III) salen complexes, excellent catalysts for the enantiomeric epoxidation of unfunctionalized alkenes.[4−6] The development of chiral salen metal complexes and catalysts in the last decade has stimulated very rapid growth.[7−8] Chiral salen-containing complexes are now used as catalysts for a variety of enantioselective reactions such as oxidation, aziridination, cyclopropanation, Diels−Alder cyclisation, addition of trimethylsilyl cyanide or zinc derivatives to aldehydes, the Strecker reaction, and for kinetic resolution of racemic epoxides.[9]

Recently, Moberg described the preparation of tetradentate N_4 ligands from chiral aziridines bearing sulfonamido functionalities. Their titanium complexes catalyse the addition of diethylzinc to benzaldehyde with high enantioselectivity (80% *ee*).[10] In the last decade, Noyori demonstrated that the use of chiral sulfonamide ligands prepared from chiral diamines gave active and enantioselective ruthenium catalysts for hydrogen-transfer reductions of ketones.[11] In other studies, high *ee* values have been achieved with bis(sulfonamide) complexes of titanium (additions of diethylzinc to aldehydes), zinc (cyclopropanation)[12] or aluminium (Diels−Alder cycloadditions).[13]

We are focussing on new chiral Schiff base ligands containing sulfonamido functionalities in place of the phenolic groups on salen ligands. As the pK_a values of $C_6H_5NHSO_2CF_3$,[14] C_6H_5NH-tosyl[15] and phenol[16] are 4.45, 8.46 and 9.89, respectively, the acidity of these sulfonamides is higher than that of phenol. Deprotonation of the sulfonamide ligand should therefore be easy and should facilitate its complexation to transition metals to form chiral complexes. Very recently, Bermejo and co-workers have described a method for the synthesis of the amino-tosylated Schiff base ligand **1**, (1*R*,2*R*)-*N*,*N*′-bis(2-*p*-tosylaminobenzylidene)-1,2-diaminocyclohexane (H_2CyTs), with unstable 2-aminobenzaldehyde as intermediate.[17] They described the X-ray crystal structure of this ligand and of the corresponding Ni and Cu complexes. In this paper we describe a different method for the synthesis of this type of molecule starting from 2-nitrobenzaldehyde and (1*R*,2*R*)-diaminocyclohexane, thus allowing easy modification of the sulfonyl moiety. This method then allowed us to obtain ligand **2**, (1*R*,2*R*)-H_2CyTf [(1*R*,2*R*)-*N*,*N*′-bis(2-trifluoromethylsulfonaminobenzylidene)-1,2-diaminocyclohexane]. The syn-

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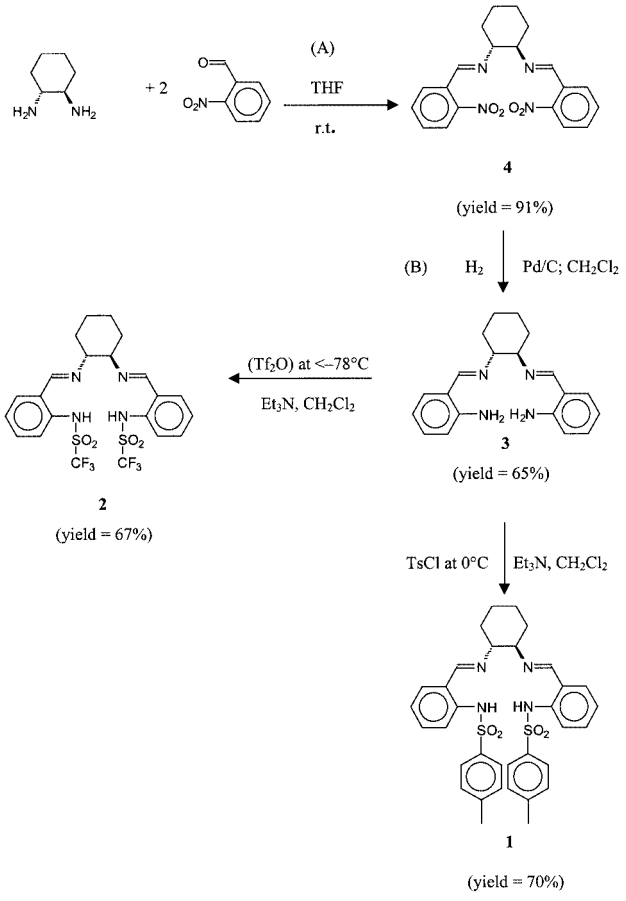
thesis of the complexes Co[(1*R*,2*R*)-CyTf] (**5**), Co[(1*R*,2*R*)-CyTs] (**6**), Cu[(1*R*,2*R*)-CyTs] (**7**) and Ni[(1*R*,2*R*)-CyTf] (**8**) are reported, as well as the X-ray crystal structures of **6** and **8**. The method we have developed should allow the easy synthesis of a wide variety of chiral sulfonamides.

Results and Discussion

Synthesis of Ligands

The synthesis of chiral sulfonamides that we have developed is based on the coupling of enantiomerically pure and commercially available (1*R*,2*R*)-diaminocyclohexane with 2-nitrobenzaldehyde (Scheme 1). The C_2-symmetric dinitro compound formed (**4**) is then reduced to **3**, and functionalisation of the diamine groups can be undertaken.

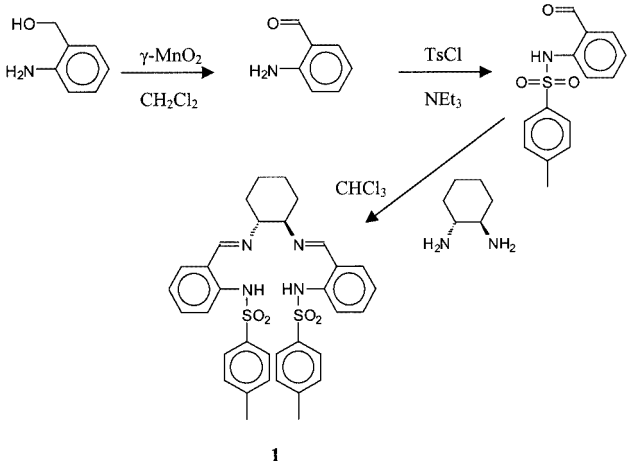


Scheme 1. General synthesis of N_4 Schiff bases **1**–**4**

The first step (A) is easily performed in anhydrous THF in the presence of molecular sieves, which collect the water formed during the condensation between the 2-nitrobenzaldehyde and the diaminocyclohexane. The following step (B) is a reduction carried out under an atmospheric pressure of hydrogen and catalysed by Pd-C (10%). In order to avoid imine reduction or hydrolysis, it is very important to keep the temperature at 0 °C and to use molecular sieves. The selectivity of this reduction step is indeed the key factor of the synthetic pathway. The diamine **3** can then react with TsCl or $(CF_3SO_2)_2O$ (TF_2O) to give the C_2-symmetric sulfonamides **1** and **2**, respectively.

Synthesis of (1R,2R)-N,N′-bis(2-p-tosylaminobenzylidene)-1,2-diaminecyclohexane, (1R,2R)-H$_2$CyTs (1)

The method described by Bermejo for the synthesis of compound **1**[17] is shown in Scheme 2. The first step involves the oxidation of 2-aminophenylmethanol by γ-MnO_2 to give 2-aminobenzaldehyde,[18] which is a very unstable compound and rapidly polymerises at room temperature.[19–20] Avoidance of the use of this intermediate therefore allows many synthetic developments. The third step, condensation between 2-tosylaminobenzaldehyde and the diaminocyclohexane, is performed at 70 °C and requires use of a Dean–Stark trap.



Scheme 2. Synthesis of **1** by Bermejo's method

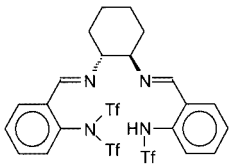
We have synthesised compound **1** from compound **3** by *N*-tosylation with tosyl chloride in dichloromethane at 0 °C in presence of triethylamine. Our method is simpler and easier, since on the one hand it avoids the use of an unstable intermediate 2-aminobenzaldehyde, while on the other it enables the synthesis of compound **3**, which is also potentially a ligand and can give rise to several other salen-type structures.

Synthesis of (1R,2R)-N,N′-bis(2-trifluoromethylsulfonaminobenzylidene)-1,2-diamino-cyclohexane, (1R,2R)-H$_2$CyTf (2)

The preparation of (1*R*,2*R*)-H_2CyTf (**2**) from diamine **3**, by treatment with Tf_2O in dry CH_2Cl_2 at low temperature (< −78 °C), requires the presence of Et_3N to neutralise the triflic acid formed during the reaction. The reaction should begin at −78 °C under a water-free atmosphere in order to avoid the triflic acid-catalysed hydrolysis of the imine functions. Several tests were carried out at higher temperatures (−20 °C, 0 °C), but resulted in the destruction of compound **3**.

Just two equivalents of triflic anhydride are enough to convert **3** completely into **2**. If an excess of this reagent is

used, the secondary product **2′** is also formed (Scheme 3).[21]



2'

Scheme 3

In the ^{1}H NMR spectra, the NH protons appear as broad signals at δ = 14.8 ppm (for **2**), 15 ppm (for **2′**) and 13.2 ppm (for **1**). It is notable that the OH proton in the salen ligand appears at δ = 13−13.5 ppm. For ligand **2**, we can assume that the protons should be easily replaceable by a metal. This trend should facilitate the formation of metal complexes with sulfonamide Schiff base **2**.

The presence of the triflate groups avoids the π-stacking interactions (face-to-face or face-to-edge) previously observed between the terminal tosyl aromatic rings or between the tosyl and the benzylidene rings in H_2CyTs.[17] These π-stacking interactions influence the conformation of the molecule and generate a competitive interaction in ligand **1**, thus reducing the available cavity for the metal.

Synthesis of Complexes

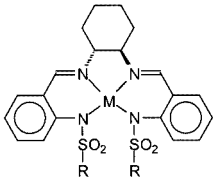
The interest in making new salen-type ligands lies in their ability to form stable complexes with transition metals, thus serving as potential precursors for homogeneous asymmetric catalysis of a variety of reactions.[7,10] All the complexes were prepared by addition of the divalent metal salts $Co(AcO)_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$ or $CuCl_2{\cdot}4H_2O$ to a MeOH/CH_2Cl_2 (1:1) solution of ligand **1** or a MeOH solution of ligand **2**. The complexes Co[(1*R*,2*R*)-CyTf], Co[(1*R*,2*R*)-CyTs], Cu[(1*R*,2*R*)-CyTs] and Ni[(1*R*,2*R*)-CyTf] (Scheme 4), which precipitated in MeOH, were obtained with high purity and in high yields. All these complexes were characterised by mass spectra.

5. M = Co, R= CF_3

6. M = Co, R= *p*-Tol

7. M = Cu, R= *p*-Tol

8. M = Ni, R= CF_3



Scheme 4. General structural formula of complexes **5**, **6**, **7** and **8**

Crystal Structure Studies of Complex 6 and Complex 8

ORTEP views of **6** and **8** are shown in Figure 1 and Figure 2, respectively. Selected bond lengths, distances and angles are displayed in Table 1 for **6** and in Table 2 for **8**. All the N-donor atoms in these complexes are bound to the metal centre. One oxygen atom of each tosyl group seems to have a weak interaction with the metal atom. The Co···O(18), Co···O(36), Ni···O(18) and Ni···O(33) distances (2.560(3) Å, 2.607(3) Å, 3.052(3) Å and 3.027(3) Å) are too long to be regarded as true coordinated bonds. The metal environment in **6** could be described as pseudo-tetrahedral and that in complex **8** as pseudo-square planar. The N(15)···N(34) distance in complex **6** is shorter than that in the free ligand (3.560(4) Å for **6** and 5.346(5) Å[17] for **1** [H_2CyTs]). In a similar way, the N(15)···N(31) distance in the free ligand **2** [7.324(8) Å] shortened after complexation to the Ni [2.824(4) Å] to produce **8**.

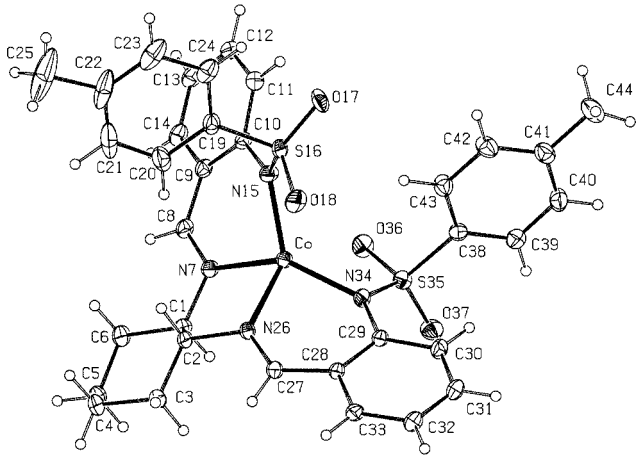


Figure 1. ORTEP view of complex **6**

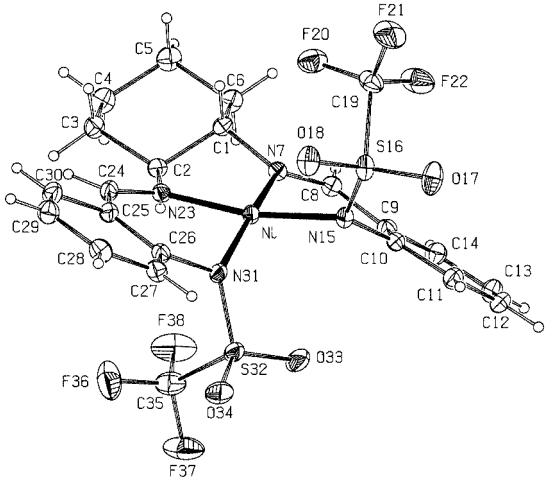


Figure 2. ORTEP view of complex **8**

Conclusion

The synthetic route that we have developed has allowed us to prepare four C_2-symmetric Schiff bases **1**−**4** in good yields. The tosylated derivative **1** was also prepared very recently by Bermejo, by a different pathway. The main advantage of our method is the formation of a stable imine/amine intermediate that can be easily modified.

The two sulfonamide ligands are indeed promising chiral inductors for asymmetric catalysis. We thus prepared various complexes of Co, Cu and Ni. The X-ray structures

Table 1. Selected distances (Å), angles (°) and bond lengths (Å) in complex **6**

N(7)···N(26)	2.661(3)
N(7)···N(15)	2.790(3)
N(15)···N(34)	3.560(4)
N(26)···N(34)	2.821(4)
N(7)−C(1)−C(2)−N(26)	−53.5(3)
C(1)−C(2)−N(26)−C(27)	−129.2(4)
C(2)−C(1)−N(7)−C(8)	−129.7(3)
Co−N(7)	2.067(2)
Co−N(26)	2.052(3)
Co−N(15)	1.996(3)
Co−N(34)	1.994(3)
N(7)−Co−N(15)	86.7(1)
N(7)−Co−N(26)	80.5(1)
N(7)−Co−N(34)	138.4(1)
N(15)−Co−N(26)	135.6(1)
N(15)−Co−N(34)	126.3(1)
N(26)−Co−N(34)	88.4(1)

Table 2. Selected distances (Å), angles (°) and bond lengths (Å) in complex **8**

N(7)···N(23)	2.538(4)
N(7)···N(15)	2.646(4)
N(23)···N(31)	2.704(4)
N(31)···N(15)	2.824(4)
N(7)−C(1)−C(2)−N(23)	47.9(2)
C(2)−C(1)−N(7)−C(8)	127.3(2)
C(1)−C(2)−N(23)−C(24)	135.5(2)
Ni−N(7)	1.860(2)
Ni−N(23)	1.874(2)
Ni−N(15)	1.910(2)
Ni−N(31)	1.905(2)
N(7)−Ni−N(15)	89.15(8)
N(7)−Ni−N(23)	85.68(8)
N(7)−Ni−N(31)	168.86(9)
N(15)−Ni−N(23)	168.97(9)
N(15)−Ni−N(31)	95.49(9)
N(23)−Ni−N(31)	91.37(8)

show that those Schiff bases act as tetradentate ligands, forming structures with the metal centre and the four N atoms with pseudo-square-planar geometry for Ni complexes and pseudo-tetrahedral geometry for Co species.

We are now focusing on the synthesis of other C_2-symmetric sulfonamide Schiff base ligands.

Experimental Section

General Remarks: Melting points (m.p., uncorrected) were determined with a Köffler Bench type WME (HEIZBANK). Elemental analysis (C, H, N, S, O, F) were obtained from the Service Central d'Analyse of the CNRS (Solaize). High-resolution mass spectra (HR LSIMS: Liquid Secondary Ionisation Mass Spectrometry) were carried out on a Finnegan MAT 95xL at the UCBL Centre de Spectroscopie de Masse. IR spectra (KBr plates) were recorded on a FT Perkin−Elmer spectrometer. $[\alpha]_D$ values were determined with a Perkin−Elmer 241 polarimeter (l = 1 dm; 25 °C; concentration c in g/mL). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AC 200 (200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, 188.29 MHz for ^{19}F) or a Bruker AC 300 FT (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 282.45 MHz for ^{19}F) spectrometer; δ values are given in ppm and J in Hz.

(1*R*,2*R*)-*N*,*N*′-Bis(2-*p*-tosylaminobenzylidene)-1,2-diaminocyclohexane (1): Compound **3** (0.5 g, 1.56 mmol) was dissolved in CH_2Cl_2 (10 mL), Et_3N (470µL, 3.28 mmol) was added, and the mixture was cooled to 0 °C. At this temperature, *p*-toluenesulfonyl chloride (0.625 g, 3.28 mmol) was added. The resulting mixture was stirred overnight (the temperature was allowed to rise at room temperature). CH_2Cl_2 (10 mL) was added, and the resulting solution was washed with water (3 × 20 mL). After separation, the organic layer was dried with Na_2SO_4 and the solvent was removed under vacuum. After addition of methanol (10 mL) to the residual oil, a yellow precipitate formed, and was collected by filtration through a Millipore filter (vv type, pore size 0.10 µm) and dried under vacuum to give ligand **1** (0.444 g). Isolated yield 70%. M.p. 175 °C. The ligand was recrystallized from CH_2Cl_2/MeOH to give yellow crystals suitable for X-ray diffraction. The crystal structure, which we obtained before publication of the Bermejo study,[17] gave the same results. $[\alpha]_D$ = −107.2 (c = 0.01 g/mL, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 13.2 (broad s, 2 H, NH), 8.47(s, 2 H, HC=N), 7.49 (dd, $^4J_{H,H}$ = 1.05, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar−H), 7.42 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar−H), 7.27 (dd, $^4J_{H,H}$ = 1.6, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar−H), 7.2 (ddd, $^4J_{H,H}$ = 1.6, $^3J_{H,H}$ = 7.5, 8.2 Hz, 2 H, Ar−H), 6.9 (ddd, $^4J_{H,H}$ = 1.05; $^3J_{H,H}$ = 7.5, 8.2 Hz, 2 H, Ar−H), 6.63 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar−H), 3.57 (m, 2 H, CH−N), 2.08 (s, 3 H, Ar−CH_3), 1.5−2 (m, 8 H, −CH_2−) ppm. ^{13}C NMR ($CDCl_3$, 300Mz, 25 °C): δ = 164 (C=N), 143, 139, 136 (3Cq), 134 (C−Ar), 129.3 (C−Ar), 127.2 (C−Ar), 122.3 (C−Ar), 120.4 (Cq), 117 (C−Ar), 73.4 (CH), 33.6 (CH_2), 24.3 (CH_2), 21.3 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 1631 (C=N), 1157−1167 ($NHSO_2$) cm^{-1}. HR LSIMS calcd. for $C_{34}H_{36}N_4O_4S_2{\cdot}H^+$(629.8): 629.2256; found 629.22553. $C_{34}H_{36}N_4O_4S_2$ (628.8): calcd. C 64.94, H 5.77, N 8.91, O 10.18, S 10.20; found C 65.09, H 5.92, N 8.97, O 10.60, S 10.40.

(1*R*,2*R*)-*N*,*N*′-Bis(2-trifluoromethylsulfonaminobenzylidene)-1,2-diaminocyclohexane (2): Compound **3** (0.47 g, 1.47 mmol) was dissolved in dry CH_2Cl_2 (8 mL), and Et_3N (430µL, 2.95 mmol) was added. After the mixture had been cooled to −78 °C under an argon atmosphere, a solution of $(CF_3SO_2)_2O$ (483µL, 2.95 mmol) in CH_2Cl_2 (8 mL) was added dropwise. The resulting solution was stirred overnight (the temperature was allowed to rise to room temperature). The solvent was evaporated and ligand **2** (0.57 g) was obtained by flash chromatography (silica, ethyl acetate/cyclohexane, 40:60). MW = 584.55. Isolated yield 67%. M.p. 136 °C. Compound **2** was recrystallized from CH_2Cl_2/cyclohexane to give yellow crystals suitable for X-ray diffraction study. $[\alpha]_D^{20}$ = −537 (c = 0.01 g/mL, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 14.8 (broad s, 2 H, NH), 8.4 (s, 2 H, HC=N), 7.7 (dd, $^4J_{H,H}$ = 0.94, $^3J_{H,H}$ = 8.3 Hz, 2 H, Ar−H), 7.4 (ddd, $^4J_{H,H}$ = 1.5, $^3J_{H,H}$ = 7.2, 8.3 Hz, 2 H, Ar−H), 7.3 (dd, $^4J_{H,H}$ = 1.5 $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar−H), 7.1 (ddd, $^4J_{H,H}$ = 0.9, $^3J_{H,H}$ = 7.2, 7.8 Hz), 3.6 (m, 2 H, CH-N), 1.3−2.1 (m, 8 H, −CH_2−) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 168 (C=N), 143.7 (Cq), 134.5 (C−Ar), 134.4 (C−Ar), 122.9 (C−Ar), 120.2(q, $^1J_{C,F}$ =323.9 Hz, 2C, CF_3), 119 (C−Ar), 118.7(Cq), 70.2 (CH), 32.8 (CH_2), 23.7 (CH_2) ppm. ^{19}F NMR ($CDCl_3$, 300 MHz, 25 °C): δ = −77.68 (s, 6F) ppm. IR (KBr): $\tilde{\nu}$ = 1651 (C=N), 1316−1199 ($NHSO_2$) cm^{-1}. HR LSIMS calculated for $C_{22}H_{22}F_6N_4O_4S_2{\cdot}H^+$ (585.6): 585.10649; found 585.10773. $C_{22}H_{22}F_6N_4O_4S_2$ (584.5): calcd. C 45.20, H 3.79, F 19.50, N 9.58, O 10.95, S 10.97; found C 45.27, H 3.90, F 19.43, N 9.40, S 11.47.

(1*R*,2*R*)-*N*,*N*′-Bis(2-aminobenzylidene)-1,2-diaminocyclohexane (3): Compound **4** (1.026 g, 2.7 mmol) was dissolved in CH_2Cl_2 (10 mL), and Pd/C(10%) (130 mg) was added, together with 4-Å molecular sieves. The mixture was stirred under a hydrogen atmosphere at 0 °C. The consumption of hydrogen was steady in the course of time. After 4 hours, the required volume of H_2 had been consumed. The mixture was filtered through Celite, the solvent was removed by evaporation, and the residue was washed with methanol and filtered through a Millipore filter (vv type, pore size 0.10 μm). Finally, it was dried under vacuum to give ligand **3** (0.56 g) as a white solid. Isolated yield: 65%. M.p. 182 °C. The ligand was recrystallized from CH_2Cl_2/MeOH to give colourless crystals suitable for X-ray diffraction study. $[\alpha]_D^{20} = -517$ (c = 0.01 g/mL, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 8.3 (s, 2 H, HC=N), 7.1 (dd, $^4J_{H,H}$ = 1.3, $^3J_{H,H}$ = 7.7 Hz, 2 H, Ar−H), 7.07(ddd, $^4J_{H,H}$ = 1.3, $^3J_{H,H}$ = 7.7, 7.8 Hz, 2 H, Ar−H), 6.64 (ddd, $^4J_{H,H}$ = 1.5, $^3J_{H,H}$ = 7.7, 7.8 Hz, 2 H, Ar−H), 6.6 (dd, $^4J_{H,H}$ = 1.5 $^3J_{H,H}$ = 7.7 Hz, 2 H, Ar−H), 6.3 (broad s, 4 H, NH_2), 3.3 (m, 2 H, CH−N), 1.5−2 (m, 2 H, $-CH_2-$) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 163.5 (C=N), 148.76 (Cq), 133.4 (C−Ar), 130.8 (C−Ar), 118.3 (Cq), 116.2 (C−Ar), 115.8 (C−Ar), 74.8 (CH), 33.9 (CH_2), 24.9 (CH_2) ppm. IR (KBr): ṽ = 3248−3473 (NH_2), 1626 (C=N) cm^{-1}. HR LSIMS calculated for $C_{20}H_{24}N_4{\cdot}H^+$(321.4): 321.20792; found 321.20724. $C_{20}H_{24}N_4$ (320.4): calcd. C 74.97, H 7.55, N 17.48; found C 75.38, H 7.67, N 17.26.

(1*R*,2*R*)-*N*,*N*′-Bis(2-nitrobenzylidene)-1,2-diaminocyclohexane (4): 2-Nitrobenzaldehyde (6.7 g, 44.3 mmol) and 4-Å molecular sieves were added to a solution of (1*R*,2*R*)-1,2-diaminocyclohexane (2.6 g, 22.7 mmol) in anhydrous THF (12 mL). The mixture was stirred overnight at room temperature under an argon atmosphere. Dichloromethane (12 mL) was added, and the resulting mixture was filtered through silica (CH_2Cl_2), the solvents were evaporated, and the residual oil was dried under vacuum to give product **4** (7.846 g) as a white solid. Isolated yield: 91%. M.p. 75 °C. $[\alpha]_D^{20}$ = +556 (c = 0.01 g/mL, CH_2Cl_2). ^{1}H NMR (DMSO, 300 MHz, 25 °C): δ = 8.5 (s, 2 H, HC=N), 8 (dd, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 7.9 Hz, 2 H, Ar−H), 7.9 (dd, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar−H), 7.7 (ddd, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 7.4, 7.5 Hz, 2 H, Ar−H), 7.6 (ddd, $^4J_{H,H}$ = 1.1 Hz; $^3J_{H,H}$ = 7.4 and 8 Hz, 2 H, Ar−H), 3.5 (m, 2 H, CH−N), 1.5−1.8 (m, 8 H, $-CH_2-$) ppm. ^{13}C NMR ($CDCl_3$, 200 MHz, 25 °C): δ = 156.8 (C=N), 148.7 (Cq), 133.6 (C−Ar), 131.35 (Cq), 130.5 (C−Ar), 130 (C−Ar), 124.2 (C−Ar), 54.7 (CH), 32.6 (CH_2), 24.3 (CH_2) ppm. IR (KBr): ṽ = 1633 (C=N), 1521−1339 (NO_2) cm^{-1}. HR LSIMS calculated for $C_{20}H_{20}N_4O_4{\cdot}H^+$ (381.4): 381.15628; found 381.15611. $C_{20}H_{20}N_4O_4$(380.4): calcd. C 63.15, H 5.30, N 14.73, O 16.83; found C 63.00, H 5.24, N 14.57, O 17.27.

[Co(1*R*,2*R*)-CyTf] (5): $Co(O_2CMe)_2{\cdot}4H_2O$ (43 mg, 0.172 mmol) was added to a solution of **2** (100 mg, 0.17 mmol) in MeOH (4 mL). The reaction mixture was heated at reflux for 1 hour. The pink solution turned brown and a copious amount of precipitate was formed, and the solid was collected and washed with methanol. Recrystallization from CH_2Cl_2/MeOH gave red crystals suitable for X-ray diffraction study (90 mg, yield 82%). HR LSIMS calculated for $C_{22}H_{20}F_6N_4O_4S_2Co{\cdot}H^+$ (642.5): 642.0240; found 642.02424.

[Co(1*R*,2*R*)-CyTs] (6): A solution of $Co(O_2CMe)_2{\cdot}4H_2O$ (44 mg, 0.176 mmol) in EtOH (2 mL) was added to a solution of **1** (107 mg, 0.17 mmol) in toluene (1 mL). The resulting solution was heated at reflux for 1.5 hours. The pink solution turned brown, and a copious amount of precipitate was formed. The solid was collected, washed with methanol and recrystallized from CH_2Cl_2/MeOH to give red crystals suitable for X-ray diffraction study (60 mg, yield 51%). HR LSIMS calculated for $C_{34}H_{34}CoN_4O_4S_2{\cdot}H^+$(686.7): 686.14316; found 686.14309.

[Cu(1*R*,2*R*)-CyTs] (7): This complex was prepared by the same procedure as used for **6**, starting from $Cu(O_2CMe).H_2O$. The product crystallises as a green, microcrystalline solid (yield 75%). No X-ray study was carried out, since one had just been published.[17] HR LSISM for $C_{34}H_{34}CuN_4O_4S_2{\cdot}H^+$(691.3): 690.13980; found 690.13980.

[Ni(1*R*,2*R*)-CyTf] (8):This complex was prepared by the same procedure as for **5**, from $NiCl_2{\cdot}6H_2O$ (44 mg, 0.184 mmol) and **2** (108 mg, 0.184 mmol) in MeOH (yield 70%). The red crystals obtained were suitable for X-ray diffraction study. ^{1}H NMR (DMSO, 300 MHz, 25 °C): δ = 8 (s, 2 H, HC=N), 7.8(d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ar−H), 7.55 (t, $^3J_{H,H}$ = 7.25 Hz, 2 H, Ar−H), 7.35 (d, $^3J_{H,H}$ = 7.6 Hz), 7.3 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar−H), 2.75 (m, 2 H, CH−N), 2.4 (m, 2 H, CH_2), 1.8 (m, 2 H, CH_2), 1.6 (m, 2 H, CH_2), 1.3 (m, 2 H, CH_2) ppm. ^{19}F NMR (DMSO, 300 MHz, 25 °C): δ = −75.84 (s, 6F, CF_3) ppm. HR LSIMS calculated for $C_{22}H_{20}F_6N_4O_4S_2Ni{\cdot}H^+$ (642.3): 641.0262; found 641.02424.

X-ray Crystallographic Study: Data were collected on a Nonius Kappa CCD diffractometer by use of graphite monochromated Mo-K_α radiation (λ = 0.71070 Å) from a fine-focus sealed tube source. The structures were solved by use of SHELXTL[22] and refined by full-matrix, least-squares on F^2. Absorption corrections were applied (Multiscan, sortav).[23] All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were included in the model at geometrically calculated positions and refined by use of a riding model. Experimental details are shown in Table 3. CCDC-194700 and CCDC-194701 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road,

Table 3. Crystal data and details of the structure determination of **6** and **8**

	6	**8**
Empirical formula	$C_{34}H_{34}CoN_4O_4S_2$	$C_{22}H_{20}F_6N_4NiO_4S_2$
Molecular mass [g/mol]	685.7	641.25
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
Crystal size (mm)	0.5 × 0.25 × 0.25	0.20 × 0.20 × 0.20
a [Å]	8.9140(1)	9.9320(2)
b [Å]	19.4390(3)	15.2950(2)
c [Å]	9.6870(2)	16.4420(3)
β [°]	103.040(1)	
V [Å^3]	1635.27(5)	2497.70(8)
Z	2	4
D (g/cm^{-3})	1.393	1.705
μ Mo-K_α (mm^{-1})	0.696	1.028
T (K)	173	295
Number of reflections collected	20905	24709
R int	0.051	0.044
Number of independent reflections	10778	9021
Number of reflections $I > 2\,\sigma(I)$	8760	6569
R [$I > 2\,\sigma(I)$]	0.059, 0.173	0.045, 0.098
R [all data]	0.075, 0.185	0.072, 0.108
Absolute structure parameter	−0.01(1)	−0.02(9)

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[21] **2′:** ^{1}H NMR($CDCl_3$, 300 MHz, 25 °C): δ = 15 (broad s, 1 H, NH), 8.3 (s, 1 H, HC=N), 8.1 (s, 1 H, HC=N), 7.7 (m, 1 H, Ar−H), 7.6 (m, 2 H, Ar−H), 7.5−7.3 (m, 3 H, Ar−H), 7.1 (m, 1 H, Ar−H), 6.85 (m, 1 H, Ar−H), 3.8 (m, 1 H, CH−N), 3.4 (m, 1 H, CH−N), 2.2−1.2 (m, 8 H, $-CH_2-$) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ = 168 (C=N), 161 (C=N), 152 (Cq−Ar), 141 (Cq−Ar), 137 (C−Ar), 135.4 (C−Ar), 135.2 (C−Ar), 135 (C−Ar), 133 (C−Ar), 132 (C−Ar), 130 (Cq−Ar), 121(C−Ar), 120.8 (C−Ar), 117(Cq−Ar), 75 (CH−N), 67 (CH−N), 32.9 (CH_2), 32.3 (CH_2), 24.4 (CH_2), 23.8 (CH_2) ppm. ^{19}F NMR ($CDCl_3$, 300 MHz, 25 °C): δ = −78.13 (NH−CF_3), −72.35 (N−CF_3), −72.27 (N−CF_3) ppm. HR LSIMS calculated for MH^+: 717.05577; found 717.05535.
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