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COMMUNICATION

Diastereoselective preparation of chiral-at-metal pentamethylcyclopentadienyl iridium(III) and -rhodium(III) complexes

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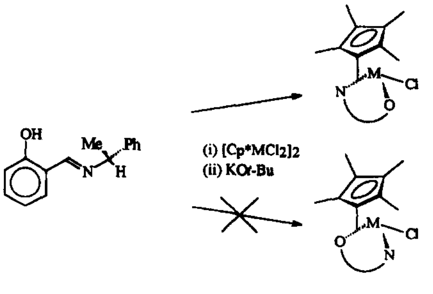
Abstract—The reaction between the chiral bidentate Schiff base ligand (S)-N-salicylidene-α-phenyethylamine (LH) and $[Cp^*MCl_2]_2$ (M = Ir, Rh) in the presence of KO*t*-Bu yields in both cases diastereomerically pure (*R*)-Cp*M(L)Cl. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: chiral-at-metal complexes; chiral Schiff base ligands; diastereoselective preparation.

There has been much interest in transition metal complexes which have applications as chiral catalysts or reagents [1]. Of these, those that do not depend wholly upon chiral ligands to induce selectivity in their reactions, but which are themselves chiral at the reacting metal centre, are particularly interesting [2]. Typically these complexes have tetrahedral or pseudo-tetrahedral geometries, containing either η^5Cp or $\eta^6C_6H_6$ derived ligands. Usually, the procedures required to resolve such compounds are somewhat arduous, involving many steps and consequently a reduced isolated yield of the desired product [3]. We report the use of a readily accessible chiral Schiff base ligand for the preparation of diastereomerically pure complexes with chiral metal centres in virtually quantitative yield.

Chiral Schiff base ligands have been known for some time [4]. They are particularly attractive ligands as they can be easily synthesised from inexpensive starting materials, and have been used to prepare complexes with a range of metals, many of these complexes having catalytic applications [5]. This is the first use of such ligands for the preparation of a fully resolved chiral metal centre, although an unsuccessful attempt to prepare related compounds has been reported [6].

LH was prepared from the direct reaction of salicylaldehyde and (*S*)-α-methylbenzylamine in a modification of the published procedure [4]. The complexes were prepared according to the conditions given in Scheme 1. The crystal structure of complex **1** is shown (Fig. 1), along with selected bond lengths and angles. The complex **1** forms with *R* configuration at the metal centre exclusively, as confirmed by X-ray crystallography and comparison of the ^{1}H NMR spectra of the reaction mixtures from the preparation of **1** and **2** with those of the crystallised material. Comparison



1. M = Ir (>95% de, 92% yield)
2. M = Rh (>95% de, 89% yield)

Scheme 1. The preparation of **1**, **2**.

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of the C=N bond length in the free ligand (1.277 Å) and the complex **1** (1.291 Å) indicates that the imine nitrogen is acting as a simple two electron donor. The C—O bond shortens by 0.04 Å on complexation (1.31 Å in **1**, 1.35 Å in LH) [7].

A recent report on the preparation of complexes of the type Cp*Ir(L′)Cl, where (L′) is a chiral aminoalcohol, has demonstrated an apparent relationship between the size of substituents on the amine nitrogen and the diastereoselectivity observed in the complexes prepared, with the greatest selectivity found for the most sterically demanding amines [8]. In the case of **1** and **2**, however, the ligand adopts a planar configuration with no real steric demand at the ligating N atom. Since the ligand used here gives rise to a very high diastereoselectivity in the resultant complexes, it seems likely that in this case there is some other explanation for the observed selectivity.

This straightforward preparation of **1** and **2** illustrates the previously unnoticed potential of chiral Schiff base ligands in the resolution of chiral metal fragments. Furthermore the use of a sterically undemanding ligand in the induction of selectivity is a remarkable example of the benefits of an electronically differentiated rather than a sterically differentiated ligand.

The various catalytic applications of **1** and **2** are currently being explored.

Selected spectroscopic data for **1**

^{1}H NMR (89.55 MHz, $CDCl_3$, 20°C, $(CH_3)_4$ Si; δ 1.49 (s, 15H, C_5Me_5), 1.89 (d, 3H, 8 Hz, HC(C*H*$_3$)), 5.59 (q, 8Hz, 1H, *H*C(CH_3)), 6.29–7.37 (m, arom, 9H), 7.79 (s, 1H, *H*C=N). IR; ν C=N 1615 cm^{-1}. For **2**: ^{1}H NMR (89.55 MHz, $CDCl_3$, 20°C, $(CH_3)_4$Si; δ 1.44 (s, 15H, C_5Me_5), 1.83 (d, 3H, 7 Hz, HC(C*H*$_3$)), 5.61 (q, 7 Hz, 1H, *H*C(CH_3)), 6.36–7.37 (m, arom, 9H), 7.86 (s, 1H, *H*C=N). IR; ν C=N 1631 cm^{-1}, Raman 1616 cm^{-1}. Satisfactory microanalysis results were obtained for both **1** and **2**. The rotation observed for **1** and for **2** are both of the same sign, and so the metal centre of **2** is assigned as having *R* configuration.

Crystal data for **1**

$C_{25}H_{29}NOClIr$; $M = 587.18$; primitive orthorhombic cell, space group $P2_12_12_1$ (#19), $a = 13.596(2)$, $b = 19.728(2)$, $c = 8.495(2)$ Å, $V = 2278.6(7)$ Å^3, $Z = 4$, $D_c = 1.712$ g/cm^3. Crystal shape irregular block $0.20 \times 0.20 \times 0.10$ mm. $F(000) = 1152.00$; $\mu = 123.5$ cm^{-1}. Data collection was performed using a Rigaku AFC7S, Cu-K_α radiation. $T = 293$ K; $2\theta_{max} = 120.1°$. 1981 reflections were measured, 1784 observed $[I > 3.00\sigma(I)]$, the data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied resulting in transmission factors ranging from 0.9665 to 1.00. *R*; *Rw* = 0.031; 0.032.

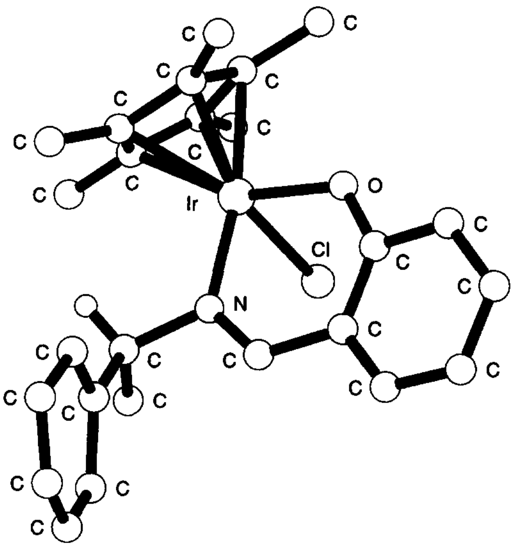

Fig. 1. The molecular structure of Cp*Ir(L)Cl, **1**. Ir—Cl 2.425(3), Ir—O 2.076(7), Ir—N 2.086(8), Ir—C (ave) 2.158 Å. Cl—Ir—O 85.3, Cl—Ir—N 83.9, O—Ir—N 88.7°

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