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Preliminary communication

Diastereoselective nucleophilic additions to imines attached to arene tricarbonylchromium moieties

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Abstract

Some highly diastereoselective 1,2-addition reactions of *N*-benzylidene-1-methylaniline tricarbonylchromium complex **1a** and related imines are reported along with the X-ray structure assignment of the major diastereomeric adduct from the reaction of **1a** with methyllithium.

The application of organotransition-metal complexes to enantioselective synthesis is an area of intense investigation [1]. 1,2- and 1,3-disubstituted arene tricarbonylchromium complexes in which the two substituents are dissimilar are chiral and a number of these compounds have been resolved using classical resolution techniques [2], and more recently enzymatic kinetic resolution [3]. These molecules have been used to prepare other chiral tricarbonylchromium complexes in a highly diastereoselective manner [4]. Much of this work has focused on the preparation of the complexes of 1-substituted benzaldehydes and acetophenones and their derivatives [4,5]. Relatively little attention, however, has been devoted to the chemistry and stereochemistry of the imine derivatives of these compounds [6,7]. We have recently reported on the potential of related ferrocenylalkyl substituted imines for asymmetric synthesis [8,9].

In 1979, Solladié-Cavallo and Tsamo reported that the addition of methylmagnesium iodide to *N*-benzylidene-1-methylaniline tricarbonylchromium complex **1a** gave a mixture (67 : 33) of diastereomeric amine products (**2a** and **3a**) [7]. For related complexes it was found that benzylmagnesium chloride was completely diastereoselective (diastereoselection = 100%) in its 1,2-addition reactions. The relative stereochemistry of these adducts, however, could not be determined. In this communication we report some highly diastereoselective reactions of **1a** and related imines and the X-ray structural assignment of the major diastereomeric adduct of **1a** and methyllithium.

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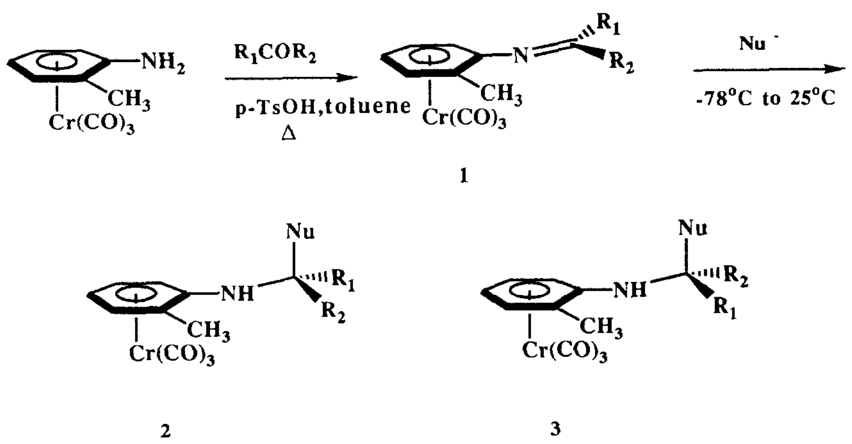
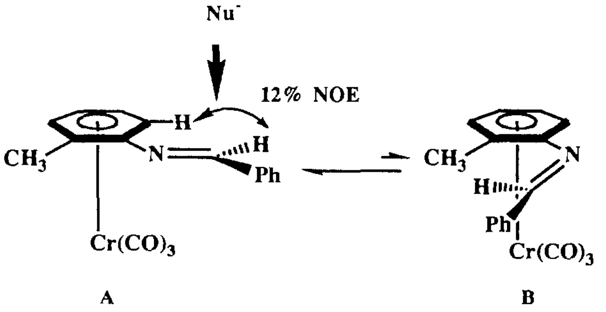


a : R_1 = H, R_2 = Ph
b : R_1 = D, R_2 = Ph
c : R_1 = H, R_2 = *t*-Bu

Scheme 1.

The racemic imine tricarbonylchromium substrate complexes **1** were prepared in good to high yield as the *E*-geometric isomers according to Scheme 1. The *E*-geometry was supported by NOE ^{1}H NMR difference spectroscopy, which showed a 12% enhancement of the signal from the aromatic proton *ortho* to the amino group when the imine methine was selectively irradiated (Scheme 2). These substrates were then treated with appropriate nucleophiles (MeLi, $NaBH_4$ or $NaBD_4$) at −78°C, followed by warming of the resulting reaction mixtures to room temperature. The product diastereoselection was determined by ^{1}H NMR (400 MHz) examination of the crude reaction mixtures and was in each case high (Table 1). The structure of the major diastereomeric adduct **2a** (R_1 = H, R_2 = Ph, Nu = Me) was unequivocally determined by single-crystal X-ray structural analysis, which revealed **2a** had the 1*R**, 2*S**, 21*S** relative stereochemistry (Fig. 1) *. The structural analysis also revealed ring C(1–6) to be significantly non-planar (χ^2 507) with "boat" deviations: δC(1–6) 0.035(3), −0.047(3), 0.032(4), 0.013(4), −0.039(4), 0.003(4) Å; δN(2) is −0.182(4) Å, Cr–C(0) (centroid) is 1.767 Å. C(0)–Cr–C(101–103) are 127.9, 122.2,



Scheme 2.

Table 1

Diastereoselection of product

Imine	Nucleophile /solvent	Diastereoselection [a] 2:3	Yield (%)
1a	MeLi/ether	90:10	42
1a	$NaBD_4$/MeOH	95:5	50
1b	$NaBH_4$/MeOH	95:5	55
1c	$NaBD_4$/MeOH	95:5	78

[a] Determined by ^{1}H NMR (400 MHz) on the crude reaction mixture.

129.5°, with C(101)–Cr–C(102,103) 88.8(1), 85.9(1)° and C(102)–Cr–C(103) 90.0(2)°. All of which suggests a displacement of CO(102) towards C(2)–N(2), but a movement of the latter away. The most significant intermolecular contact is

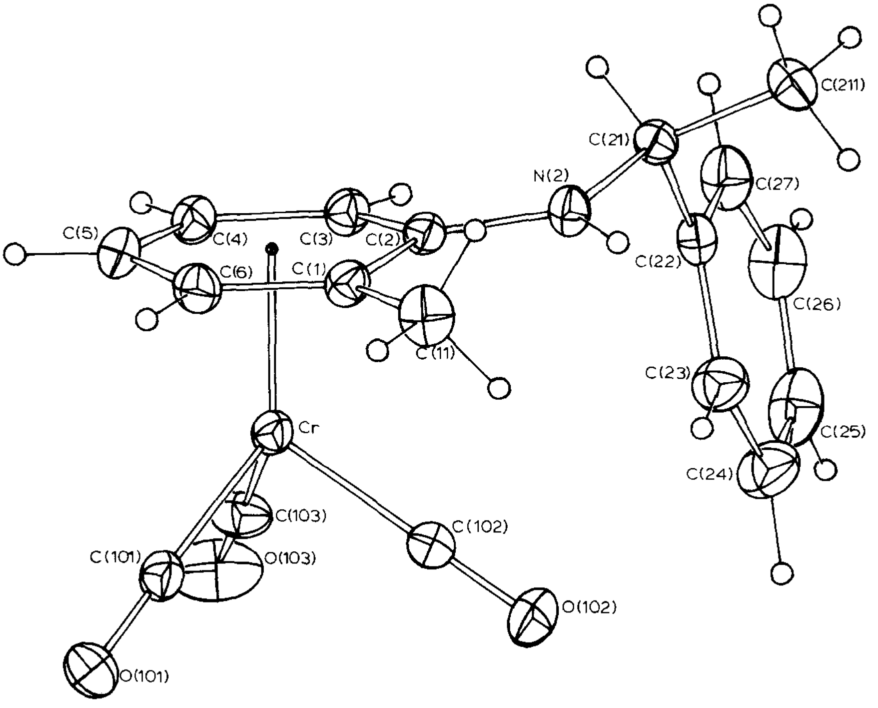


Fig. 1. Projection of a single molecule. 20% Thermal ellipsoids are shown for the hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Cr–C(1–6) are 2.267(3), 2.374(3), 2.267(3), 2.215(3), 2.219(3), 2.197(4) Å, C(2)–N(2), 1.359(4) Å; Cr–C(101–103), 1.813(3), 1.819(3), 1.822(4) Å.

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* *Crystal/refinement data*: $C_{18}H_{17}CrNO_3$, $M = 347.3$ Monoclinic, space group $P2_1/c$, a 8.584(2), b 12.617(4), c 16.359(4) Å, β 109.32(2)°, U 1672 Å^3. D_c 1.38 g cm^{-3}, $Z = 4$. Full matrix refinement, $R = 0.035$, R_w (statistical weights) = 0.042 for 2160 observed ($I > 3\sigma(I)$) out of 2738 unique absorption corrected reflections measured to $2\theta_{max}$ 50° (Enraf-Nonius CAD-4 diffractometer, $2\theta/\theta$ scan mode, monochromatic Mo-K_α radiation (λ 0.71073 Å, μ(Mo) 7.3 cm^{-1})). Anisotropic thermal parameter refinement for non-hydrogen atoms; (x, y, z, U_{iso})$_H$ included constrained at estimated values. $T \sim 295$ K.

O(101) $\cdots$ H(2) ($\underline{x}, \frac{1}{2}+\underline{y}, \frac{1}{2}-\underline{z}$), 2.35 Å. C(2)–N(2)–C(21) is 124.8(2)°, N(2)–C(21)–C(211,22) are 107.5(2), 114.8(2) and C(211)–C(21)–C(22) 110.1(2)°.

Two possible conformations for *E*-**1a** are shown in Scheme 2. Conformation **A** would be expected to be favoured over conformation **B** from steric considerations, and this was confirmed by NOE difference ^{1}H NMR spectroscopy. Addition of methyllithium to conformer **A** to the face of the imine that is *anti* to the sterically demanding tricarbonylchromium moiety provides a ready rationale for the observed product stereochemistry.

The reactions outlined in Scheme 1 thus appear to provide a facile and highly diastereoselective route to chiral amines, and the application of these and related compounds to asymmetric synthesis is currently under intensive investigation.

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