Diastereoselective Nucleophilic Additions to Imines attached to Tricarbonyl(arene)chromium Moieties

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A range of imine complexes has been prepared which possess planar chirality associated with the attached tricarbonyl(1,2-disubstituted arene)chromium moiety. Nucleophilic addition to the imine group of these complexes occurs with high diastereoselectivity, providing an efficient route to the asymmetric synthesis of chiral amines. The stereochemical outcome of the additions may be rationalized in terms of a favoured conformer for the complexes, with nucleophilic attack occurring on the face of the imine *anti* to the sterically demanding $Cr(CO)_3$ group. Related studies have also been carried out on imine complexes in which the chiral auxiliary is instead a carbon centre attached to the imine N atom. In these latter systems high diastereoselectivity was also observed, but was not superior to that achieved with the related free amines.

Tricarbonyl(arene)chromium complexes containing 1,2- and 1,3-disubstituted arenes possess planar chirality and are useful chiral auxiliaries for the asymmetric synthesis of chiral molecules.[1] While the diastereoselective addition of nucleophiles to chiral *ortho*-substituted tricarbonyl(η^6-benzaldehyde)-chromium(0) and related complexes to give the corresponding chiral carbinol adducts is well documented,[2] reactions of the imine derivatives of these compounds to give chiral amines have been less intensively investigated.[3–5] This is particularly surprising since chiral amines have a wide application in organic chemistry as resolving agents and chiral ligands, bases and auxiliaries for asymmetric synthesis.[6] In 1979 Solladie-Cavallo and Tsamo[4] reported on the diastereoselectivity of the 1,2 addition of Grignard reagents to (*N*-benzylidene-*o*-methylaniline)tricarbonylchromium and related complexes. More recently we briefly reported some highly diastereoselective 1,2-addition reactions of methyllithium, hydride and deuteride to the imine complexes $[Cr(CO)_3\{C_6H_4(N{=}CHR)Me\text{-}o\}]$ (R = Ph or Bu^t) and the N=CDR analogue.[7] We now report the full details of this investigation, together with the diastereoselectivity and stereochemical outcome of analogous 1,2-addition reactions with the related imine $[Cr(CO)_3\{C_6H_4(CH{=}NBu^t)Me\text{-}o\}]$. In addition the novel complexes $[Cr(CO)_3\{C_6H_5(CHMeN{=}CRPh)\}]$ (R = H or Me) have been synthesised and the diastereoselectivity of addition of $H^-(D^-)$ to their imine group investigated. Unlike the previous imine complexes, these substrates do not possess planar chirality, and any asymmetric induction will instead be associated with the stereogenic carbon centre attached to the imine nitrogen atom.

Experimental

The NMR spectra were obtained on either a Varian Unity 400 or a JEOL FX90Q Fourier-transform spectrometer in $CDCl_3$, infrared spectra in cyclohexane using a FTIR Bio-Rad FTS-7 spectrometer. Optical rotations were obtained in CH_2Cl_2 on a JASCO model DIP-370 digital polarimeter. Mass spectra were recorded with a quadrupole V.G. analytical MM12-12 spectrometer in FAB mode. Microanalyses were carried out at the Research School of Chemistry at Australian National University, Canberra. The purity of all compounds was determined to be > 95% from ^1H NMR analysis. In some cases the chromium complexes were not stable and consequently good microanalytical data could not be obtained. Melting points were determined on a Gallenpoint apparatus and are uncorrected.

General Method for Preparation of Tricarbonyl(arene)-chromium Compounds.[8]—The reactions were carried out under N_2 in dry di-*n*-butyl ether–tetrahydrofuran (thf) (12:1). The solvents were passed through a column of basic alumina, then N_2 was bubbled through them for 30 min prior to use. The compound $[Cr(CO)_6]$ and an excess of the arene were refluxed at 135–140 °C in the above solvent mixture under N_2 overnight. The reaction mixture was then cooled, filtered through Celite and rotary evaporated to remove the solvent. The residue was dissolved in a small amount of diethyl ether and then light petroleum (b.p. 35–60 °C) was added, which resulted in the formation of yellow crystals of the product complex.

General Methods for Preparation of Imines from a Tricarbonyl(arene)chromium Complex and an Aldehyde or Ketone.—(1) A Dean–Stark reflux apparatus was employed. The chromium complex and the aldehyde were dissolved in toluene and a small amount of toluene-*p*-sulfonic acid added as catalyst. The reaction vessel was flushed with N_2 and a drying tube placed on the condenser. The reaction mixture was refluxed at 120–140 °C until water ceased to be produced. It was then cooled, filtered and evaporated to dryness. The residue was washed and recrystallized from a suitable solvent.

(2) The arene chromium compound and the aldehyde were dissolved in dry diethyl ether. Activated 5A molecular sieves were added and the reaction mixture left stirring at ambient temperature for several days. It was then filtered, the sieves washed several times with ether and the washings combined with the filtrate. This was rotary evaporated to dryness and the residue recrystallized from a suitable solvent.

General Method for Reduction of the Chromium Imine Complexes.—The complexed imines were reduced with either $NaBH_4$ or $NaBD_4$ using a ten-fold excess of the reducing agent. The imine complex was dissolved in methanol, the $NaBH_4$ was dissolved in a small amount of water and then added to the imine. The reaction was left for 15 min at room temperature. The mixture was then filtered and the excess of $NaBH_4$ broken down with acetone. Dichloromethane, then water, were added and the dichloromethane layer was separated, washed with water three times, dried over anhydrous sodium carbonate and then rotary evaporated to dryness.

General Method for the Reaction of Chromium Imine Complexes with LiMe.—The imine complex was weighed into a three-necked flask which was alternately evacuated then flushed with N_2 to remove any trace of air or moisture. Dry thf was added and the flask cooled to −78 °C using a CO_2–acetone bath. An excess (1.15 molar equivalents) of LiMe (1.4 mol dm^{-3} in diethyl ether) was added and the reaction left for 15 min at −78 °C. The bath was then removed and the reaction allowed to come to room temperature for 20 min. Water and CH_2Cl_2 were added. The CH_2Cl_2 layer was separated, washed with water (3 ×), dried (sodium carbonate), then filtered and evaporated to dryness. The resulting yellow solid was recrystallized from $CHCl_3$.

The chromium imine complexes were also prepared by first making the organic imines and treating them with $[Cr(CO)_6]$, as described above.

Preparation of the Organic Imines.—One equivalent of the amine and one equivalent of the aldehyde or ketone were dissolved in toluene and a catalytic amount of toluene-*p*-sulfonic acid added. The reaction was carried out using a Dean–Stark apparatus as described above in Method (1). These imines were then treated with $[Cr(CO)_6]$. A five- to ten-fold excess of the imine was refluxed in di-*n*-butyl ether–thf (12:1) with $[Cr(CO)_6]$ under N_2 for 24–48 h (see general method).

Tricarbonyl(η⁶-o-*toluidine*)*chromium* **1**. Hexacarbonylchromium (2 g, 9.08 mmol) and *o*-toluidine (12.5 cm^3, 0.117 mol) in dibutyl ether–thf (90:10, 130 cm^3) gave 1.47 g (66% yield) of bright yellow crystals, m.p. 123–124 °C (Found: C, 49.15; H, 3.50; N, 5.60. Calc. for $C_{10}H_9CrNO_3$: C, 49.40; H, 3.75; N, 5.75%). Mass spectrum: *m/z* 243, M^+. IR (cyclohexane): 1955 and 1869 cm^{-1} (C≡O). NMR: ^1H, δ 5.54 (1 H, d, J = 6.4, aromatic H), 5.42 (1 H, t, J = 6.4, aromatic H), 4.94 (1 H, d, J = 6.4, aromatic H), 4.84 (1 H, t, J = 6.0 Hz, aromatic H), 3.62 (2 H, br s, NH_2) and 2.11 (3 H, s, CH_3); ^{13}C, δ 128.8, 98.5, 95.1, 91.2, 84.6, 78.4 and 16.9.

(N-*Benzylidene*-o-*methylbenzene*)*tricarbonylchromium* **2** (R = Ph). Complex **1** (1 g, 4.11 mmol) and benzaldehyde (0.44 g, 4.14 mmol) in toluene were refluxed (Dean–Stark apparatus), followed by recrystallization from light petroleum (b.p. 40–60 °C) to give 1.9 g (87% yield) of deep red crystalline product (*E* isomer), m.p. 82–83 °C (Found: C, 59.90; H, 3.85; N, 3.95. Calc. for $C_{17}H_{13}CrNO_3$: C, 61.65; H, 3.65; N, 4.23%). Mass spectrum: *m/z* 331, M^+. IR (cyclohexane): 1970, 1906 and 1896 cm^{-1} (C≡O). NMR: ^1H, δ 8.41 (1 H, s, imine H), 7.90 (2 H, m, aromatic H), 7.50 (3 H, m, aromatic H), 5.36 (2 H, m, complexed aromatic H), 5.23 (2 H, m, complexed aromatic H) and 2.17 (3 H, s, CH_3); ^{13}C, δ 165.1, 135.1, 132.4, 129.4, 128.9, 103.8, 93.4, 92.0, 89.6 and 17.2. The minor (*Z*) isomer had δ 8.37 (s, imine H) and remained in the mother-liquor after recrystallization.

(N-*Benzyl*-η⁶-o-*toluidine*)*tricarbonylchromium* **3** (R = Ph, Nu = H). Complex **2** (R = Ph) (26.2 mg, 0.08 mmol) in MeOH (5 cm^3) was treated with $NaBH_4$ (29.8 mg, 0.79 mmol) in water (1 cm^3) to give 18.7 mg (71% yield) of yellow solid. Mass spectrum: *m/z* 333, M^+. IR: 1964, 1894 and 1883 cm^{-1} (C≡O). ^1H NMR: δ 7.4 (5 H, br s, free aromatic H), 5.57 (1 H, d, J = 8, complexed aromatic H), 5.84 (1 H, t, J = 8, complexed aromatic H), 4.83 (2 H, m, J = 8 Hz, complexed aromatic H), 4.23 (2 H, m, CH_2), 3.77 (1 H, br s, NH) and 2.13 (3 H, s, CH_3).

Tricarbonyl(α-*deuterio*-N-*benzyl*-η⁶-o-*toluidine*)*chromium* **3** (R = Ph, Nu = D). Complex **2** (R = Ph) (15.4 mg, 0.046 mmol) was treated with $NaBD_4$ (21.5 mg, 0.5 mmol) to give 14.6 mg (78%) of product as a yellow crystalline solid, m.p. 73–75 °C (Found: C, 61.75; H, 4.75; N, 4.00. Calc. for $C_{17}H_{14}CrDNO_3$ (all D seen as H): C, 61.10; H, 4.75; N, 4.20%). Mass spectrum: *m/z* 334, M^+. IR: 1964, 1894 and 1883 cm^{-1} (C≡O). NMR: ^1H, δ 7.4 (5 H, br s, free aromatic H), 5.57 (1 H, d, J = 8, aromatic H), 5.48 (1 H, t, J = 8, aromatic H), 4.83 (2 H, m, J = 8 Hz, aromatic H), 4.23 (1 H, br s, CH), 3.76 (1 H, br s, NH) and 2.13 (3 H, s, CH_3); ^{13}C, δ 137.0, 130.9, 129.0, 128.1, 127.9, 98.6, 95.1, 91.2, 83.9, 74.3, 48.0 (t) and 17.2.

Tricarbonyl(N-1-*phenylethyl*-η⁶-o-*toluidine*)*chromium* **3** (R = Ph, Nu = Me). Complex **2** (R = Ph) (114 mg, 0.344 mmol) in dry thf (2 cm^3) was treated with an excess of LiMe (350 μl) at −78 °C followed by recrystallization from $CHCl_3$ to give a yellow crystalline solid (50 mg, 42% yield) (Found: C, 61.70; H, 4.70; N, 3.50. Calc. for $C_{18}H_{17}CrNO_3$: C, 62.25; H, 4.95; N, 4.05%). Mass spectrum: *m/z* 347, M^+. IR: 1968 and 1895 cm^{-1} (C≡O). NMR: ^1H, δ 7.41 (3 H, m, free aromatic H), 7.34 (2 H, m, free aromatic H), 5.41 (1 H, d, J = 5.6, complexed aromatic H), 5.33 (1 H, t, J = 5.6, complexed aromatic H), 4.84 (1 H, t, J = 6, complexed aromatic H), 4.74 (1 H, d, J = 6, complexed aromatic H), 4.54 (0.08 H, t, CH), 4.35 (0.92 H, t, J = 6.4, CH), 3.78 (1 H, br s, NH), 2.22 (0.24 H, s, CH_3 of aryl), 2.11 (2.76 H, s, CH_3 of aryl), and 1.55 (3 H, d, J = 6.4 Hz, CH_3); ^{13}C, δ 141.9, 130.5, 129.0, 127.9, 127.0, 97.0, 94.1, 90.7, 85.0, 75.8, 53.7, 23.6 and 17.3.

tert-*Butyl*(o-*methylbenzylidene*)*amine*. *o*-Methylbenzaldehyde (5 g, 41.7 mmol) and *tert*-butylamine (6.09 g, 83.3 mmol) were dissolved in light petroleum (b.p. 40–60 °C) (100 cm^3). Molecular sieves (activated, 5A) were added and the mixture stirred for 2 d at room temperature. After work-up, 6.67 g (92% yield) of an oil was obtained. NMR: ^1H, δ 8.57 (1 H, s, HC=N), 7.83–7.18 (4 H, m, aromatic H), 2.47 (3 H, s, CH_3) and 1.29 [9 H, s, $C(CH_3)_3$].

[η⁶-tert-*Butyl*(o-*methylbenzylidene*)*amine*]*tricarbonylchromium* **6**. The above amine (6.67 g, 38.33 mmol) and $[Cr(CO)_6]$ (1.85 g, 8.27 mmol) in dibutyl ether (50 cm^3) and thf (5 cm^3) were refluxed under N_2 for 45 h to give 1.46 g (57%) of yellow-orange crystals, m.p. 83–84 °C (Found: C, 58.00; H, 5.50; N, 4.15. Calc. for $C_{15}H_{17}CrNO_3$: C, 57.90; H, 5.50; N, 4.50%). Mass spectrum: *m/z* 312, $[M + H]^+$. IR: 1975 and 1910 cm^{-1} (C≡O). NMR: ^1H, δ 8.09 (1 H, s, imine H), 6.24–6.18 (1 H, dd, J = 6.4 Hz, complexed aromatic H), 5.44–5.08 (3 H, m, complexed aromatic H), 2.35 (3 H, s, CH_3 of aryl) and 1.26 [9 H, s, $C(CH_3)_3$]; ^{13}C, δ 149.6, 109.0, 100.7, 93.8, 93.2, 92.6, 90.0, 58.0, 29.6 and 18.3.

N-2,2-*Dimethylpropylidene*-o-*toluidine*. *o*-Toluidine (2.5 g, 23.4 mmol) and pivaldehyde (2.8 cm^3, 25.8 mmol) in dry ether (30 cm^3) with activated 5A molecular sieves were stirred for 48 h to give 3.59 g (88% yield) of a pale yellow oil. NMR: ^1H, δ 7.59 (1 H, s, imine H), 7.20–7.07 (3 H, m, aromatic H), 6.74–6.61 (1 H, m, aromatic H), 2.22 (3 H, s, CH_3 of aryl) and 1.18 [9 H, s, $C(CH_3)_3$].

Tricarbonyl(η⁶-2,2-*dimethylpropylidene*-o-*toluidine*)-*chromium* **2** (R = Bu^t). The above toluidine derivative (3.59 g, 20.5 mmol) and $[Cr(CO)_6]$ (1.50 g, 6.83 mmol) were refluxed for 48 h under N_2 in dibutyl ether–thf (10:1, 40 cm^3) to give yellow crystals of the chromium complex (1.41 g, 40% yield), m.p. 35–36 °C (Found: C, 57.00; H, 5.35; N, 3.95. Calc. for $C_{15}H_{17}CrNO_3$: C, 57.90; H, 5.5; N, 4.50%). Mass spectrum: *m/z* 311, M^+. IR: 1968, 1900 and 1890 cm^{-1} (C≡O). NMR: ^1H, δ 7.73 (1 H, s, imine H), 5.34–5.25 (2 H, m, aromatic H), 5.149 (1 H, dt, J = 7.2, aromatic H), 5.01 (1 H, d, J = 6.8 Hz, aromatic H), 2.11 (0.18 H, s, CH_3 of aryl), 2.03 (2.82 H, s, CH_3 of aryl) and 1.19 [9 H, s, $C(CH_3)_3$].

Tricarbonyl[η⁶-N-(1,2,2-*trimethylpropyl*)-o-*toluidine*]-*chromium* **3** (R = Bu^t, Nu = Me). An excess of LiMe was added to complex **2** (R = Bu^t) (0.213 g, 0.685 mmol) in dry thf at −78 °C under N_2 to give 0.197 g (88% yield) of yellow solid, m.p. 93–95 °C (Found: C, 58.80; H, 6.90; N, 4.50. Calc. for $C_{16}H_{21}CrNO_3$: C, 58.70; H, 6.45; N, 4.30%). Mass spectrum: *m/z* 327, M^+. IR: 1965, 1958, 1900 and 1888 cm^{-1} (C≡O). NMR: ^1H, δ 5.50 (1 H, d, J = 6, complexed aromatic H), 5.45 (1 H, t, J = 6.4, complexed aromatic H), 4.87 (1 H, d, J = 7.2, complexed aromatic H), 4.78 (1 H, t, J = 6.4, complexed aromatic H), 3.53 (1 H, br d, J = 6.4, NH), 3.07 (1 H, qnt, J = 6.8, CH), 2.08 (3 H, s, CH_3 of aryl), 1.07 (3 H, d, J = 6.4 Hz, CCH_3), 1.03 [8.28 H, s, $C(CH_3)_3$] and 0.97 [0.72 H, s, $C(CH_3)_3$].

α-Deuteriobenzaldehyde. Benzil (5.5 g, 0.026 mol) was placed in a dry round-bottomed flask and dry 1,4-dioxane (12 cm^3) and D_2O (5 cm^3) were added. Potassium cyanide (2 g, 0.0307 mmol) was added in four portions at 2 min intervals to the stirred benzil suspension and stirring continued for 20 min. The mixture was then diluted with water (50 cm^3) and extracted with two portions (25 cm^3) of ether. The ether extracts were washed with 5% $NaHCO_3$ (25 cm^3), water (50 cm^3) and saturated NaCl (25 cm^3). The organic layer was dried over $MgSO_4$, then filtered and rotary evaporated to give a pale oil (1.18 g, 42% yield) which was crystalline at 0 °C. NMR: ^1H, δ 8.14–8.12 (1 H, m), 7.90–7.88(1 H, m), 7.65:7.59 (1 H, m) and 7.55 (2 H, m) (all aromatic H).

Tricarbonyl(η⁶-*α-deuteriobenzylidene-o-toluidine*)*chromium* **5**. Complex **1** (339 mg, 1.40 mmol) and PhCDO (150 mg, 1.4 mmol) in toluene (20 cm^3) with toluene-*p*-sulfonic acid as catalyst were refluxed for 4 h, resulting in 450 mg (96%) of a red solid, m.p. 200–202 °C (Found: C, 61.75; H, 3.85; N, 3.95. Calc. for $C_{17}H_{12}CrDNO_3$: C, 61.45; H, 3.65; N, 4.20%). Mass spectrum: *m/z* 333, $[M + H]^+$. IR: 1971, 1906 and 1896 cm^{-1} (C≡O). NMR: ^1H, δ 7.91 (2 H, m, aromatic H), 7.52 (3 H, m, aromatic H), 5.36 (2 H, d, complexed aromatic H), 5.23 (2 H, m, complexed aromatic H) and 2.17 (3 H, s, CH_3 of aryl); ^{13}C, δ 165.2, 135.0, 132.4, 129.4, 128.9, 103.8, 93.5, 91.9, 89.6, 87.5 and 17.2.

Reduction of complex **5**. To complex **5** (394 mg, 1.19 mmol) in MeOH (15 cm^3) was added $NaBH_4$ (0.45 mg, 11.9 mmol) and the reaction mixture stirred for 20 min, then worked up to give 217 mg (55%) of a yellow solid. Mass spectrum: *m/z* 334, M^+. IR: 1956 and 1875 cm^{-1} (C≡O). NMR: ^1H, δ 7.38 (5 H, m, free aromatic H), 5.56 (1 H, d, J = 6.4, complexed aromatic H), 5.44 (1 H, t, J = 6.4 Hz, complexed aromatic H), 4.84 (2 H, m, complexed aromatic H), 4.20 (1 H, br s, PhCD*H*), 3.75 (1 H, br s, NH) and 2.01 (3 H, s, CH_3); ^{13}C, δ 137.0, 131.0, 128.9, 128.0, 127.8, 98.6, 95.1, 91.3, 83.9, 74.2, 47.9 (t, CHD) and 17.1.

Complex **3** (R = Bu^t, Nu = D). To complex **2** (R = Bu^t) (50 mg, 0.159 mmol) in MeOH (10 cm^3) was added $NaBD_4$ (65 mg, 1.58 mmol). The reaction was stirred for 15 min to give after work-up a yellow solid (29.2 mg, 58%). Mass spectrum: *m/z* 314, M^+. IR: 1969, 1891 and 1883 cm^{-1} (C≡O). NMR: ^1H, δ 5.58 (1 H, d, J = 6.4, aromatic H), 5.48 (1 H, t, J = 6.4, aromatic H), 4.83 (2 H, t, J = 6.4, aromatic H), 3.51 (1 H, br s, NH), 2.77 (1 H, br s, CH), 2.12 (3 H, s, CH_3) and 1.02 [9 H, s, $C(CH_3)_3$].

Complex **3** (R = Bu^t, Nu = H). To complex **2** (R = Bu^t) (394 mg, 1.19 mmol) dissolved in MeOH (15 cm^3) was added $NaBH_4$ (0.45 g, 11.9 mmol) and the reaction mixture stirred for 15 min, resulting in a yellow crystalline solid (0.217 g, 55% yield) (Found: C, 57.55; H, 6.40; N, 4.25. Calc. for $C_{15}H_{19}CrNO_3$: C, 57.50; H, 6.10; N, 4.45%). Mass spectrum: *m/z* 313, M^+, IR: 1969, 1891 and 1883 cm^{-1} (C≡O). NMR: ^1H, δ 5.58 (1 H, m, aromatic H), 5.47 (1 H, m, aromatic H), 4.84 (2 H, m, aromatic H), 3.51 (1 H, br s, NH), 2.80 (2 H, m, CH_2), 2.12 (3 H, s, CH_3) and 1.03 [9 H, s, $C(CH_3)_3$].

(N-tert-*Butyl-α-deuterio-o-methylbenzylamine*)*tricarbonylchromium* **7** *and* **8**. To complex **6** (52 mg, 0.166 mmol) in CH_2Cl_2 (4 cm^3) was added $NaBD_4$ (60 mg, 1.58 mmol) in water (1 cm^3) and the reaction mixture stirred for 30 min. Work-up resulted in 31.6 mg (60% yield) of yellow solid. The isomer ratio **7**:**8** was 97 : 3. Mass spectrum: *m/z* 314, M^+. IR: 1968 and 1900 cm^{-1} (C≡O). NMR: ^1H, δ 5.61 (1 H, d, J = 6, aromatic H), 5.32 (1 H, t, J = 6, aromatic H), 5.22 (2 H, t, J = 6, aromatic H), 3.56 (0.02 H, s, CH), 3.39 (0.98 H, s, CH), 2.23 (3 H, s, CH_3 of aryl), 1.28 [0.18 H, s, $C(CH_3)_3$] and 1.16 ([8.82 H, s, $C(CH_3)_3$].

Tricarbonyl[η⁶-(R)-1-*phenylethylamine*]*chromium* **13**. Hexacarbonylchromium (1.6 g, 7.27 mmol) and (*R*)-(+)-phenylethylamine (1.1 g, 9.07 mmol) in dibutyl ether–thf (10 : 1, 70 cm^3) were refluxed under N_2 for 20 h to give, after work-up, a crude yield of 1.45 g (77.9%) of dark yellow oil (solid at 0 °C). As it was difficult to remove all traces of solvent, the crude product was used in subsequent reactions. Mass spectrum: *m/z* 257, M^+. IR: 1972, 1908 and 1897 cm^{-1} (C≡O). NMR: ^1H, δ 5.64 (1 H, d, J = 6.4, aromatic H), 5.39 (1 H, t, J = 6.4, aromatic H), 5.34 (1 H, d, J = 5.6, aromatic H), 5.31 (2 H, m, J = 6.4, aromatic H), 3.82 (1 H, q, J = 6.4, CH), 1.55 (2 H, qnt, J = 6.4, NH_2), 1.35 (3 H, d, J = 6.8, CCH_3) and 1.38 (2 H, m, J = 6.8 Hz, NH_2). α (589 nm, 1.01%, CH_2Cl_2) −21.1°.

Tricarbonyl[η⁶-(S)-1-*phenylethylamine*]*chromium* **13**. Hexacarbonylchromium (3.1 g, 0.014 mmol) and (*S*)-(−)-phenylethylamine (1.7 g, 0.014 mol) were refluxed in dibutyl ether–thf (10:1, 60 cm^3) for 20 h to give 3.32 g (91.7% crude yield) of brown-yellow oil. The crude product was used in subsequent reactions because of difficulty in removing solvent. Mass spectrum: *m/z* 257, M^+. IR: 1972, 1908 and 1897 cm^{-1} (C≡O). NMR: ^1H, δ 5.626 (1 H, d, J = 6.8, aromatic H), 5.373 (1 H, t, J = 5.6, aromatic H), 5.327 (1 H, d, J = 6.8, aromatic H), 5.287 (2 H, d, J = 5.6, aromatic H), 3.823 (1 H, q, J = 6.4, CH), 1.381 (2 H, br d, J = 6, NH_2) and 1.35 (3 H, d, J = 6.4 Hz, CH_3). α (589 nm, 0.442%, CH_2Cl_2) +19.9°.

[N-*Benzylidene*-η⁶-(S)-1-*phenylethylamine*]*tricarbonylchromium* **9**. The (*S*)-amine complex **13** (1.24 g, 4.82 mmol) and benzaldehyde (0.512 g, 4.82 mmol) in dry ether (80 cm^3) and activated 5A molecular sieves (20 g) were stirred under N_2 for 48 h. After work-up, 1.086 g of yellow crystals were obtained (65% yield), m.p. 88–88.5 °C (Found: C, 62.60; H, 4.70; N, 3.95. Calc. for $C_{18}H_{15}CrNO_3$: C, 62.60; H, 4.40; N, 4.05%). IR: 1973 and 1905 cm^{-1} (C≡O). Mass spectrum: *m/z* 346, $[M + H]^+$. NMR: ^1H, δ 8.37 (1 H, s, imine H), 7.79 (2 H, m, free aromatic H), 7.44 (3 H, m, free aromatic H), 5.66 (1 H, d, J = 6.8, complexed aromatic H), 5.38–5.27 (4 H, m, complexed aromatic H), 4.15 (1 H, q, J = 6.8, CH) and 1.51 (3 H, d, J = 6.8 Hz, CCH_3); ^{13}C, δ 161.1, 135.9, 131.0, 128.5, 128.4, 116.5, 92.4, 92.1, 91.5, 67.4 and 25.3. α (589 nm, 0.538%, CH_2Cl_2) +267.5°.

Reduction of complex (*S*)-**9** *with* $NaBD_4$. To the complex (*S*)-**9** (102.1 mg, 0.295 mmol) in MeOH (6 cm^3), was added $NaBD_4$ (121.3 mg) in water (1 cm^3) and the reaction was stirred for 20 min. Work-up resulted in 60 mg of product (58% yield). Mass spectrum: *m/z* 348, M^+. IR: 1975 and 1907 cm^{-1} (C≡O). NMR: ^1H, δ 7.36–7.25 (5 H, br s, free aromatic H), 5.63 (1 H, d, J = 6, complexed aromatic H), 5.42 (1 H, d, J = 7.2, complexed aromatic H), 5.36 (3 H, m, complexed aromatic H), 3.85 (1 H, br s, DCH), 3.53 (1 H, q, J = 6.8 Hz, CH_3CH) and 1.50 (1 H, br s, NH).

[N-*Benzylidene*-η⁶-(R)-1-*phenylethylamine*)*tricarbonylchromiun* **9**. The (*R*)-amine complex **13** (1.1 g, 4.28 mmol) and benzaldehyde (0.44 g, 4.15 mmol) in dry ether (30 cm^3) with activated 5A sieves (20 g) were stirred for 48 h. After work-up and recrystallization from light petroleum (b.p. 40–60 °C), 0.93 g of yellow crystals was obtained (65% yield), m.p. 86–87 °C (Found: C, 62.10; H, 4.75; N, 4.00. Calc. for $C_{18}H_{15}CrNO_3$: C, 62.60; H, 4.40; N, 4.05%). Mass spectrum: *m/z* 346, $[M + H]^+$. IR: 1976 and 1908 cm^{-1} (C≡O). NMR: ^1H [of (*E*) isomer], δ 8.39 (1 H, s, imine H), 7.79 (2 H, br s, free aromatic H), 7.44 (3 H, br s, free aromatic H), 5.68 (1 H, d, J = 5.2, complexed aromatic H), 5.35 (4 H, br m, complexed aromatic H), 4.18 (1 H, br d, J = 6.4, CH) and 1.54 (3 H, d, J = 6 Hz, CH_3). α (589 nm, 0.223%, CH_2Cl_2) −254.7°.

Reduction of complex (*R*)-**9** *with* $NaBD_4$. To the complex (*R*)-**9** (26.6 mg, 1.077 mmol) MeOH (4 cm^3) was added $NaBD_4$ (28.8 mg) in water (1 cm^3). The reaction was stirred for 15 min then worked up to give 14.4 mg of yellow solid (53.5% yield). Mass spectrum: *m/z* 349, $[M + H]^+$. IR: 1976 and 1908 cm^{-1} (C≡O). NMR: ^1H, δ 7.36–7.28 (5 H, m, free aromatic H), 5.65 (1 H, d, J = 6, complexed aromatic H), 5.44 (1 H, d, J = 7.2, complexed aromatic H), 5.35–5.29 (3 H, m, complexed aromatic H), 3.88 (0.08 H, s, PhDC*H*), 3.87 (0.92 H, br s, PhDC*H*), 3.55 (1 H, q, J = 6.4, CH_3CH) and 1.41 (3 H, d, J = 6.4 Hz, CCH_3). α (589 nm, 0.335%, CH_2Cl_2) −14.9°.

Reduction of complex (*R*)-**9** *with* $NaBH_4$. To complex (*R*)-**9** (25.0 mg) in MeOH (4 cm^3) was added $NaBH_4$ (27 mg) and the reaction mixture stirred for 15 min. Work-up resulted in 16 mg (63%) of the amine complex. Mass spectrum: *m/z* 348, $[M + H]^+$. IR: 1977 and 1908 cm^{-1} (C≡O). NMR: ^1H, δ 7.36–7.27

(5 H, m, free aromatic H), 5.65 (1 H, d, J = 6.8, complexed aromatic H), 5.44 (1 H, d, J = 6.4, complexed aromatic H), 5.32 (3 H, m, complexed aromatic H), 3.88 (2 H, s, CH_2), 3.55 (1 H, q, J = 6.8, CH) and 1.41 (3 H, d, J = 6.4 Hz, CH_3).

Tricarbonyl[N-(α-*methylbenzylidene*)-η^6-(S)-1-*phenylethylamine*)*chromium* **10**. The (*S*)-amine complex **3** (320 mg, 1.24 mmol) and acetophenone (149 mg, 1.24 mmol) with activated 5A sieves (10 g) in dry ether (30 cm^3) were stirred for 6 d. Work-up gave 200 mg (44.7%) of product. Ratio of isomers 93:7 (Found: C, 63.80; H, 4.85; N, 3.60. Calc. for $C_{19}H_{17}CrNO_3$: C, 63.50; H, 4.75; N, 3.90%). Mass spectrum: m/z 360, $[M + H]^+$. IR: 1974, 1972 and 1906 cm^{-1} (C≡O). α (589 nm, 1.2%, CH_2Cl_2) +180°. NMR: ^1H, δ 7.84 (1 H, br s, free aromatic H), 7.40 (4 H, br m, free aromatic H), 5.93 (1 H, d, complexed aromatic H), 5.44–5.25 (4 H, m, complexed aromatic H), 4.85 (0.07 H, q, CH), 4.53 (0.93 H, q, J = 6.4, CH), 2.34 (2.79 H, s, =CCH_3), 2.12 (0.21 H, s, =CCH_3), 2.11 (0.21 H, d, CH_3) and 1.44 (2.79 H, d, J = 6.4 Hz, CCH_3); ^{13}C, δ 160.1, 129.9, 128.6, 128.3, 128.2, 127.0, 117.8, 92.9, 92.7, 92.0, 91.8, 91.6, 57.8, 24.7 and 15.3.

Reduction of complex (*S*)-**10**. To complex **10** (182 mg, 0.505 mmol) in MeOH (5 cm^3) was added $NaBH_4$ (197.7 mg, 5.2 mmol) in water (1 cm^3). The reaction mixture was stirred for 1 h then worked up to give 110 mg (60%) of complex **12**. Mass spectrum: m/z 362, $[M + H]^+$. IR: 1973 and 1905 cm^{-1} (C≡O). NMR: ^1H, δ 7.35–7.27 (5 H, m, free aromatic H), 5.56–5.24 (5 H, m, complexed aromatic H), 3.86 (1 H, d, J = 6.4, CH), 3.33 (1 H, d, J = 6, CH), 1.32 (3 H, d, J = 6.8, CH_3) and 1.27 (3 H, d, J = 6.8 Hz, CH_3).

N-(α-*Methylbenzylidene*)-(R)-1-*phenylethylamine*. (*R*)-(+)-Phenylethylamine (4 g, 0.033 mol) and acetophenone (4.1 g, 0.033 mol) were refluxed in toluene (60 cm^3) with toluene-*p*-sulfonic acid as catalyst for 48 h. Work-up gave 5.25 g (71%) of product in an 89:11 isomeric ratio. α (589 nm, 0.52%, CH_2Cl_2) −74.1°. NMR: ^1H, δ 7.86–7.75 (2 H, m, aromatic H), 7.38–7.17 (8 H, m, aromatic H), 4.82 (0.89 H, q, J = 6.6, CH), 4.42 (0.11 H, q, J = 6.4, CH), 2.31 (0.33 H, s, CH_3), 2.24 (2.67 H, s, CH_3), 1.54 (2.67 H, d, J = 6.6, $CHCH_3$) and 1.40 (0.33 H, d, J = 6.4 Hz, CH_3); ^{13}C, δ 162.9, 146.1, 141.3, 129.2, 128.2, 127.9, 126.6, 126.4, 126.3, 59.6, 24.9 and 15.1.

Chromium complexing of N-(α-*Methylbenzylidene*-(R)-1-*phenylethylamine*. The compound $[Cr(CO)_6]$ (1.0 g) and the amine (1.1 g) were refluxed in dibutyl ether (20 cm^3)–thf (4 cm^3) for 24 h. After work-up the crude complex **10** (2.11 g, 69% yield) was obtained as a yellow oil. It was washed several times in light petroleum (b.p. 40–60 °C) and found by NMR spectroscopy to be 70% in the form with chromium attached to the amine phenyl group and 30% in the form in which the chromium is bound to the other phenyl group. The ratio of the two geometric isomers of the major product was 90:10. Data for the major product are given. Mass spectrum: m/z 360, $[M + H]^+$. NMR: ^1H, δ 7.84 (1 H, m, free aromatic H), 7.40 (4 H, m, free aromatic H), 5.93 (1 H, d, J = 6.4, complexed aromatic H), 5.42–5.25 (4 H, m, complexed aromatic H), 4.84 (0.1 H, q, CH), 4.52 (0.9 H, q, J = 6.8, CH), 2.34 (2.7 H, s, CH_3), 2.11 (0.3 H, s, CH_3), 1.43 (2.7 H, d, J = 6.8, CH_3) and 1.32 (0.3 H, d, J = 6.8 Hz, CH_3).

Reduction of N-(α-*Methylbenzylidene*)-(R)-1-*phenylethylamine*. To the imine (86.4 mg, 0.387 mmol) in MeOH (10 cm^3) was added $NaBH_4$ (146.5 mg, 3.87 mmol) in water (1 cm^3). Work-up after 5 h resulted in 86.4 mg (92.9%) of product, as an 85:15 mixture of diastereoisomers. NMR: ^1H, δ 7.34–7.19 (10 H, m, aromatic H), 3.76 (0.3 H, q, J = 6.8, CH), 3.49 (1.7 H, q, J = 6.8, CH), 1.71 (1 H, br s, NH), 1.34 (0.9 H, d, J = 6.8 Hz, CCH_3) and 1.26 (5.1 H, d, J = 6.8, CCH_3). α (589 nm, 2.57%, CH_2Cl_2) +119.2°.

Reduction of complex (*R*)-**10**. The reduction was carried out on the crude mixture of complex (*R*)-**10** (21.9 mg, 0.61 mmol) with $NaBH_4$ (22.6 mg, 0.61 mmol) to give 14.86 mg (65%) of complex **12**. Data for major product are given. α (589 nm, 0.57%, CH_2Cl_2) −7.0°. NMR: ^1H, δ 7.37–7.23 (5 H, m, free aromatic H), 5.54–5.22 (5 H, m, complexed aromatic H), 3.94 (0.24 H, q, CH), 3.86 (0.76 H, q, J = 6.8, CH), 3.33 (0.76 H, q, J = 6.8, CH), 3.28 (0.24 H, q, CH), 1.33 (2.28 H, d, J = 6.4, CH_3) and 1.27 (2.28 H, d, J = 6.8 Hz, CH_3).

N-(α-*Methylbenzylidene*)-(S)-1-*phenylethylamine*. (*S*)-(−)-Phenylethylamine (2.896 g, 0.0238 mmol) and acetophenone (2.867 g, 0.023 mmol) was refluxed in toluene (80 cm^3) with toluene-*p*-sulfonic acid as catalyst for 4 d. Work-up resulted in 4.28 g (80.3%) of a pale straw-coloured oil. The ratio of geometric isomers was 91:9. Mass spectrum: m/z 224, $[M + H]^+$. α (589 nm, 2.66%, CH_2Cl_2) +78°. NMR: ^1H, δ 7.84–7.19 (10 H, m, aromatic H), 4.81 (0.91 H, q, J = 6.8, CH), 4.42 (0.09 H, q, J = 6.4, CH), 2.30 (0.27 H, s, =CCH_3), 2.11 (2.73 H, s, =CCH_3), 1.53 (2.37 H, d, J = 6.8, $CHCH_3$) and 1.39 (0.23 H, d, J = 6.8 Hz, $CHCH_3$).

Reduction of N-(α-*methylbenzylidene*)-(S)-1-*phenylethylamine with* $NaBH_4$. To the imine (0.434 g, 1.94 mmol) in MeOH (20 cm^3) was added $NaBH_4$ (0.736 g, 19.4 mmol) in water (2 cm^3). Work-up after 5.5 h gave 0.375 g (86%) of clear oil of α,α-dimethyldibenzylamine, as an 84:16 mixture of isomers. NMR: ^1H, δ 7.31–7.17 (10 H, m, aromatic H), 3.74 (0.32 H, q, J = 6.4, CH), 3.48 (1.68 H, q, J = 6.8, CH), 1.70 (1 H, br s, NH), 1.32 (0.96 H, d, J = 6.4, CCH_3) and 1.24 (5.04 H, d, J = 6.8 Hz, CCH_3). α (589 nm, 3.96%, CH_2Cl_2) −127.7°.

N-*Benzylidene*-(S)-1-*phenylethylamine*. 1-Phenylethylamine (2 g, 0.0164 mol) and benzaldehyde (1.75 g, 0.0165 mol) were refluxed in toluene (60 cm^3) with toluene-*p*-sulfonic acid as catalyst for 20 h to give 4.55 g (88%) of the imine. Mass spectrum: m/z 210, $[M + H]^+$. NMR: ^1H, δ 8.37 (1 H, s, imine H), 7.799–7.76 (2 H, m, aromatic H), 7.44–7.21 (8 H, m, aromatic H), 4.52 (1 H, q, J = 6.4, CH_3CH) and 1.59 (3 H, d, J = 6.8 Hz, CH_3). α (589 nm, CH_2Cl_2) +76.4°.

Reduction of N-*benzylidene*-(S)-1-*phenylethylamine*. To the imine (110 mg, 0.50 mmol) in MeOH (5 cm^3) was added $NaBD_4$ (216 mg, 5.14 mmol) in water (1 cm^3). The mixture was stirred for 3 h. After work-up, 90.1 mg (78%) of *N*-α-deuteriobenzyl-1-phenylethylamine were obtained. NMR: ^1H, δ 7.35–7.23 (10 H, m, aromatic H), 3.81 (1 H, dq, J = 6.4, CH_3CH), 3.64 (1 H, br s, DCH) and 1.36 (3 H, d, J = 6.4 Hz, CH_3). α (589 nm, 1.98%, CH_2Cl_2) −45.5°.

Determination of the Geometric Purity of Imines and Product Diastereoselection.—The geometric purities of the imine complexes **2** (R = Ph or Bu^t), **5**, **6** and **9** and of PhCH=N–CHMePh were determined from ^1H NMR (400 MHz) analysis by integration of the low-field CH=N signals for the *E* (major) and *Z* (minor) geometric isomers. In the case of **2** (R = Ph) and **5** the aromatic CH_3 signals for the *E* (δ 2.17) and *Z* (δ 2.37) isomers were used to determine the geometric purity. For the imine PhCMe=N–CHMePh and complex **10** the *E*:*Z* ratio was determined from integration of the $C(CH_3)$=N signals for the two isomers (this signal was further downfield for the major *E* isomer).

The product diastereoselection for the reactions of complexes **2**, **5** and **6** with hydride and deuteride was determined by ^1H NMR (400 MHz) examination of the crude reaction mixtures, using the well resolved singlets for the benzylic methine CHDNHR proton of the diastereomeric products. The analogous reductions of **2** (R = Ph or Bu^t) and **6** with $NaBH_4$ gave the corresponding amines in which the diastereotopic benzylic amine protons (CH_AH_BNHR) gave well resolved doublets in ^1H NMR analysis. These amine compounds were prepared to assist us in the above determination of the ratio of isomers **3** and **4** (R = Ph or Bu^t; Nu = D) and **7** and **8** from the reduction of **2** and **6**, respectively, with $NaBD_4$.

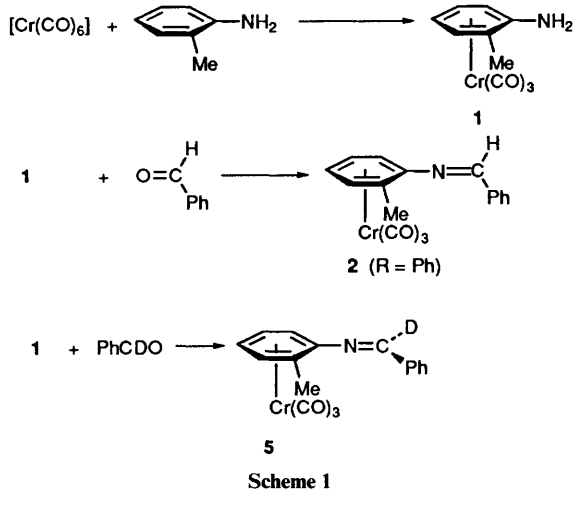
For the reaction of complex **2** (R = Ph) with LiMe, integration of the ring Me groups of the major (δ 2.085) and minor (δ 2.100) diastereomeric adducts was used to determine the diastereoselection. This ratio was also consistent with that determined from ^{13}C NMR spectroscopic analysis. For the analogous reaction of **2** (R = Bu^t), integration of the

singlets for the Bu^t groups of the major (δ 1.003) and minor (δ 0.968) diastereomeric adducts was used.

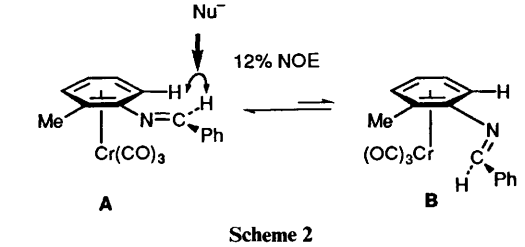
In the case of deuteride attack on PhCH=N–CHMePh and complex **9** and of hydride addition to PhCMe=N–CHMePh and complex **10**, the diasteromeric ratio was determined by averaging the integrals for the diastereomeric pairs of methine and methyl signals for the two diastereomeric products.

Results and Discussion

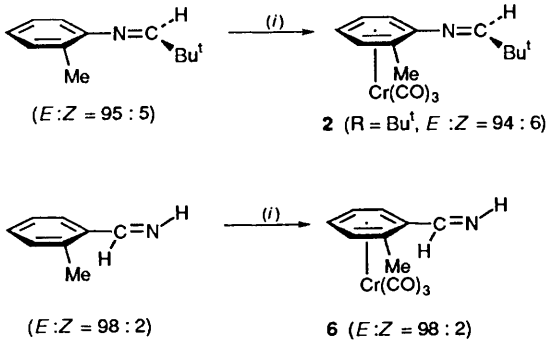
Synthesis and 1,2-*Addition reactions of Imine Complexes* **2**, **5** *and* **6**.—The imine complex **2** (R = Ph) was prepared from tricarbonyl(η^6-*o*-toluidine)chromium(0) **1**[8] and benzaldehyde under standard conditions (refluxing toluene with azeotropic water removal) in 87% yield as a 91:9 mixture of *E* and *Z* geometric isomers (Scheme 1). Recrystallization of this mixture gave pure (*E*)-**2** (R = Ph) which was used in all subsequent reactions. The deuterio analogue **5** of **2** (R = Ph) was prepared in a similar manner from PhCDO.[9] The *E* geometry of **2** (R = Ph) was supported by nuclear Overhauser effect (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). On the other hand, the imine complexes **2** (R = Bu^t, *E*:*Z* = 94:6) and **6** (*E*:*Z* = 98:2) were prepared from the reaction of the free imines *o*-MeC$_6$H$_4$–N=CHBu^t (*E*:*Z* = >95:<5) and *o*-MeC$_6$H$_4$–CH=NBu^t (*E*:*Z* = 98:2), respectively, with [Cr(CO)$_6$] under standard conditions (Scheme 3). In each case a simple recrystallization afforded the pure *E* geometric isomers which were employed in all subsequent reactions.



Scheme 1



Scheme 2



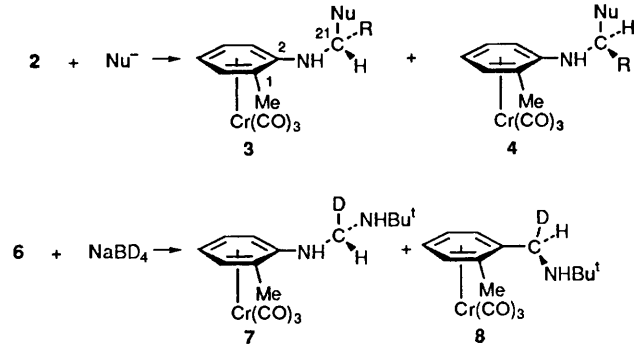
Scheme 3 (*i*) [Cr(CO)$_6$]

The organometallic imine substrates **2** (R = Ph or Bu^t), **5** and **6** were then treated with appropriate nucleophiles ($NaBD_4$, $NaBH_4$ and LiMe) at −78 °C, followed by warming of the reaction mixtures to room temperature. In each case a mixture of diastereomeric amine complexes (**3** and **4** or **7** and **8**) was formed (Scheme 4). The product diastereoselection was determined by ^{1}H NMR (400 MHz) examination of the crude reaction mixtures (see Experimental section). The results are summarized in Table 1. In each case the product diastereoselection is high (92–97%) except for entry 3, where a 87:13 ratio of diastereomeric products was observed. Comparison of the reductions of **2** (R = Bu^t) and **6** with D$^-$ reveals that the diastereoselectivity of addition is significantly higher for **6**, which is consistent with the closer proximity of the tricarbonyl(arene)chromium chiral auxiliary to the carbon reaction centre in it. The reaction of **6** with LiMe was unsuccessful (Table 1, entry 7) and only **6** was recovered.

The structure and stereochemistry of the major diastereomeric adduct **3** (R = Ph; Nu = Me) was unequivocally determined by single-crystal X-ray analysis, as previously reported by us.[7] This showed the 1*R**, 2*S**, 21*S** relative stereochemistry (see structure **3** for numbering). The stereochemical assignments made to the other major diastereomeric amine adducts **3** (R = Ph or Bu^t; Nu = Me or D) and **7** are based on this known stereochemistry.

The stereochemical outcome of the reaction of complex **2** (R = Ph) with LiMe can be readily rationalized by consideration of the two possible conformations for **2** shown in Scheme 2. Conformer **A** would be expected to be favoured over **B** on steric grounds, as confirmed by NOE difference ^{1}H NMR spectroscopy. Attack by LiMe on **A** then occurs almost exclusively on the face of the imine that is *anti* to the sterically demanding tricarbonylchromium moiety.

There are several possible origins for the minor diastereomeric products in Table 1, namely *anti* attack on conformer **B**, *syn*



Scheme 4 Nu$^-$ = D$^-$, H$^-$ or Me$^-$

Table 1 1,2-Addition reactions of imine complexes **2** (R = Ph or Bu^t), **5** and **6** with nucleophiles

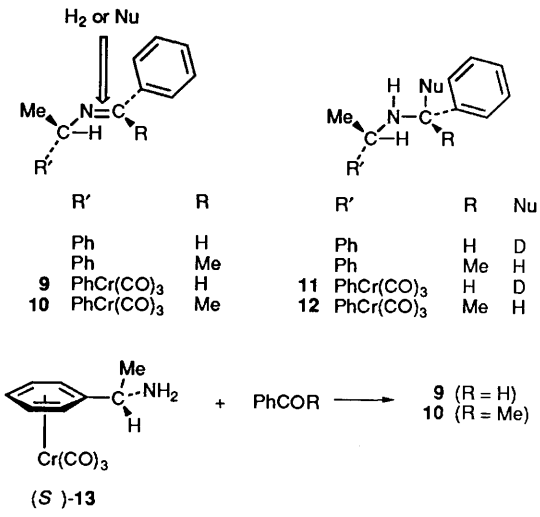
Entry	Complex	Nucleophile	Yield of adducts (%)	Diastereoselection **3**:**4**
1	**2** (R = Ph)	$NaBD_4$	78	95:5
2	**2** (R = Ph)	LiMe	42	92:8
3	**2** (R = Bu^t)	$NaBD_4$	55	87:13
4	**2** (R = Bu^t)	LiMe	88	95:5
5	**5**	$NaBH_4$	55	5:95
6	**6**	$NaBD_4$	58	97:3 (**7**:**8**)
7	**6**	LiMe	0	—

addition to **A** [despite the presence of the large $Cr(CO)_3$ blocking group], and *E*/*Z* isomerization during reaction. Such geometric isomerization, however, has been shown not to occur during the reduction of imine **2** (R = Bu^t, pure *E* isomer) with $NaBD_4$. This reaction did not proceed to completion under the conditions employed and 29% of **2** (R = Bu^t) was also isolated. This recovered imine complex was still 100% of the *E* geometric isomer. Hence, the relatively poor diastereoselectivity in this reaction cannot be attributed to the formation of the *Z* isomer and its subsequent reduction to **4**.

Synthesis and 1,2-Addition Reaction of Organic Imines and the Related Complexes **9** *and* **10**.—The catalytic hydrogenation of optically active *N*-(α-methylbenzylidene)-1-phenylethylamine and related free imines is known to give *N*,*N*-dibenzylamines with good to modest diastereoselectivity.[10] For example, catalytic hydrogenation of *N*-(α-methylbenzylidene)-(*S*)-1-phenylethylamine (*E*:*Z* = 88:12) gave a 85:15 mixture of (*S*)(*S*)-(α-methylbenzyl)-1-phenylethylamine and the *meso* compound [(*S*)(*R*)]. It has been found that the *E* and *Z* geometric isomers of this benzylideneamine isomerize under the reaction conditions and that their ratio does not affect the diastereoselectivity of the hydrogenation.[10b,c] The stereochemical outcome of these reactions has been rationalized in terms of reduction of the imine ground-state conformation which would be expected to be favoured in terms of allylic 1,3-strain considerations.[10b,c,11] Hydrogenation occurs from the face of the imine *anti* to the bulky aryl group.

We reasoned that if the steric demand of the aryl group was increased, by complexation with tricarbonylchromium, then an enhanced diastereoselectivity in the reduction step would result. To this end, the tricarbonyl(arene)chromium imine complexes **9** and **10** were prepared from either (*S*)- or (*R*)-tricarbonyl(η^6-1-phenylethylamine)chromium(0) **13** and benzaldehyde or acetophenone (Scheme 5). In some cases a better yield of the desired imine complex could be realized when the condensation reaction was performed at room temperature in the presence of 5A molecular sieves rather than in refluxing toluene.[13] It should be noted that, unlike the imine complexes **2**, **5** and **6**, **9** and **10** do not possess planar chirality. Instead, the chiral auxiliary (as with the free imines) is the chiral carbon attached to the imine nitrogen atom. In each case (Table 2) a mixture of *E* and *Z* geometric isomers resulted, which were difficult to separate. Consequently all subsequent reductions of **9** and **10** were performed on the mixture. Complex (*R*)-**10** could also be prepared by treatment of the free imine with $[Cr(CO)_6]$. This resulted in a mixture of (*R*)-**10** (70%; *E*:*Z* = 90:10 from ^{1}H NMR analysis of the imine CH=N proton signals of the geometric isomers) and a regioisomer (30%) resulting from the complexation of tricarbonylchromium to the aryl group of the methylbenzylidene moiety. These regioisomers could be separated by recrystallization. For comparison, the uncomplexed imines were also reduced under similar reaction conditions. It is of interest that starting with (*S*)-(−)-1-phenylethylamine the imines had a positive rotation, but the product amines (see Scheme 5) had a negative rotation. In contrast, previous workers report[10a,b] a negative rotation for the (*S*)-imines. However, one worker noted a reverse in sign on going from phenylethylamine to the imine.[14] We chose to study the reduction of imines with $NaBH_4$ and $NaBD_4$ rather than reduction under catalytic hydrogenation conditions. The stereochemical results are reported in Table 2.

From Table 2 it is evident, within the limits of the experimental errors arising from our ^{1}H NMR integral measurements, that there is no significant difference in the product diastereoselectivities for the complexed imines (*S*)- and (*R*)-**9** and the corresponding uncomplexed (*S*)-imine, even though there is a significant difference in the *E*:*Z* ratio of the complexed and uncomplexed imines. Clearly *E*:*Z* isomerization must be occurring during the course of the reduction reactions. The imine PhCH=N–CHMePh and complex **9** derived from



Scheme 5

Table 2 Reduction of imines and imine complexes with $NaBD_4$ or $NaBH_4$

Compound	*E*:*Z*	Reductant	Yield of adducts (%)	Diastereoselectivity
(*S*)-PhCH=N–CHMePh	76:24	$NaBD_4$	78	91:9[a]
(*S*)-**9**	98:2	$NaBD_4$	58	94:6[b]
(*R*)-**9**	98:2	$NaBD_4$	54	92:8[b]
(*S*)-PhCMe=N–CHMePh	91:9	$NaBH_4$	86	84:16[a]
(*S*)-**10**	93:7	$NaBH_4$	60	72:28[b]
(*R*)-PhCMe=N–CHMePh	89:11	$NaBH_4$	93	85:15[a]
(*R*)-**10**	90:10	$NaBH_4$	80	76:24[b]

[a] Minor diastereoisomer is the *meso* compound. [b] Minor diastereoisomer is the *meso* compound after decomplexation.

benzaldehyde show a much higher diastereoselectivity in their reduction reactions than do the corresponding compound, derived from acetophenone. The reduction by $NaBH_4$ of the free imine (*R*)-PhCMe=N–CHMePh proceeds with an almost identical diastereoselectivity to that of its reported catalytic hydrogenation. However, its tricarbonylchromium complex **10** appears to be less diastereoselective in its reduction with $NaBH_4$. It must be concluded that the tricarbonylchromium moiety is projected away from the site of nucleophilic attack on the imine group and consequently has little influence on the diastereoselectivity of these reductions. Decomplexation of **12** in air in the presence of sunlight gave $NH(CHMePh)_2$. Thus, the stereochemical outcome for the reduction of PhCMe=N–CHMePh and complex **10** by $NaBH_4$ is the same.

In conclusion, highly diastereoselective 1,2-addition reactions have been achieved on imines attached to tricarbonyl-(*o*-substituted arene)chromium moieties possessing planar chirality. The absolute stereochemistry of the amine products has been established and explained on the basis of nucleophilic attack on a favoured conformer at the face of the imine remote from the bulky $Cr(CO)_3$(arene) group. High diastereoselectivity has also been shown for nucleophilic addition to related iminechromium complexes where asymmetric induction arises from a chiral carbon centre adjacent to the reaction site. The application of these methods to the asymmetric synthesis of biologically interesting compounds is currently under investigation.

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