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Epoxide ring opening catalysed by imidochromium complexes‡

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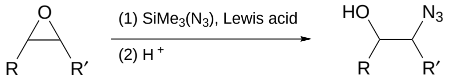
tert-Butylimidochromium complexes catalysed ring opening of epoxides by $SiMe_3(N_3)$ to give azidohydrins in good yields. The proposed mechanism for the chromium-mediated epoxide azidolysis involves the intermediacy of a chromium–azide species which delivers nucleophilic azide to the epoxide substrate. The azido complexes $[\{Cr(NBu^t)_2Cl\}_2(\mu\text{-}N_3)_2]$ **1** and $[Cr(Bu^tN{=}NN{=}NSiMe_3)(N_3)Cl_2]$ **2** have been isolated in the reactions of $SiMe_3(N_3)$ with $[Cr(NBu^t)_2Cl_2]$ and $[Cr(NBu^t)Cl_3(dme)]$ (dme = 1,2-dimethoxyethane), respectively. The structure of complex **1** has been established by X-ray crystallography. The mean Cr–N (imide) and Cr–N (azide) distances are 1.605 and 2.061 Å, respectively. Reaction of $[Cr(NBu^t)Cl_3(thf)_2]$ (thf = tetrahydrofuran) with (*S*,*S*)-diop {4,5-[bis(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane} gave the dimeric complex $[\{Cr(NBu^t)Cl_3\}_2\{\mu\text{-}(S,S)\text{-diop}\}]$, which has been characterised by X-ray crystallography. The Cr–N and Cr–P distances are 1.593(9) and 2.449(4) Å, respectively.

Epoxides are an important class of building blocks for complex organic compounds.[1] With the advent of asymmetric epoxidation of allylic alcohols[2] and alkenes,[3] optically pure epoxides have been made easily available as valuable starting materials for stereospecific syntheses. Of practical importance is the synthesis of azidohydrins *via* ring opening of epoxides with $SiMe_3(N_3)$, which is known to be catalysed by organometallic Lewis acids such as V, Ti,[4] Zr[5] and Yb[6] (Scheme 1).



Scheme 1

While organoimido complexes (M=NR) have been successfully used as well defined promoters for alkene metathesis and ring-opening metathesis polymerisation of cyclic alkenes,[7] there are few reports on the applications of these complexes in organic transformations. Recently we found that imidochromium complexes catalyse regioselective ring opening of epoxides[8] and *N*-toluene-*p*-sulfonylaziridines,[9] demonstrating that these complexes have potential applications in organic syntheses. The salient features of this new class of Lewis acids include high solubilities in organic solvents, little tendency to oligomerise, high tolerance to heteroatom functional groups, and their well defined organometallic chemistry. The study of chromium-mediated epoxide ring opening is of significance because Jacobsen and co-workers[10–12] recently discovered that chiral chromium complexes are unique catalysts for enantioselective ring opening of *meso*-epoxides[10] and kinetic resolution of racemic epoxides.[11] Herein we describe the isolation of azido(imido)chromium complexes, which are believed to be the active species of chromium-mediated epoxide ring opening and the preparation of a chiral imidochromium catalyst for enantioselective epoxide ring opening.

Experimental

All manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were purified, distilled and degassed prior to use. Proton NMR spectra were recorded on a JEOL EX 400 or Bruker ALX 300 spectrometer, chemical shifts (δ, in ppm) being referenced to $SiMe_4$. Infrared spectra were obtained on a Perkin-Elmer 16PC FT-IR spectrophotometer, mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Brunel University, UK.

CAUTION: high-valent chromium complexes are potentially carcinogenic; avoid contact with skin and inhalation.

Materials

The compounds $[Cr(NBu^t)_2Cl_2]$,[13] $[Cr(NBu^t)Cl_3(thf)_2]$ (thf = tetrahydrofuran), $[Cr(NBu^t)Cl_3(dme)]$ (dme = 1,2-dimethoxyethane),[14] and $[\{Ti(NBu^t)Cl_2(NH_2Bu^t)_2\}_3]$[15] were prepared as described elsewhere. The epoxide substrates and (*S*,*S*)-diop {4,5-[bis(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxolane} were obtained from Aldrich and used as received.

Typical procedure for ring opening of styrene oxide

To a stirred solution of styrene oxide (1 mmol) and $[Cr(NBu^t)Cl_3(dme)]$ (0.05 mmol) in dry CH_2Cl_2 (15 cm^3) at room temperature was added $SiMe_3(N_3)$ (3 mmol). After stirring overnight, the reaction mixture was treated with dilute H_2SO_4 (1 mol dm^{-3}, 10 cm^3). The organic layer was collected and dried with anhydrous $MgSO_4$. Evaporation of the volatiles gave an oil, which was loaded onto a column of silica gel. The azidophenylethanol products were eluted with 15% Et_2O–hexane, isolated as an inseparable mixture. The ratio of the products was determined by ^1H NMR spectroscopy.

Spectroscopic data for the azidohydrins and chlorohydrin. 2-*Azido-2-phenylethanol.* ^1H NMR ($CDCl_3$): δ 1.90 (t, *J* = 6.5, 1 H, OH), 3.76 (t, *J* = 6.5, 2 H, CH_2OH), 4.68 [t, *J* = 6.4 Hz, $CH(N_3)$] and 7.32–7.41 (m, 5 H, aromatic). IR (cm^{-1}): 3386 (br) [ν(OH)] and 2102 [ν(N_3)]. Chemical ionisation (CI) mass spectrum: *m*/*z* 163 (M^+).

2-*Chloro-2-phenylethanol.* ^1H NMR ($CDCl_3$): δ 2.06 (dd, *J* = 6.4, 7.7, 1 H, OH), 3.94 (dt, *J* = 1.8, 6.8, 2 H, CH_2OH), 5.00

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‡ *Non-SI unit employed*: $\mu_B = 9.27 \times 10^{-24}$ J T^{-1}.

(t, $J = 6.6$ Hz, 1 H, CHCl) and 7.33–7.43 (m, 5 H, aromatic). CI mass spectrum: m/z 156 (M^+).

2-*Azido*-1-*phenylethanol*. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.38 (s br, 1 H, OH), 3.44 (dd, $J = 4.2$, 12.6, 1 H, $\mathrm{CH_2N_3}$), 3.50 (dd, $J = 7.8$, 12.6 Hz, 1 H, $\mathrm{CH_2N_3}$), 4.90–4.93 (m, 1 H, C*H*OH) and 7.32–7.39 (m, 5 H, aromatic).

Preparation of $[\{\mathrm{Cr(NBu^t)_2Cl}\}_2(\mu\text{-}\mathrm{N_3})_2]$ 1

The compound $\mathrm{SiMe_3(N_3)}$ (0.44 cm^3, 3.31 mmol) was added to a solution of $[\mathrm{Cr(NBu^t)_2Cl_2}]$ (0.22 g, 0.83 mmol) in hexane (10 cm^3). The reaction mixture was refluxed overnight. The solvent was removed *in vacuo* and the residue recrystallised from toluene. Dark red crystals were obtained after cooling the solution to −10 °C overnight {yield 25% with respect to $[\mathrm{Cr(NBu^t)_2Cl_2}]$ used}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.64 (s, 36 H, $\mathrm{Bu^t}$). IR (cm^{-1}): 1198 ν(Cr=$\mathrm{NBu^t}$) and 2098 ν($\mathrm{N_3}$) (Found: C, 35.2; H, 6.8; N, 26.8. Calc. for $\mathrm{C_{16}H_{36}Cl_2Cr_2N_{10}}$: C, 35.4; H, 6.6; N, 25.8%).

Preparation of $[\mathrm{Cr(Bu^tN{=}N{-}N{=}NSiMe_3)(N_3)Cl_2}]$ 2

The compound $\mathrm{SiMe_3(N_3)}$ (0.50 cm^3, 3.77 mmol) was added to a solution of $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ (0.30 g, 0.94 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3). The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue recrystallised from $\mathrm{CH_2Cl_2}$–diethyl ether to give a dark yellow solid (yield 75%). IR (cm^{-1}): 2110 ν($\mathrm{N_3}$). CI mass spectrum: m/z 264 ($M^+ - \mathrm{N_2}$ − isobutene). μ_eff(Evans method,[16] $\mathrm{CHCl_3}$) = 3.52 μ_B (Found: C, 23.4; H, 5.2; N, 25.4. Calc. for $\mathrm{C_{10}H_{27}Cl_2CrN_8Si_2}$: C, 23.9; H, 5.1; N, 27.9%).

Ring opening of cyclohexene oxide by $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ with (*S*,*S*)-diop

A mixture of cyclohexene oxide (0.61 mmol), $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ (10 mmol), (*S*,*S*)-diop (10 mmol) and $\mathrm{SiMe_3(N_3)}$ (1.83 mmol) was stirred in $\mathrm{CH_2Cl_2}$ (5 cm^3) at room temperature for 3 d. The reaction mixture was worked up as described earlier and the products were identified as racemic mixtures of 2-azidocyclohexanols (30%) and 2-chlorocyclohexanol (20%) by GLC.

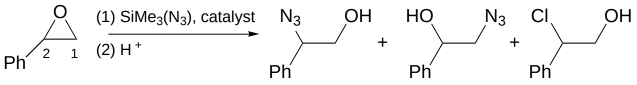
Preparation of $[\{\mathrm{Cr(NBu^t)Cl_3}\}_2\{\mu\text{-}(S,S)\text{-diop}\}]$ 4

The compound (*S*,*S*)-diop (0.27 g, 0.54 mmol) was added to a solution of $[\mathrm{Cr(NBu^t)Cl_3(thf)_2}]$ (0.20 g, 0.54 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3). The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue washed with toluene. Recrystallisation from $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$ afforded green prisms, suitable for X-ray diffraction study {Yield 33% with respect to $[\mathrm{Cr(NBu^t)Cl_3(thf)_2}]$ used} (Found: C, 55.7; H, 5.8; N, 2.5. Calc. for $\mathrm{C_{53}H_{66}Cl_6Cr_2N_2O_2P_2}$: C, 55.3; H, 5.7; N, 2.6%).

X-Ray crystallography

Crystal data and experimental details for complexes **1** and **4** are listed in Table 2. Measurements for **1** were made on an Enraf-Nonius CAD-4 diffractometer. X-Ray-quality crystals of $[\{\mathrm{Cr(NBu^t)_2Cl}\}_2(\mu\text{-}\mathrm{N_3})_2]$ **1** were obtained from a toluene solution at −10 °C. Lattice parameters for **1** were obtained from 25 reflections with 2θ 19.02–27.70°. All reflections were corrected for Lorentz-polarisation effects. All data reduction and refinement was performed using the NRCVAX packages.[17] The structure was solved by the Patterson method and refined on *F* by full-matrix least-squares analysis. All hydrogen atoms were refined isotropically and all other atoms anisotropically. Hydrogen atoms on the organic ligands were calculated in idealised positions and included in the structure-factor calculation. X-Ray-quality crystals of $[\{\mathrm{Cr(NBu^t)Cl_3}\}_2\{\mu\text{-}(S,S)\text{-diop}\}]$ **4** were obtained by slow diffusion of ether into a $\mathrm{CH_2Cl_2}$ solution. Measurements were made on a Rigaku AFC7R diffractometer at 25 °C. Intensity data were corrected for Lorentz-polarization effects. The structure was solved by direct methods (SIR 92[18]) and refined by full-matrix least-squares analysis with hydrogen atoms placed in calculated positions.

Table 1 Catalytic ring opening of styrene oxide by $\mathrm{SiMe_3(N_3)}$



I **II** **III**

Catalyst[a]	Solvent	% Yield I	 II	 III	Reaction time
$[\mathrm{Cr(NBu^t)_2Cl_2}]$	$\mathrm{CH_2Cl_2}$	90	0	7	12 h
$[\{\mathrm{Cr(NBu^t)_2Cl}\}_2(\mathrm{N_3})_2]$	$\mathrm{CH_2Cl_2}$	90	0	0	10 h
$[\mathrm{Cr(NBu^t)Cl_3(dme)}]$	$\mathrm{CH_2Cl_2}$	63	30	3	5 h
	thf	42	10	2	12 h
	MeCN	4	0	0	24 h
$[\mathrm{CrL(NBu^t)Cl_2}]$[b]	$\mathrm{CH_2Cl_2}$	0	0	0	5 d
$[\mathrm{Mo(NBu^t)_2Cl_2(dme)}]$	$\mathrm{CH_2Cl_2}$	45	0	0	2 d
$[\{\mathrm{Ti(NBu^t)Cl_2(NH_2Bu^t)_2}\}_3]$	$\mathrm{CH_2Cl_2}$	45	0	9	20 h

[a] Catalyst loading was 10 mol % except for the reactions with $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$, in which 5 mol % catalyst was used. [b] L = (η-$\mathrm{C_5H_5}$)Co{PO(OEt)$_2$}$_3$.

CCDC reference number 186/650.

Results and Discussion

Catalytic azidolysis of styrene oxide

tert-Butylimidochromium complexes $[\mathrm{Cr(NBu^t)_2Cl_2}]$ and $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ catalyse ring opening of styrene oxide with $\mathrm{SiMe_3(N_3)}$ to give the vicinal azidohydrins in good yields and the results are summarised in Table 1. Typically reaction of styrene oxide with $\mathrm{SiMe_3(N_3)}$ in the presence of 10 mol % of $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ afforded a 1:2 mixture of azidohydrins **I** and **II** in 93% yield.

Depending on the purity of the catalyst and experimental conditions, some chlorohydrin **III** was also detected. It is apparently derived from the chloride of the catalyst because none was detected when the azidochromium complex $[\{\mathrm{Cr(NBu^t)Cl(N_3)}\}_2(\mu\text{-}\mathrm{N_3})_2]$ (see later) was employed as the catalyst. The corresponding reactions with $[\mathrm{Cr(NBu^t)_2Cl_2}]$ and $[\mathrm{Mo(NBu^t)_2Cl_2}]$[19] were slower but selective, yielding the 2-azido-alcohol **I** exclusively. The preference for the formation of **I** by the ring opening of styrene oxide may be explained in terms of the stability of the benzylic carbocation intermediate, which is susceptible to nucleophilic attack by azide. The activity of imidometal complexes in epoxide ring opening was found to decrease in the order $\mathrm{Cr^V} > \mathrm{Ti^{IV}} > \mathrm{Cr^{VI}} > \mathrm{Mo^{VI}}$, which reflects the trend in Lewis acidity of the metal centre. The lower Lewis acidity of $[\mathrm{Cr(NBu^t)_2Cl_2}]$ compared with that of $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ may be reasoned by the fact that the former complex, although in a higher oxidation state, is stabilised by two strongly π-donating imides and is therefore a weaker Lewis acid. No catalytic reaction was observed when co-ordinatively saturated $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{Co\{PO(OEt)_2\}_3Cr(NBu^t)Cl_2}]$[20] was used as catalyst, suggesting that a vacant site on chromium is essential for the catalytic ring opening. However, there is no appreciable difference in catalytic activity between $[\mathrm{Cr(NBu^t)Cl_3(dme)}]$ and the more substitutionally labile $[\mathrm{Cr(NBu^t)Cl_3(thf)_2}]$, indicating that dissociation of the ether ligands in the imidochromium(V) complexes is not a rate-limiting step in the chromium-catalysed azidolysis reaction. The catalytic epoxide ring opening is rather insensitive to the choice of solvent, although the yield for $\mathrm{CH_2Cl_2}$ was found to be slightly higher than that for thf. This is in contrast to the Cr(salen) [$\mathrm{H_2}$salen = *N*,*N*′-bis(salicylidene)-ethane-1,2-diamine] system,[10] in which epoxide ring opening

Table 2 Crystallographic data for $[\{Cr(NBu^t)_2Cl\}_2(\mu\text{-}N_3)_2]$ **1** and $[\{Cr(NBu^t)Cl_3\}_2\{\mu\text{-}(S,S)\text{-diop}\}]$ **4**

	1	**4**
Chemical formula	$C_8H_{18}ClCrN_5$	$C_{53}H_{66}Cl_6Cr_2N_2O_2P_2$
M	271.71	1141.77
Crystal dimensions/mm	0.40 × 0.50 × 0.60	0.23 × 0.24 × 0.34
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	10.552(4)	18.822(4)
b/Å	12.429(4)	27.220(4)
c/Å	11.320(2)	10.984(3)
β/°	97.13(3)	
U/Å^3	1473.2(7)	5627(1)
Z	4	4
T/°C	25	25
λ/Å	0.710 69	0.710 73
D_c/g cm^{-3}	1.225	1.348
Scan type	θ–2θ	ω–2θ
$2\theta_{max}$/°	50	45
μ/cm^{-1}	7.338	7.68
$F(000)$	570	2376
Reflections measured	2586	8308
Observed reflections	1611 $[I > 2\sigma(I)]$	2701 $[I > 3\sigma(I)]$
Weighting scheme	$1/\sigma^2(F_o)$	$1/[\sigma^2(F_o) + (0.006F_o^2/4)]$
R [a]	0.045	0.052
R' [b]	0.032	0.047
Goodness of fit [c]	2.22	2.25

[a] $R = (\Sigma|F_o| - |F_c|)/|F_o|$. [b] $R' = [(\Sigma w^2|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2)]^{\frac{1}{2}}$. [c] Goodness of fit $= [\Sigma w(|F_c| - |F_o|)^2/(N_{obs} - N_{param})]^{\frac{1}{2}}$.

was found to be faster in thf and ether. The catalytic reaction is very slow in acetonitrile possibly because the imidochromium complexes have a strong affinity for N-donor ligands and bind to acetonitrile very tightly.

Azido(imido)chromium complexes

No reactions between styrene oxide and the imido complexes were observed; nor was there any between $SiMe_3(N_3)$ and epoxide under the reaction conditions. This suggests that the first step of the catalytic azidolysis may involve the interaction of the imido complexes with $SiMe_3(N_3)$. Indeed Jacobsen and co-workers[10] demonstrated that the structurally characterised $[Cr(salen)(N_3)]$ species is responsible for the Cr(salen)-mediated epoxide azidolysis. The formation of the diazide species $[Cr(NBu^t)_2(N_3)_2]$ from $[Cr(NBu^t)_2Cl_2]$ and $SiMe_3(N_3)$ was previously reported by Wilkinson and co-workers.[21] However, despite many attempts we were only able to isolate the dinuclear species $[\{Cr(NBu^t)_2Cl\}(\mu\text{-}N_3)_2]$ **1**, which has been characterised by X-ray crystallography, from the reaction of $[Cr(NBu^t)_2Cl_2]$ with $SiMe_3(N_3)$, even under refluxing conditions [equation (1)].

$$2[Cr(NBu^t)_2Cl_2] + 2SiMe_3(N_3) \longrightarrow [\{Cr(NBu^t)_2Cl\}_2(\mu\text{-}N_3)_2] + 2SiMe_3Cl \quad (1)$$

Fig. 1 shows a perspective view of the molecule; selected bond lengths and angles are given in Table 3. The two $Cr(NBu^t)_2Cl$ cores are bridged by two azides with Cr–N (azide)–Cr and N (azide)–Cr–N (azide) angles 109.6(2) and 70.4(1)°, respectively. The mean Cr–N (imido), Cr–N (azide) and Cr–Cl distances are 1.605, 2.061 and 2.288(2) Å, respectively. The short Cr–N (imido) bond lengths and large Cr–N–C angles (*ca.* 165.65°) are consistent with the formulation of Cr–N triple bond. The IR spectrum of **1** shows N≡N and $Cr{=}NBu^t$ stretches at 2098 and 1198 cm^{-1}, respectively.

On the other hand, reaction of $[Cr(NBu^t)Cl_3(dme)]$ with $SiMe_3(N_3)$ afforded an air-stable brown solid analysed as $[Cr(NBu^t)(N_3)Cl_2\{Me_3Si(N_3)\}]$ **2**. The IR spectrum displays a band at *ca.* 1500 cm^{-1}, tentatively assigned as the N=N stretch, along with the $\nu(N_3)$ band at 2110 cm^{-1}. The measured magnetic moment of *ca.* 3.52 μ_B suggests that complex **2** is probably a trivalent chromium species. On the basis of the analytical and spectral data, it is tentatively formulated as a chromium(III) tetrazene complex $[Cr^{III}(Bu^tN{=}N{-}N{=}NSiMe_3)(N_3)Cl_2]$. It may be noted that dipolar cycloaddition of the imido-metal moiety with azide to give tetrazene is not without precedent. Reactions of imido complexes of Os,[22] Zr[23] and Ru[24] with organic azides have been reported to give the respective tetrazene species.

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Cr···Cr′	3.368(2)	Cr–Cl	2.288(2)
Cr–N(1)	2.020(4)	Cr–N(1′)	2.101(4)
Cr–N(4)	1.607(4)	Cr–N(5)	1.603(4)
N(1′)–Cr	2.101(4)	N(1)–N(2)	1.221(5)
N(2)–N(3)	1.119(5)		
Cr′–Cr–Cl	121.16(5)	Cr′–Cr–N(1)	36.0(1)
Cr′–Cr–N(1′)	34.3(1)	Cr′–Cr–N(4)	115.1(2)
Cr′–Cr–N(5)	113.6(2)	Cl–Cr–N(1)	86.8(1)
Cl–Cr–N(4)	94.9(2)	Cl–Cr–N(5)	96.8(2)
N(1)–Cr–N(1′)	70.4(1)	N(1)–Cr–N(4)	98.1(2)
N(1)–Cr–N(5)	95.4(2)	N(1′)–Cr–N(4)	123.1(2)
N(1′)–Cr–N(5)	123.4(2)	N(4)–Cr–N(5)	112.9(2)
Cr′–N(1)–Cr′	109.6(2)	Cr–N(1)–N(2)	122.0(3)
Cr–N(1)–N(2)	128.4(3)	N(1)–N(2)–N(3)	179.1(5)
Cr–N(4)–C(1)	162.2(4)		

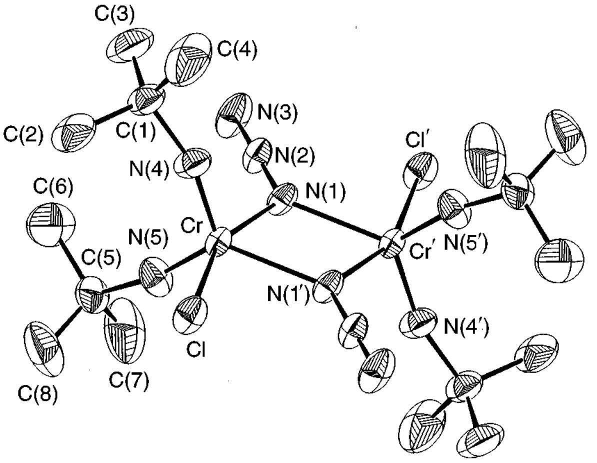
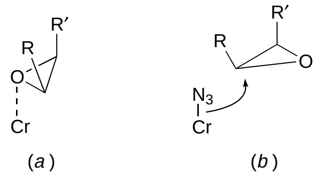


Fig. 1 Perspective view of $[\{Cr(NBu^t)_2Cl\}_2(\mu\text{-}N_3)_2]$ **1**



Scheme 2

Proposed mechanism for the Cr-mediated epoxide ring opening

Two mechanisms have been proposed for the metal-catalysed azidolysis of epoxides (Scheme 2): (*a*) Lewis-acid activation and (*b*) nucleophilic delivery of azide. As in the case for Cr(salen)-catalysed epoxide ring opening,[10] we believe that the nucleophilic delivery mechanism is operative in the imidochromium system. This is supported by fact that the azido complexes **1** and **2** are capable of catalysing azidolysis of styrene epoxide in yields comparable to those for their precursors. It should be noted that azidolysis of styrene oxide with **1** is only marginally faster than that for $[Cr(NBu^t)_2Cl_2]$, indicating that the delivery of azide to epoxide rather than the formation of a $Cr{-}N_3$ intermediate is rate limiting. These results are consistent with the mechanism depicted in Scheme 3. Reaction of the precatalyst $[Cr(NBu^t)_2Cl_2]$ with $SiMe_3(N_3)$ gives the azido(imido)-

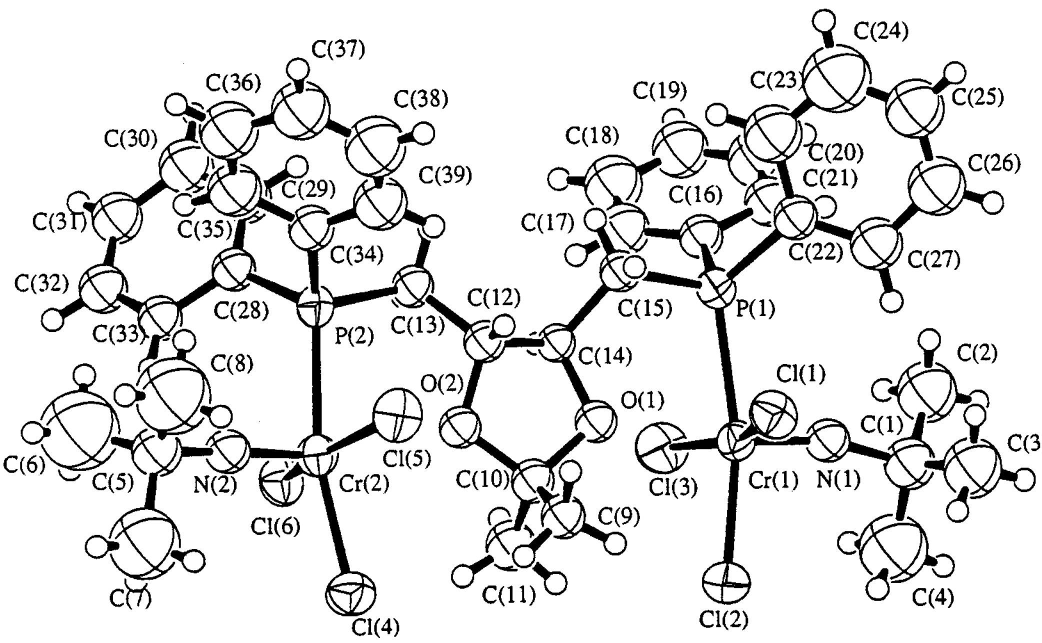
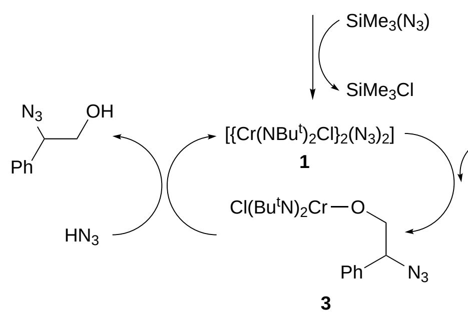
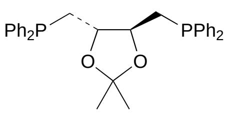


Fig. 2 Perspective view of $[\{\mathrm{Cr(NBu^t)Cl_3}\}_2\{\mu\text{-}(S,S)\text{-diop}\}]$ **4**



Scheme 3



(*S*, *S*)-diop

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Cr(1)–N(1)	1.593(9)	Cr(2)–N(2)	1.603(9)
Cr(1)–Cl(1)	2.272(4)	Cr(2)–Cl(4)	2.279(4)
Cr(1)–Cl(2)	2.287(4)	Cr(2)–Cl(5)	2.274(4)
Cr(1)–Cl(3)	2.281(4)	Cr(2)–Cl(6)	2.273(4)
Cr(1)–P(1)	2.449(4)	Cr(2)–P(2)	2.450(4)
Cr(1)–O(1)	2.58(1)	Cr(2)–O(2)	2.43(1)
Cl(1)–Cr(1)–Cl(2)	91.8(1)	Cl(1)–Cr(1)–Cl(3)	162.3(2)
Cl(1)–Cr(1)–P(1)	85.0(1)	Cl(1)–Cr(1)–N(1)	100.1(4)
Cl(2)–Cr(1)–Cl(3)	93.7(1)	Cl(2)–Cr(1)–P(1)	166.9(1)
Cl(2)–Cr(1)–N(1)	97.7(4)	Cl(3)–Cr(1)–P(1)	85.8(1)
Cl(3)–Cr(1)–N(1)	95.8(4)	P(1)–Cr(1)–N(1)	95.4(4)
Cl(4)–Cr(2)–Cl(5)	92.2(1)	Cl(4)–Cr(2)–Cl(6)	90.2(1)
Cl(4)–Cr(2)–P(2)	165.0(1)	Cl(4)–Cr(2)–N(2)	101.3(4)
Cl(5)–Cr(2)–Cl(6)	158.7(1)	Cl(5)–Cr(2)–P(2)	86.4(1)
Cl(5)–Cr(2)–N(2)	96.3(4)	Cl(6)–Cr(2)–P(2)	85.8(1)
Cl(6)–Cr(2)–N(2)	104.1(4)	P(2)–Cr(2)–N(2)	93.6(4)
Cr(1)–N(1)–C(1)	165.6(9)	Cr(2)–N(2)–C(5)	169(1)

chromium complex **1** and $\mathrm{SiMe_3Cl}$. This is followed by the rate-limiting nucleophilic delivery of the Cr-bound azide to the epoxide and the formation of chromium azidoalkoxide complex **3**. It may be noted that a related Cr(salen) cyclopentoxide complex has been isolated recently from the reaction of cyclopentene oxide with $[\mathrm{Cr(salen)(N_3)}]$.[25] Reaction of **3** with $\mathrm{HN_3}$, which is presumably formed by protonation of $\mathrm{SiMe_3(N_3)}$, gives the azidohydrin and complex **1**, thus completing the catalytic cycle. The elegant work by Jacobsen and co-workers[25] has unambiguously confirmed that it is $\mathrm{HN_3}$, instead of $\mathrm{SiMe_3(N_3)}$, that is responsible for the turnover of the alkoxide intermediate.

Chiral imidochromium complex

The success of imidochromium complexes in azidolysis of cyclohexene oxide[8] prompts us to explore the possibility of enantioselective ring opening of *meso*-epoxides with chiral imidochromium complexes. To this end, ring opening of *meso*-epoxides with $\mathrm{SiMe_3(N_3)}$ in the presence of $[\mathrm{Cr(NBu^t)Cl_3(thf)_2}]$ and chiral phosphines such as (*S*,*S*)-diop was attempted.

Unfortunately the reaction of cyclohexene oxide with $\mathrm{SiMe_3(N_3)}$ in the presence of catalytic $[\mathrm{Cr(NBu^t)Cl_3(thf)_2}]$ and (*S*,*S*)-diop only yielded racemic mixtures of the azidohydrins and chlorohydrins in 50% overall yield. The solid-state structure of the phosphine adduct of the imidochromium(V) complex may provide some insights into the inability of this complex to effect asymmetric ring opening. The 2:1 adduct $[\{\mathrm{Cr(NBu^t)Cl_3}\}_2\{\mu\text{-}(S,S)\text{-diop}\}]$ **4** was obtained by reaction of $[\mathrm{Cr(NBu^t)Cl_3(thf)_2}]$ with 1 equivalent of (*S*,*S*)-diop. The 1:1 phosphine adduct $[\mathrm{Cr(NBu^t)Cl_3}\{(S,S)\text{-diop}\}]$ was not obtained even when an excess of phosphine was used. Fig. 2 shows a perspective view of the molecule; selected bond lengths and angles are given in Table 4. The structure consists of two $\mathrm{Cr(NBu^t)Cl_3}$ fragments, which are bridged together *via* the phosphorus and oxygen atoms of (*S*,*S*)-diop. The geometry around each Cr can be described as distorted octahedral with the imide ligand opposite to the isopropylidene oxygen of (*S*,*S*)-diop. The Cr(1)–N(1) and Cr(1)–P(1) distances of 1.593(3) and 2.449(4) Å are comparable to those in $[\mathrm{Cr(NBu^t)Cl_3(PEtPh_2)_2}]$ [1.634(7) and 2.479 Å, respectively].[26] The Cr–O distances [2.43(1) and 2.58(1) Å] are long apparently due to the *trans* influence of the *tert*-butylimide. In this co-ordination mode it seems that the steric effect of the ligand is not sufficient to direct the orientation of the substrate in the transition state to achieve enantioselective ring opening. This may explain why no stereoselectivity was observed for catalytic ring opening with complex **4**. The preparation of monomeric chiral imidochromium complexes with C_2-symmetric chiral ligands is underway.

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