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Organoimido Complexes as a New Class of Lewis Acid Catalysts for Regioselective Ring-Opening of Epoxides

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Abstract: Organoimido complexes of Group VI transition metals were found to catalyze ring-opening of epoxides by trimethylsilyl azide and amines with good regioselectivities.

Organoimide ligands (RN^{2-}) are strong π donors and capable of stabilizing electrophilic high-valent metal centers. Although the chemistry of imido complexes of the type $M(NR)_2X_2$ (M = group VI transition metal), which are isolobal with $(\eta^5\text{-}C_5H_5)_2M'X_2$ (M' = group IV transition metal),[1] are well documented; there are few studies of the application of imido complexes to organic synthesis, apart from their uses in olefin metathesis polymerization.[2] Because of the presence of low-lying vacant d orbitals, high-valent imidometal compounds are anticipated to be good Lewis acid catalysts. The attractive features of this new class of Lewis acid catalysts include (a) high solubility and low tendency to oligomerize, (b) tunable Lewis acidity; and (c) high tolerance to functional group. We report here the nucleophilic ring-opening of epoxides catalyzed by organoimido complexes .

Ring opening of epoxides by trimethylsilyl azide ($TMSN_3$) and amines was found to be promoted by organoimido complexes $M(NBu^t)_2Cl_2$ (M= Cr,[3] Mo[4]), $Cr(NBu^t)Cl_3(dme)$[5] (dme = 1,2-dimethoxyethane) and $W(NBu^t)_2(NHBu^t)_2$[6]; and the results are summarized in Table 1. The catalytic activity of the imido complexes decreases in the order Cr(V) > Cr(VI) ≈ Mo(VI) » W(VI), which roughly parallels with the order of electrophilicity of the metal center. The ring opening of styrene oxide by $TMSN_3$ with bis-imido catalysts $M(NBu^t)_2Cl_2$ (M = Cr, Mo) and $W(NBu^t)_2(NHBu^t)_2$ are slower but more selective than those for $Cr(NBu^t)Cl_3(dme)$, giving the 2-azido alcohol exclusively. The preferential α-attack on styrene oxide can be explained in terms of the stability of the intermediate benzylic carbocation. It seems likely that active intermediate for the catalytic ring-opening reactions is a high-valent $M\text{-}N_3$ species, which reacts with epoxide to give azidohydrin. A similar mechanism has been suggested for the analogous Ti(IV)-catalyzed reactions.[7] Indeed, $Cr(NBu^t)_2(N_3)_2$[8] was found to react with styrene oxide to give azidohydrin in good yield. Interestingly, while $M(NBu^t)_2Cl_2$ complexes are rather inactive toward the ring opening of 1,2-epoxyhexane, $W(NBu^t)_2(NHBu^t)_2$ can catalyze the ring opening reaction regioselectively presumably via a different mechanism. The imido complexes also catalyze ring opening of epoxides by amines. For example, the reaction of Bu^tNHTMS with styrene oxide in the presence of the Cr-imido catalysts gave predominately the 2-aminoalcohol in high yield. However, the regioselectivity decreases when Et_2NH was used as the nucleophile. Catalytic ring-opening reactions by amines are slower than those by $TMSN_3$ possibly because $Cr(NBu^t)_2Cl_2$ reacts with amines to give the imido-amido compound $Cr(NBu^t)_2(NRR')Cl$, which are weaker Lewis acids than the parent dichloride catalyst.

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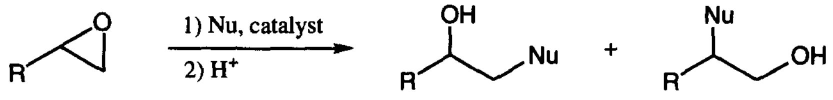
Table 1. Regioselective ring opening of epoxides catalyzed by imido complexes[a]



R	Nu	Catalyst	yield (%)		Time
Ph	$\mathrm{TMSN_3}$	$\mathrm{Cr(NBu^t)Cl_3(dme)}$	31	64	3 h
Ph	$\mathrm{TMSN_3}$	$\mathrm{Cr(NBu^t)_2Cl_2}$	0	95	12 h
Ph	$\mathrm{TMSN_3}$	$\mathrm{Mo(NBu^t)_2Cl_2(dme)}$	0	45	2 d
Ph	$\mathrm{TMSN_3}$	$\mathrm{W(NBu^t)_2(NHBu^t)_2}$	0	95	5 d
n-Bu	$\mathrm{TMSN_3}$	$\mathrm{Cr(NBu^t)Cl_3(dme)}$	26	39	3 d
n-Bu	$\mathrm{TMSN_3}$	$\mathrm{W(NBu^t)_2(NHBu^t)_2}$	0	80	5 d
Ph	$\mathrm{Bu^tNHTMS}$	$\mathrm{Cr(NBu^t)Cl_3(dme)}$	27	33	5 d
Ph	$\mathrm{Bu^tNHTMS}$	$\mathrm{Cr(NBu^t)_2Cl_2}$	7	68	10 d
Ph	$\mathrm{Et_2NH}$	$\mathrm{Cr(NBu^t)Cl_3(dme)}$	15	25	5 d
Ph	$\mathrm{Et_2NH}$	$\mathrm{Cr(NBu^t)_2Cl_2}$	8	23	10 d

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[a] Typical procedure:to a stirred solution of styrene oxide (1 mmol) and $\mathrm{Cr(NBu^t)_2Cl_2}$ (0.05 mmol) in dry $\mathrm{CH_2Cl_2}$ (15 mL) at room temperature was added $\mathrm{TMSN_3}$ (3 mmol). After stirring overnight, the reaction mixture was treated with dil. $\mathrm{H_2SO_4}$ and worked up by normal procedures to give azidophenylethanol in almost quantitative yield.

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