Synthesis and Reactivity of Organoimido Complexes of Chromium

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Organoimido groups are excellent spectator ligands for high-valent organometallic compounds due to their strong π-donating capability. Of interest are imidochromium complexes that are used as catalysts for olefin polymerization. This microreview provides an overview of the organometallic chemistry of high-valent imidochromium complexes. Synthetic routes to alkyl- and arylimido complexes of chromium in oxidation states VI–IV will be presented. The reactivity of imidochromium complexes including imido group transfer and cycloaddition will be described. The use of imidochromium complexes as catalysts for regioselective ring opening of epoxides will be discussed.

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1. Introduction

Transition metal imido complexes have attracted much attention because of their proposed intermediacy in the industrially important ammoxidation of propylene,[1] and also due to their applications to organic transformations such as aziridination[2] and aminohydroxylation[3] of olefins, amidation of hydrocarbons,[2b] amination of silyl enol ethers,[4] hydroamination of unsaturated hydrocarbons,[5,6] imine metathesis,[7] and activation of alkane C−H bonds.[8] In addition, because of their high π-donor strength, organoimido groups (NR^{2-}; R = alkyl or aryl) prove to be excellent spectator ligands for high-valent organometallic complexes. Well-defined ring-opening metathesis polymerization[9] and ring-closing metathesis[10] catalysts based on Mo^{VI} imido alkylidene complexes have been developed, while the last decade has witnessed significant progress in the organometallic chemistry of high oxidation state (imido)Cr complexes, due in part to their catalytic activities toward olefin polymerization.[11,12] This microreview reviews the synthesis and reactivity of organoimido complexes of Cr in oxidation states VI−III. General reviews on organoimido complexes of transition metals have also appeared.[13−15]

2. Synthesis of Imidochromium Complexes

2.1. (Imido)Cr^{VI} Complexes

Nugent synthesized the first (organoimido)Cr^{VI} complex $[Cr(NtBu)_2(OSiMe_3)_2]$ (**1**) by treatment of $[CrO_2Cl_2]$ with $tBuSiMe_3NH$.[16] Treatment of **1** with BCl_3 afforded the dichloride compound $[Cr(NtBu)_2Cl_2]$ (**2**).[17] The bis(adamantyl)imido complex $[Cr(NAd)_2Cl_2]$ (Ad = 1-adamantyl) was synthesized similarly, from $[CrO_2Cl_2]$, $Ad(SiMe_3)NH$, and BCl_3,[18] while $[Cr(NR)_2Cl_2]$ reacted with donor ligands L to give monoadducts $[Cr(NR)_2Cl_2(L)]$ [R = tBu,[17] Ad;[18] L = pyridine (py), PMe_2Ph, and tBuNC]. The pyridine adduct $[Cr(NtBu)_2Br_2(py)]$ (**3**) was also synthesized from **1** and Me_3SiBr in the presence of pyridine.[19] Treatment of **2** either with [Ag(OTf)] (OTf = triflate) or with

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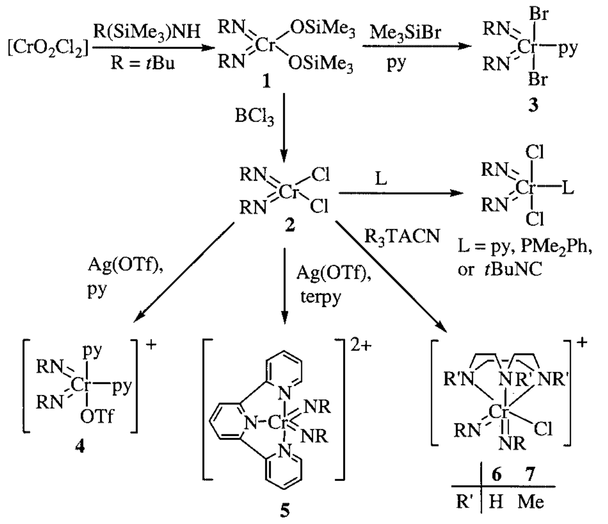
MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

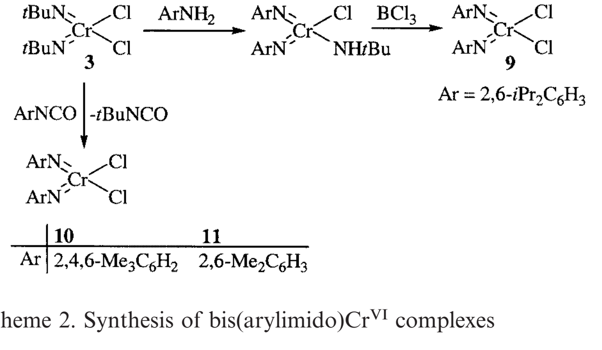
Ag(OAc) (OAc = acetate) afforded [Cr(N*t*Bu)$_2$(OTf)$_2$] and [Cr(N*t*Bu)$_2$(OAc)$_2$], respectively, while treatment of [Cr(N*t*Bu)$_2$(OTf)$_2$] with pyridine (py) or 2,2′:6′,2′′-terpyridine (terpy) gave cationic [Cr(N*t*Bu)$_2$(py)$_2$(CF$_3$SO$_3$)]$^+$ (**4**)[17] or dicationic [Cr(N*t*Bu)$_2$(terpy)]$^{2+}$ (**5**),[20] respectively. Treatment of **2** with R′$_3$TACN (TACN = 1,4,7-triazacyclononane) or KTp* [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate] afforded [Cr(N*t*Bu)$_2$(R′$_3$TACN)Cl]$^+$ (**6**, R = H; **7**, R = Me)[21] and [Tp*Cr(N*t*Bu)$_2$Cl],[22] respectively (Scheme 1).



Scheme 1. Synthesis of bis(imido)Cr^{VI} complexes

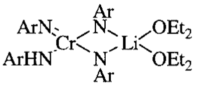
Compound **2** afforded the bis(aryl oxide) compound [Cr(N*t*Bu)$_2$(OC$_6$H$_3$*i*Pr$_2$-2,6)$_2$] (**8**) on treatment with NaOC$_6$H$_3$*i*Pr$_2$-2,6,[20] and [Cr(N*t*Bu)$_2$(NPPh$_3$)$_2$] on treatment with LiNPPh$_3$,[17] while with *t*BuNHLi it afforded [Cr(N*t*Bu)$_2$(NH*t*Bu)$_2$], which was deprotonated with *n*BuLi to give the homoleptic (imido)Cr complex [Li$_2$Cr(N*t*Bu)$_4$]. NMR spectroscopy suggested that [Li$_2$Cr(N*t*Bu)$_4$] has a structure similar to [Li$_2$W(N*t*Bu)$_4$]$_2$, with terminal linear imido and bridging bent imido groups.[23]

The bis(arylimido)Cr^{VI} complex [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(NH*t*Bu)Cl] was prepared by imido group exchange between **2** and 2,6-*i*Pr$_2$C$_6$H$_2$NH$_2$. Treatment of [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(NH*t*Bu)Cl] with BCl$_3$ afforded [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$Cl$_2$] (**9**).[24] Alternatively, [Cr(NAr)$_2$Cl$_2$] (**10**, Ar = 2,4,6-Me$_3$C$_6$H$_2$; **11**, Ar = 2,6-Me$_2$C$_6$H$_3$) were synthesized from **2** and ArNCO through Wittig-like [2 + 2] exchange of imido groups[25] (Scheme 2).



Scheme 2. Synthesis of bis(arylimido)Cr^{VI} complexes

Interestingly, treatment of **2** with 2,6-*i*Pr$_2$C$_6$H$_3$NCO resulted in the formation of the Cr^V dimer [Cr(μ-N*t*Bu)(N-C$_6$H$_3$*i*Pr$_2$-2,6)Cl]$_2$ rather than **9**.[24] Unlike **2**,[17] **3**,[18] and **9**,[26] which all formed monoadducts with donor ligands, **10** reacted with PMe$_3$ or py to yield six-coordinate [Cr(NR)$_2$Cl$_2$(L)$_2$] (L = py, PMe$_3$).[25] Treatment of **10** with NaSR afforded the dithiolate compounds [Cr(NC$_6$H$_3$Me$_2$-2,4,6)$_2$(SR)$_2$] (R = C$_6$F$_5$, 2,4,6-Me$_3$C$_6$H$_2$, 2,4,6-*i*Pr$_3$C$_6$H$_2$),[25] while with 4 equiv. of ArNHLi (Ar = 2,4,6-Me$_3$C$_6$H$_2$), **10** gave [Cr(NAr)(NHAr)(μ-NAr)$_2$Li(OEt$_2$)$_2$] (**13**, Figure 1). The amido group in **12** could not be further deprotonated by *n*BuLi.[27]



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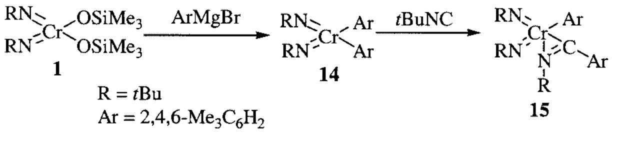
Ar = 2,4,6-Me$_3$C$_6$H$_2$

Figure 1. Structure of [Cr(NAr)(NHAr)(μ-NAr)$_2$Li(OEt$_2$)$_2$] (Ar = 2,4,6-Me$_3$C$_6$H$_2$)

Similarly, treatment of **9** with 2,6-*i*Pr$_2$C$_6$H$_3$NHLi afforded [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(NHC$_6$H$_3$*i*Pr$_2$-2,6)Cl], which also resisted further deprotonation.[26]

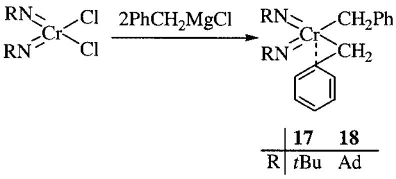
(Imido)Cr^{VI} Complexes Containing σ-Alkyl and Related Ligands

[Cr(N*t*Bu)$_2$(C$_6$H$_2$Me$_3$-2,4,6)$_2$] (**14**), the first isolated stable Cr^{VI} σ-aryl complex, was synthesized by alkylation of **1** with 2,4,6-Me$_3$C$_6$H$_2$MgBr. Similarly, alkylation of [Cr(NR)$_2$Cl$_2$] with Li(fmes) [fmes = 2,4,6-(CF$_3$)$_3$C$_6$H$_2$] yielded [Cr(NR)$_2$(fmes)$_2$] (R = *t*Bu, Ad).[18b] X-ray diffraction studies of [Cr(NR)$_2$(fmes)$_2$] revealed pseudo-tetrahedral coordination of Cr, complemented by two secondary Cr···F interactions with the *ortho*-CF$_3$ groups of the fmes ligands. Treatment of **14** with *t*BuNC afforded the η^2-(iminoacyl) complex [Cr(N*t*Bu)$_2$(C$_6$H$_2$Me$_3$-2,4,6)(η^2-*t*BuN=CC$_6$H$_2$Me$_3$-2,4,6)] (**15**, Scheme 3).[28]



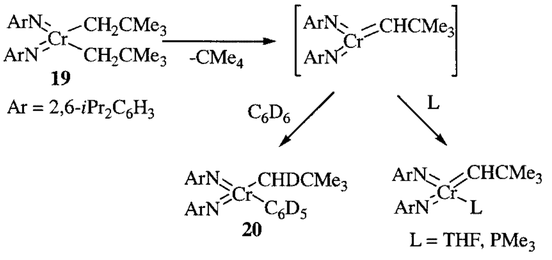
Scheme 3. Synthesis of [Cr(N*t*Bu)$_2$(C$_6$H$_2$Me$_3$-2,4,6)$_2$] and its reaction with *t*BuNC

Treatment of **2** or **3** with Me$_3$SiCH$_2$MgCl or Zn(CH$_2$SiMe$_3$)$_2$ gave [Cr(N*t*Bu)$_2$(CH$_2$SiMe$_3$)$_2$], isolated as an oil.[17,19] Alkylation of **3** with *o*-C$_6$H$_4$[(CHSiMe$_3$)Li(TMEDA)]$_2$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) afforded crystalline [Cr(N*t*Bu)$_2${*o*-C$_6$H$_4$(CHSiMe$_3$)$_2$}] (**16**).[19] Treatment of **3** with Cp$_2$Mg(THF)$_{2.5}$ (Cp = η^5-C$_5$H$_5$) afforded [CpCr(N*t*Bu)$_2$Br], which could be alkylated to give the monoalkyl compounds [CpCr(N*t*Bu)$_2$R] (R = Me, CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph).[19] Crystalline [Cr(NR)$_2$(CH$_2$Ph)(η^2-CH$_2$Ph)] (**17**, R = *t*Bu;[29] **18**, R = Ad[18]) were isolated after alkylation of [Cr(NR)$_2$Cl$_2$] with PhCH$_2$MgCl (Scheme 4).



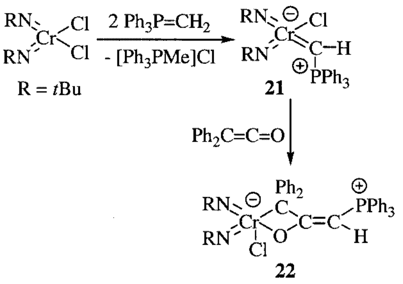
Scheme 4. Synthesis of dibenzylbis(imido)Cr^{VI} complexes

The Cr−C$_\alpha$ and Cr−C$_{ipso}$ distances for the η^2-benzyl ligand in **17** are 207.1(2) and 235.7(2) pm, respectively.[28] The solid-state ^{13}C CP/MAS NMR spectrum of **17** displays two different resonance signals at δ = 157.9 and 124.4 ppm, assigned to the η^1- and η^2-*ipso*-phenyl carbon atoms, respectively.[29] Similarly, the dialkyl compounds [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$R$_2$] (R = CH$_3$, CH$_2$Ph, CH$_2$CMe$_3$)[30] and [Cr(NC$_6$H$_2$Me$_3$-2,4,6)$_2$R$_2$] (R = CH$_2$Ph, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph)[25] have been prepared by alkylation of **9** and **10**, respectively, with RMgCl. In the solid state, [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(CH$_2$CMe$_3$)$_2$] (**19**) shows weak α-agostic interactions between Cr and the methylene hydrogen atoms of the neopentyl ligands. Complex **19** reacted with C$_6$D$_6$ at room temperature to give [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(CHDCMe$_3$)(C$_6$D$_5$)] (**20**) and CHDCMe$_3$, through an (alkylidene)Cr^{VI} intermediate that could be trapped by THF or PMe$_3$ to form adducts [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(=CHCMe$_3$)L] (L = THF, PMe$_3$). The conversion of **19** into **20** was found to follow first-order kinetics, suggesting that the rate-determining step is the α-hydrogen elimination of **19** to give the transient three-coordinate alkylidene intermediate, which rapidly reacted with C$_6$D$_6$. Neither [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(=CHCMe$_3$)L] nor base-free [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(=CHCMe$_3$)] reacted with simple olefins (Scheme 5).[30]



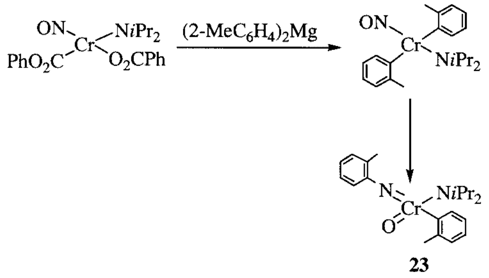
Scheme 5. Synthesis and C−H bond activation by an (alkylidene)Cr^{VI} complex

The (methylidene)(α-phosphonio) complex [Cr(N*t*Bu)$_2$Cl{CH(PPh$_3$)}] (**21**) was synthesized by transylidation of **2** with Ph$_3$P=CH$_2$. The NMR spectroscopic data for **21** (δ$_{H\alpha}$ = 11.84 ppm; δ$_{C\alpha}$ = 200.1 ppm) are characteristic for alkylidene complexes. The high barrier to rotation about the Cr−C bond [$\Delta G^{\ddagger}$(336 K) = 75 kJ·mol^{-1}] for **21** is indicative of the Cr=C double bond character. Treatment of **21** with Ph$_2$C=C=O resulted in the nucleophilic attack of Cα on the ketene and the formation of the chromaoxetane [Cr(N*t*Bu)$_2${η^2-(*O*,*C*)-OC(CHPPh$_3$)CPh$_2$}Cl] (**22**, Scheme 6).[31]



Scheme 6. Synthesis of (methylidene)(phosphanyl)Cr^{VI} complex and its reaction with ketene

Alkylation of [Cr(NO)(N*i*Pr$_2$)(O$_2$CPh)$_2$] with (2-MeC$_6$H$_4$)$_2$Mg afforded the (imido)(oxo) compound [Cr(O)(NC$_6$H$_4$Me-2)(N*i*Pr$_2$)(C$_6$H$_4$Me-2)] (**23**), presumably through N−O cleavage in the intermediate [Cr(NO)(C$_6$H$_4$Me-2)$_2$(N*i*Pr$_2$)] (Scheme 7).[32]

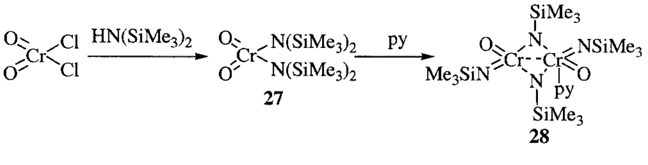


Scheme 7. Isolation of a mono(arylimido)Cr^{VI} complex from the alkylation of a (nitrosyl)Cr complex

2.2. (Imido)Cr^{V} Complexes

Treatment of [CpCrCl$_2$]$_2$ with Me$_3$SiN=NSiMe$_3$ gave the (silylimido)Cr^{V} complex [CpCr(μ-NSiMe$_3$)(NSiMe$_3$)]$_2$ (**24**), which reacted with MeOH to yield the parent imido species [CpCr(NH)(NSiMe$_3$)]$_2$.[33] Reduction of **2** with cobaltocene gave dinuclear [Cr(μ-N*t*Bu)(N*t*Bu)Cl]$_2$ (**25**).[17] Similarly, **9** reacted with LiCp or NaCp to give [Cr(μ-NC$_6$H$_2$*i*Pr$_2$-2,6)(NC$_6$H$_2$*i*Pr$_2$-2,6)Cl]$_2$ (**26**).[26] Both **25** and **26** are diamagnetic, due to spin coupling through the imido bridges or Cr···Cr interaction [the Cr−Cr separation in **26** is 247.5(2) pm[26]].

Treatment of [CrO$_2$Cl$_2$] with (Me$_3$Si)$_2$NH afforded [CrO$_2${N(SiMe$_3$)$_2$}$_2$] (**27**), which reacted with pyridine to give the imido-bridged Cr^{V} dimer [Cr$_2$(μ-NSiMe$_3$)$_2$(NSiMe$_3$)$_2$(O)$_2$(py)] (**28**, Scheme 8).[34]

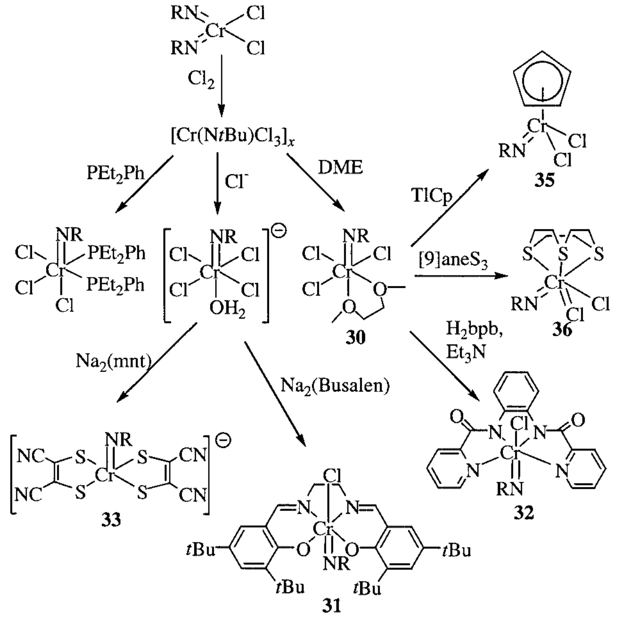


Scheme 8. Synthesis of a dinuclear (imido)(oxo)Cr^{V} complex

Treatment of **27** with *t*BuOH resulted in desilylation of the amido ligands and the formation of the (nitrido)Cr^{VI}

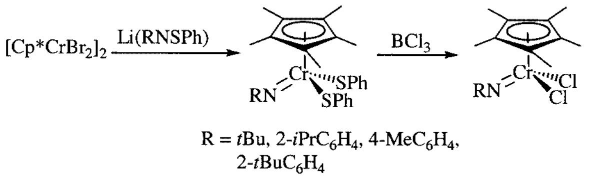
compound [Cr(N)(O*t*Bu)$_3$] (**29**). Complex **29** could also be prepared directly by addition of excess *t*BuOH to a reaction mixture of [NH$_4$]$_2$[Cr$_2$O$_7$], Me$_3$SiCl, HN(SiMe$_3$)$_2$, and Et$_3$N.[35]

Chlorination of **2** afforded mono(imido)Cr^{V} species [Cr(N*t*Bu)Cl$_3$]$_x$, which reacted with Lewis bases to give six-coordinate [Cr(N*t*Bu)Cl$_3$L$_2$] [L = PEt$_2$Ph, THF, py, 0.5DME (DME = 1,2-dimethoxyethane), 0.5bpy (bpy = 2,2′-bipyridine)].[36] Treatment of [Cr(N*t*Bu)Cl$_3$]$_x$ with CtCl in CH$_2$Cl$_2$ gave [Ct][Cr(N*t*Bu)Cl$_4$(H$_2$O)] {[Ct]$^+$ = [*n*Bu$_4$N]$^+$, [PPh$_4$]$^+$, or [N(PPh$_3$)$_2$]$^+$}.[36,37] Treatment of [Cr(N*t*Bu)Cl$_3$(DME)] (**30**) with H$_2$(bpb) [bis(2-pyridinecarboxamido)benzene] or with H$_2$(Busalen) [bis(2,4-di-*tert*-butylsalicylidene)diaminoethane] in the presence of a base afforded [Cr(N*t*Bu)(Busalen)Cl] (**31**)[37] and [Cr(N*t*Bu)(Cl)(bpb)] (**32**),[38] respectively. Treatment of [PPh$_4$][Cr(N*t*Bu)Cl$_4$(H$_2$O)] with Na$_2$(mnt) [mnt^{2-} = 1,2-maleonitriledithiolate(2−)] gave [PPh$_4$][Cr(N*t*Bu)(mnt)$_2$] (**33**)[36b] (Scheme 9), while treatment of **30** with NaO*t*Bu resulted in the isolation of [Cr(O*t*Bu)$_4$] together with [Cr(N*t*Bu)$_2$(O*t*Bu)$_2$], presumably through disproportionation of the trialkoxide intermediate [Cr(N*t*Bu)(OR)$_3$].[36b]



Scheme 9. Synthesis of mono(imido)Cr^{V} complexes

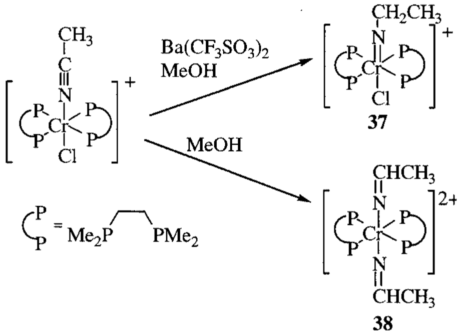
Treatment of **30** with NaL$_{\mathrm{OEt}}$ (L$_{\mathrm{OEt}}^-$ = [CpCo{P(O)(OEt)$_2$}$_3$]$^-$), TlCp (Cp = η^5-C$_5$H$_5$), or [9]aneS$_3$ gave [L$_{\mathrm{OEt}}$Cr(N*t*Bu)Cl$_2$] (**34**), [CpCr(N*t*Bu)Cl$_2$] (**35**),[37] or [([9]ane[S$_3$])Cr(N*t*Bu)Cl$_2$]$^+$ (**36**),[39] respectively. Attempts to prepare (imido)(pentamethylcyclopentadienyl)Cr^{V} complexes from **30** and LiCp* or TlCp* (Cp* = η^5-C$_5$Me$_5$) were unsuccessful. Half-sandwich Cp*Cr^{V} imido complexes [Cp*Cr(NR)(SPh)$_2$] (R = *t*Bu, 2-*i*PrC$_6$H$_4$, 4-MeC$_6$H$_4$, 2-*t*BuC$_6$H$_4$) were prepared from [Cp*CrBr$_2$]$_2$ and Li(RNSPh).[40] Chlorination of [Cp*Cr(NR)(SPh)$_2$] with BCl$_3$ afforded [Cp*Cr(NR)Cl$_2$] (Scheme 10).[27]



Scheme 10. Synthesis of (imido)Cp*Cr^{V} complexes

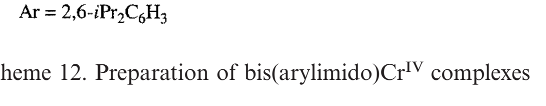
2.3. (Imido)Cr^{IV} and -Cr^{III} Complexes

Addition of a solution of Ba(CF$_3$SO$_3$)$_2$ in MeOH to [Cr(DMPE)$_2$(MeCN)Cl][BPh$_4$] [DMPE = 1,2-bis(dimethylphosphanyl)ethane] in MeCN afforded the (ethylimido)Cr^{IV} complex *trans*-[Cr(NEt)Cl(DMPE)$_2$]$^+$ (**37**). In contrast, addition of MeOH to [Cr(DMPE)$_2$(MeCN)Cl][BPh$_4$] in MeCN yielded the bis(ethylideneamido) complex *trans*-[Cr(N=CHMe)$_2$(DMPE)$_2$][BPh$_4$]$_2$ (**38**). It was proposed that the formation of complexes **37** and **38** involved hydride transfer from MeOH or methoxide to the carbon atom of the MeCN ligand (Scheme 11). Reduction of **30** with Na/Hg in the presence of DMPE gave [Cr(N*t*Bu)(DMPE)$_2$Cl]$^+$ (**39**).[36a] Complexes **37**−**39** are diamagnetic and show well-resolved ^{1}H NMR spectra in solution (Scheme 11).[41]



Scheme 11. Reaction between *trans*-[Cr(DMPE)$_2$(MeCN)Cl]$^+$ and MeOH

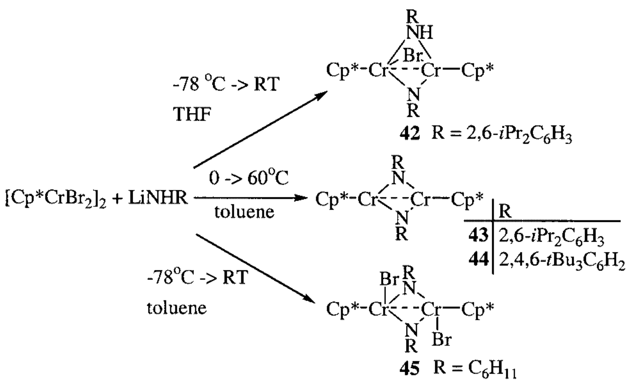
Heating of the dialkyl compounds [Cr(NC$_6$H$_2$Me$_3$-2,4,6)$_2$R$_2$] (R = CH$_2$Ph, CH$_2$CMe$_3$, CHCMe$_2$Ph) with PMe$_3$ in aromatic solvents afforded dinuclear (imido)Cr^{IV} complex [Cr(μ-NC$_6$H$_2$Me$_3$-2,4,6)(NC$_6$H$_2$Me$_3$-2,4,6)]$_2$.[25] Treatment of **10** with MgEtBr in the presence of PMe$_3$ resulted in the formation of [Cr$_2$(μ-NC$_6$H$_2$Me$_3$-2,4,6)$_2$(NC$_6$H$_2$Me$_3$-2,4,6)$_2$Br$_2$(PMe$_3$)],[25] while reduction of **9** with Mg in the presence of PMe$_3$ afforded [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(PMe$_3$)$_2$] (**40**), which reacted with PhCHN$_2$ to give the diazoalkane compound [Cr(NC$_6$H$_3$*i*Pr$_2$-2,6)$_2$(PMe$_3$)(N$_2$CHPh)] (**41**, Scheme 12).[26]



Scheme 12. Preparation of bis(arylimido)Cr^{IV} complexes

The (imido)Cr^{IV} porphyrins [$Cr(NC_6H_4X$-4)(TPP)] have been prepared from [Cr(TPP)] (TPP = tetraphenylporphyrin dianion) and aryl azides 4-$XC_6H_4N_3$ (X = Me, Cl, I, MeO). Unlike the diamagnetic [Cr(O)(TPP)] and *trans*-[$Cr(NEt)Cl(DMPE)_2]^+$, [$Cr(NC_6H_4X$-4)(TPP)] are high spin, with measured μ_{eff} values of ca. 2.83 μ_B at 293 K. Treatment of [Cr(TPP)(NC_6H_4Me-4)] with [$V(O)(acac)_2$] (Hacac = 2,4-pentanedione) and [Fe(salen)(MeIm)] [salen = bis(salicylideneiminato)-1,2-diaminoethane, MeIm = 1-methylimidazole] afforded extremely moisture-sensitive imido-bridged dimetallic Cr−V and Cr−Fe species.[42]

The natures of the products of reactions between [$Cp^*CrBr_2]_2$ and LiNHR were found to be dependent both upon the reactant used and upon the reaction conditions. Thus, treatment of [$Cp^*CrBr_2]_2$ with 2,6-*i*$Pr_2C_6H_3NHLi$ in THF at −78 °C and subsequent rapid workup afforded dinuclear Cr^{III} complex [$(Cp^*Cr)_2(\mu$-Br)(μ-$NHC_6H_3iPr_2$-2,6)(μ-$NC_6H_3iPr_2$-2,6)] (**42**), which has a magnetic moment of 1.12 μ_B per Cr atom. The short Cr−Cr separation in **42** [264.7(5) and 265.1(5) pm)] is indicative of Cr···Cr interaction. On the other hand, addition of [$Cp^*CrBr_2]_2$ to ArNHLi in toluene at 0 °C, followed by heating at 60 °C, gave the dinuclear (imido)Cr^{III} complexes [$Cp^*Cr(\mu$-NAr)$]_2$ (Ar = 2,6-*i*$Pr_2C_6H_3$, **43**; 2,4,6-*t*$Bu_3C_6H_2$, **44**). The Cr−Cr separations in **43** and **44** − of 259.1(1) and 256.4(1) pm, respectively − are indicative of Cr···Cr interaction. In contrast, treatment of [$Cp^*CrBr_2]_2$ with $C_6H_{11}NHLi$ (C_6H_{11} = cyclohexyl) in toluene at −78 °C gave the paramagnetic dinuclear (imido)Cr^{IV} complex [$Cp^*CrBr(\mu$-$NC_6H_{11})]_2$ (**45**), presumably through 2 III → IV + II disproportionation (Scheme 13).[43]



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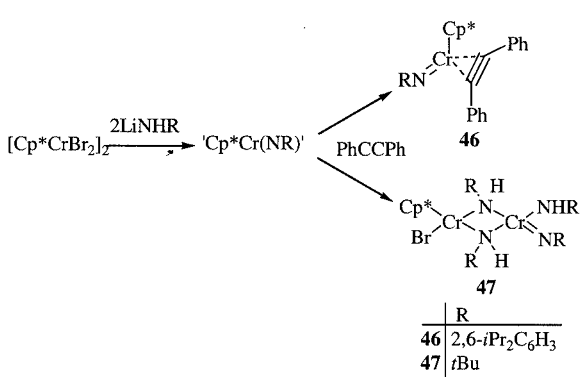
Scheme 13. Reactions of [$Cp^*CrBr_2]_2$ with RNHLi

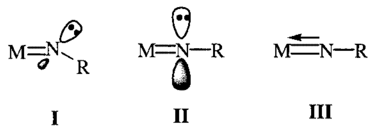
It seems likely that complexes **42**−**45** were formed by dimerization of the "Cp*Cr(NR)" intermediates that could be trapped by donor ligands. Thus, treatment of "$Cp^*Cr(NC_6H_3iPr_2$-2,6)", prepared in situ from [$Cp^*CrBr_2]_2$ and 2,6-*i*$Pr_2C_6H_3NHLi$, with PhC≡CPh gave [$Cp^*Cr(NC_6H_3iPr_2$-2,6)(η^2-PhC≡CPh)] (**46**). The C−C distance of the acetylene ligand in **46** is fairly long [129.5(5) pm], indicative of C=C double bond character, and so the Cr oxidation state for **46** could be assigned as either III or V. Complex **46** has a measured μ_{eff} of 2.20 μ_B at room temperature and showed an isotropic EPR signal at *g* = 2.007 with α_N = 3.7 G. In contrast, treatment of "Cp*Cr(N*t*Bu)" (prepared in situ) with PhC≡CPh gave [$Cp^*CrBr(\mu$-$NHtBu)_2Cr(NHtBu)(NtBu)$] (**47**, Scheme 14).[43]



Scheme 14. Trapping of [Cp*Cr(NR)] intermediates by diphenylacetylene

3. Linear versus Bent Binding Modes of Imido Ligands

Imido groups bind to transition metal atoms either in linear or in bent fashion (Scheme 15). In general, linear imido ligands have M−N−C angles greater than 160°, whereas the bond angles for bent ones are less than 150°, although the dividing line between these two binding modes is not clear-cut. In valence bond description terms, the bent imido group − with sp^2-hybridized nitrogen atom − is regarded as a 4e donor (structure **I**). On the other hand, the linear imido group − with sp-hybridized nitrogen atom − can be either a 4e or a 6e donor, depending upon whether there are one or two M−N π bonds (structures **II** and **III**, respectively).[15]



Scheme 15. Valence bond description of linear and bent imido ligands[15]

The bent and linear binding modes for imido ligands have recently been investigated both theoretically[44−49] and experimentally.[50−55] Nitrogen NMR studies indicate that complexes possessing both linear and bent imido groups are fluxional in solution and that the energy barrier to bending of the M−N−C unit is relatively small,[51] consistently with the results of theoretical studies.[32,44,49] It appears that both electronic and steric factors affect the geometry of the imido ligands. Thus, while the observation of one bent imido ligand in [$Mo(NPh)_2(Et_2NCS_2)_2$] [Mo−N−C angle of

139.4(4)°; cf. 169.4(4)° for the linear one] has been interpreted in terms of the 18e rule,[53] the more bulky 2,6-diisopropylphenylimido analogue [$Mo(NC_6H_3iPr_2\text{-}2,6)_2(Et_2NCS_2)_2$] possesses essentially linear imido groups [Mo−N−C angle of 169.9(2)°], presumably due to steric effects.[54]

The vast majority of (imido)Cr complexes so far isolated contain essentially linear imido ligands (type **III**). One of the imido ligands in **6** was found to be bent [Cr−N−C(imido) angle = 151.8(4)°], but this bending was attributed to crystal packing rather than electronic effects. It may be noted that both imido groups in the Mo analogue [$Mo(TACN)(NtBu)_2Cl$][ClO_4] are essentially linear [Mo−N−C(imido) angles are 171.1(3) and 161.5(3)°].[22] An example of a strongly bent (imido)Cr complex is **23**, the Cr−N−C(imido) angle of which is 146.2(3)°. The bent Cr−N−C(imido) angle in **23** was explained in terms of π-conflict between the oxo and the imido groups. In order to investigate the origin of the bending of the Cr−N−C(imido) unit in **23**, DFT calculations were performed on a simplified model compound [$Cr(NMe)(O)(NMe_2)Me$], which lacks the steric bulk present in **23**. It was found that the DFT-optimized geometry of [$Cr(NMe)(O)(NMe_2)Me$] satisfactorily reproduced the pertinent structural features in **23**. The calculated Cr−N−C(imido) angle of 149.0° is similar to that found in **23**, suggesting that electronic factors play a significant role in the distortion in **23**.[32]

4. Electrochemistry of (Imido)Cr Complexes

The reduction couples observed in the range of −1.2 to −2.0 V vs. $Cp_2Fe^{+/0}$ for bis(imido)Cr^{VI} complexes have been attributed to metal-centered $Cr^{VI/V}$ reduction. For example, the diaryl compound **14** underwent 1e reduction in THF at $E_{1/2} = -1.31$ V vs. Ag/AgCl (ca. −1.65 V vs. $Cp_2Fe^{+/0}$).[28] The $Cr^{VI/V}$ couple for the diaryl oxide compound **8** was found at −1.2 V vs. $Cp_2Fe^{+/0}$,[20] which is less negative than that for **14**, indicating that the σ-aryl moiety is a stronger donor than the aryl oxide. As would be expected, the $Cr^{VI/V}$ couple for dicationic **5** has a less negative $Cr^{VI/V}$ potential (−0.74 vs. $Cp_2Fe^{+/0}$).[20] Attempts to isolate bis(imido)Cr^{V} complexes by reduction of **5** or **14** with reducing agents were unsuccessful. For **6**, in addition to the Cr-centered reduction wave at −1.29 V vs. $Cp_2Fe^{+/0}$, a quasi-reversible oxidation couple was observed at 0.86 V and attributed to imido-centered oxidation. A similar oxidation potential (0.99 V) was found for the Mo analogue [$Mo(TACN)(NtBu)_2Cl$]$^+$.[21] Cyclic voltammograms of (imido)Cr^{V} complexes showed irreversible reduction waves that were assigned to $Cr^{V/IV}$ reduction. For example, the $Cr^{V/IV}$ reduction for **31** was found at −0.71 V, which is more negative than that for the oxo analogue [$Cr(O)(L)$]$^+$ [L = 2,3-dimethyl-*N,N'*-bis(salicylidene)butane-2,3-diamine] (0.63 V vs. standard calomel electrode), reflecting the higher donor strength of imide relative to oxo.[37]

5. Reactivity of (Imido)Cr Complexes

5.1. Hydrolysis

(Imido)Cr complexes are generally moisture-sensitive and readily hydrolyze to (oxo)Cr complexes. However, cationic bis(imido)Cr^{VI} complexes **5** and **6** are air-stable and inert to hydrolysis. Treatment of **1** with 1 equiv. of water in diethyl ether afforded the (imido)(oxo) complex [$Cr(O)(NtBu)(OSiMe_3)_2$], which reacted with PCl_5 to give [$Cr(O)(NtBu)Cl_2$].[19] Treatment of **2** with [$O(Ph_2SiOH)_2$] in the presence of pyridine gave a dinuclear chromosiloxane complex [$\{Cr(O)(NtBu)(OPh_2SiO)_2\}_2$] (**48**, Figure 2), the oxo group of which was presumably derived from the silanol.[56]

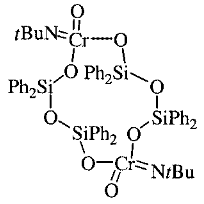


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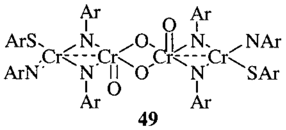
Figure 2. Structure of [$\{Cr(O)(NtBu)(OPh_2SiO)_2\}_2$]

Treatment of [$Cr(NAr)_2(SAr)_2$] (Ar = 2,4,6-$Me_3C_6H_2$) with PMe_2Ph, followed by workup in the presence of adventitious oxygen, afforded an interesting tetranuclear (imido)(oxo)Cr cluster [$Cr_4(\mu\text{-}O)_2(\mu\text{-}NAr)_4(O)_2(NAr)_2(SAr)_2$] (**49**, Figure 3) in low yield.[57]



49

Ar = 2,4,6-$Me_3C_6H_2$

Figure 3. Structure of [$Cr_4(\mu\text{-}O)_2(\mu\text{-}NAr)_4(O)_2(NAr)_2(SAr)_2$] (Ar = 2,4,6-$Me_3C_6H_2$)

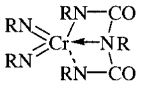
5.2. Cycloaddition

The [2 + 2] cycloaddition reactions between imido complexes and doubly bonded X=Y systems, presumably through four-membered metallacyclic intermediates (Scheme 16), are well documented.

Scheme 16. [2 + 2] cycloadditions between M=NR and X=Y

Treatment of **1** with PhCHO afforded the (imido)(oxo)-Cr^{VI} complex [$Cr(NtBu)(O)(OSiMe_3)_2$] and PhCH=NtBu.[58] While **2** underwent cycloaddition and imido group exchange with aryl isocyanates ArNCO to give [$Cr(NAr)_2Cl_2$], no reactions were found between [$Cr(NAr)_2Cl_2$] and tBuNCO.[25] Treatment of

$[Cr(NtBu)_2\{N(SiMe_3)_2\}_2]$ with *t*BuNCO resulted in isocyanate insertion into the Cr−amide bond to give the *N*,*N*′,*N*′′-tri-*tert*-butylbiureto complex $[Cr(NtBu)_2\{(tBuNCO)_2NtBu\}]$ (**50**, Figure 4) rather than cycloaddition of Cr=N*t*Bu with isocyanate.[59]



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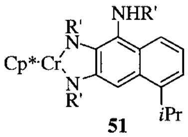
R = *t*Bu

Figure 4. Structure of $[Cr(NtBu)_2\{(tBuNCO)_2NtBu\}]$

Treatment of “$Cp^*Cr(NC_6H_3iPr_2$-2,6)” (prepared in situ) with 2,6-$Me_2C_6H_4NC$ resulted in coupling of the isocyanide with Cr=$NC_6H_3iPr_2$-2,6 and the formation of a Cp^*Cr^{III} complex containing an *N*,*N*-bis(2,6-diisopropylphenyl)-4-isopropyl-1-(2,6-xylylamino)naphthaline-2,3-diamido ligand (**51**, Figure 5).[40]



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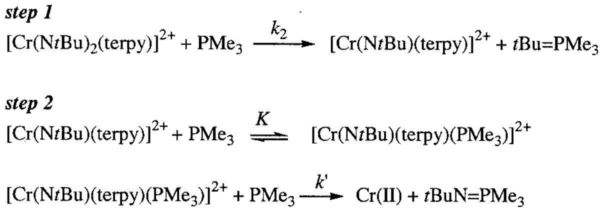
R = 2,6-$iPr_2C_6H_3$, R' = 2,6-$Me_2C_6H_3$

Figure 5. Structure of the product obtained on treatment of “Cp* $Cr(NC_6H_3iPr_2$-2,6)” with 2,6-$Me_2C_6H_3NC$

Recent theoretical studies on olefin polymerization with bis(imido)Cr^{VI} catalysts revealed that the [2 + 2] cycloadditions between C=C and Cr=NR double bonds proceed with very low energy barriers. It was suggested that the resulting azachromacycles could be a starting point for further modification of the (alkyl)Cr^{VI} cations in the catalytic cycle.[12]

5.3. Imido Group Transfer

Organoimido complexes are less reactive than acylimido (M=NCOR) and tosylimido ($M=NSO_2R$) complexes toward imido group transfer. (Imido)Cr complexes undergo imido transfer with strong reducing agents such as tertiary phosphanes[20,36b,37,42] and isocyanides.[57,60] Imido transfer from (imido)Cr^{IV}−porphyrin compounds to benzaldehyde, CS_2, and styrene has also been reported,[42] and imido group transfer to phosphanes from (imido)Cr^V complexes was found to be catalyzed by light.[36,37] It was noted that the reactivity of (imido)Cr complexes toward imido transfer could be correlated with the electron deficiency at the Cr center.[20] Thus, while no reaction was found between the diaryl oxide compound **8** ($E_{1/2} = -1.2$ V vs. $Cp_2Fe^{+/0}$) and PMe_3, dicationic **5** ($E_{1/2} = -0.74$ V vs. $Cp_2Fe^{+/0}$) readily underwent imido transfer with tertiary phosphanes to give phosphanimines. Under pseudo-first-order conditions, the reaction between **5** and PMe_3 was found to follow biphasic kinetics, with $k_{obs1} \propto [PMe_3]$ and $k_{obs2} \propto [PMe_3]^2$. The kinetic data are consistent with a two-step mechanism as shown in Scheme 17.[20]



Scheme 17. Proposed mechanism for imido transfer from $[Cr(NtBu)(terpy)]^{2+}$ to PMe_3

For step 1, rate = $k_2[Cr][PMe_3]$. For step 2, at $K[PMe_3] >> 1$, rate = $Kk'[Cr][PMe_3]^2$ with $k_3 = kK'$. At 25 °C in acetonitrile solution, $k_2 = 0.48 \pm 0.10$ $\text{M}^{-1}\cdot s^{-1}$ and $k_3 = Kk' = 1.44 \pm 0.16$ $\text{M}^{-2}\cdot s^{-1}$.[20]

Treatment of $[Cr(NC_6H_2Me_3\text{-}2,4,6)_2(SC_6H_2Me_3\text{-}2,4,6)_2]$ with 2,6-$Me_2C_6H_3NC$ at reflux resulted in the formation of the mono(imido)Cr^{IV} complex $[Cr(NC_6H_2Me_3\text{-}2,4,6)(SC_6H_2Me_3\text{-}2,4,6)_2(CNC_6H_4Me_2\text{-}2,6)_2]$ and the carbodiimide 2,4,6-$Me_3C_6H_2N=C=NC_6H_3Me_2$-2,6. It seems likely that the imido transfer to the isocyanide occurred through a (η^2-carboimide)Cr intermediate.[57] Treatment of $[Cr(NC_6H_2Me_3\text{-}2,4,6)_2(SC_6F_5)_2]$ with 2,6-$Me_2C_6H_3NC$ resulted in the isolation of *mer*-$[Cr(SC_6F_5)_3(NCC_6H_2Me_2\text{-}2,6)_3]$ and *trans*-$[Cr(SC_6F_5)_2(NCC_6H_2Me_2\text{-}2,6)_4]$, together with other unidentified products.[60] No imido transfer was found between 2,6-$Me_2C_6H_3NC$ and either $[Cr(NC_6H_2iPr_3\text{-}2,4,6)(SC_6H_2Me_3\text{-}2,4,6)_2]$ or $[Mo(NAr)_2(SC_6H_3iPr_2\text{-}2,6)_2]$ (R = 2,4,6-$Me_3C_6H_2$ or 2,6-$iPr_2C_6H_3$), probably because of steric effects.[57][60]

5.4. Addition of Alkyl Group to Imido Ligand

Nugent and Harlow studied the addition of alkyl groups to coordinated imido groups in attempts to model the C−N formation step in ammoxidation of propylene. Thus, treatment of **1** with Ph_2Zn, followed by hydrolysis, afforded organic products including *tert*-butylaniline and biphenyl. It was believed that the former product was formed by the Cr-to-N migration of the phenyl ligand in a mono(phenyl)Cr^{VI} intermediate, whereas the latter product originated from reductive elimination of a diphenylCr^{VI} species.[61] Similarly, the reaction between **1** and benzyl radical, generated from toluene and dibenzyl peroxide, resulted in addition of benzyl radical to the imido nitrogen atom. Upon hydrolysis, *t*BuN=CHPh was produced, along with CO_2, bibenzyl, and methylbiphenyls.[1b] The (amido)Cr^{IV} species $[Cr\{N(C_6H_4Me_3\text{-}2,4,6)(4\text{-}tBuC_6H_4)Cl]_2(\mu\text{-}NC_6H_4Me_3\text{-}2,4,6)Cl]_2$, obtained from the alkylation of **9** with 4-$tBuC_6H_4CH_2MgCl$, has been isolated and characterized structurally.[25] No alkyl group migration was found for the alkylation of **1** with 2,4,6-$Me_3C_6H_2MgBr$, apparently because of the steric bulk of the mesityl group.[28] However, thermal decomposition of $[Cr(NtBu)_2\{C(O)C_6H_2Me_3\text{-}2,4,6\}_2]$, prepared by carbonylation of **14**, yielded 2,4,6-$Me_3C_6H_2C(O)NHtBu$, presumably through migration of the acyl group to the imido nitrogen atom.[28]

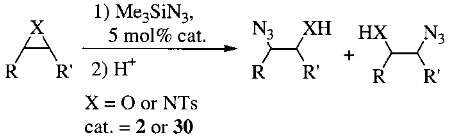
6. Reactions Catalyzed by (Imido)Cr Complexes

6.1. Olefin Polymerization

Chromium catalysts play important roles in the manufacture of polyolefins in industry. To this end, much effort has been devoted to the development of new, well-defined molecular chromium catalysts for olefin polymerization.[62] The catalytic activity of bis(imido)Cr^{VI} complexes and half-sandwich Group-5 CpM(NR) systems, which are isolobal with Group-4 metallocenes, toward olefin polymerization has been investigated.[11] Gibson and co-workers reported that **2** in conjunction with an activator such as MAO (methylaluminoxanes) and Et_2AlCl was capable of polymerization of ethylene to give poly(ethylene)s of high molecular weights with little branching. $[Mo(N\mathit{t}Bu)_2Cl_2]$ was found to be a less active polymerization catalyst than the Cr congener.[11a] The dibenzyl compound $[Cr(N\mathit{t}Bu)_2(CH_2Ph)_2]$ was able to polymerize ethylene in the presence of boron activators $[PhNMe_2H][B(C_6F_5)_4]$, $[CPh_3][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ to give poly(ethylene)s of high molecular weights.[11c,29] Both $[Cr(NC_6H_4Me_2\text{-}2,6)_2Me_2]$ and $[Mo(NC_6H_4Me_2\text{-}2,6)_2Me_2]$ are active catalysts for polymerization of ethylene in the presence of $B(C_6F_5)_3$.[11c] Treatment of $[Cr(N\mathit{t}Bu)_2(CH_2Ph)_2]$ with $[CPh_3][B(C_6F_5)_4]$ afforded an oily cationic species $[Cr(N\mathit{t}Bu)_2(\eta^2\text{-}CH_2Ph)]^+$, which reacted with PMe_3 to give the monophosphane adduct. On the other hand, $[Cr(N\mathit{t}Bu)_2(CH_2Ph)_2]$ reacted with $[PhNMe_2H][B(C_6F_5)_4]$ to yield a mixture of mono- and bis(dimethylaniline) adducts $[Cr(N\mathit{t}Bu)_2(\eta^2\text{-}CH_2Ph)(NMe_2Ph)_n]^+$ (n = 1 or 2). Solutions containing $[Cr(N\mathit{t}Bu)_2(\eta^2\text{-}CH_2Ph)]^+$ or $[Cr(N\mathit{t}Bu)_2(\eta^2\text{-}CH_2Ph)(NMe_2Ph)_n]^+$ are capable of catalyzing ethylene polymerization in the absence of a co-catalyst.[11c] A recent theoretical study on $[Cr(NR)_2(C_3H_7)(C_2H_4)]^+$ (R = H, *t*Bu) revealed a facile reductive elimination involving β-hydrogen transfer from the alkyl chain, suggesting that the active species for the bis(imido)Cr^{VI}-based catalysts contain Cr in a lower oxidation state.[12b] Recently, Siemeling and co-workers reported that an *ansa*-bis(imido)Cr^{VI} complex $[(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)(\eta^2\text{-}CH_2Ph)]$ (**52**), prepared from $[Cr(NCMe_2CH_2CH_2CMe_2N)Cl_2]$ and $PhCH_2MgCl$, and complex **17**, were capable of catalyzing polymerization of acrylonitrile in the absence of a co-catalyst to give poly(acrylonitrile)s with high molecular weights. Complexes **17** and **52** also catalyzed the copolymerization of acrylonitrile and methyl methacrylate.[63]

6.2. Ring-Opening of Epoxides and Aziridines

Coordinatively unsaturated imido complexes are good Lewis acid catalysts because of the presence of low-lying vacant metal d-orbitals, their high solubility in organic solvents, and their low tendency to dimerize or oligomerize in organic solvents. In view of this, the use of (imido)metal complexes as Lewis acid catalysts for ring-opening of epoxides and aziridines has been investigated. (Imido)Cr complexes **2** and **30** were capable of catalyzing ring-opening of epoxides[64] and tosylaziridines[65] with Me_3SiN_3 in good yield and with good regioselectivity (Scheme 18).



Scheme 18. Ring-opening of epoxides and aziridines catalyzed by (imido)Cr complexes

Treatment of styrene oxide (R = Ph, R′ =H) with Me_3SiN_3 and a catalytic amount of **2** exclusively gave 2-azido-1-phenylethanol, consistent with the Lewis acid mechanism for epoxide ring-opening. The catalytic activity of (imido)metal complexes was found to decrease in the order **30** > **2** > $[Mo(N\mathit{t}Bu)_2Cl_2]$.[64] It is believed that (azido)(imido)Cr complexes are the active intermediates for the Cr-mediated azidolysis of epoxides. Indeed, treatment of **2** with Me_3SiN_3 afforded dinuclear $[Cr(\mu\text{-}N_3)(N\mathit{t}Bu)_2Cl]_2$, an active catalyst for epoxide ring-opening.[65] In an attempt to prepare a chiral (imido)Cr complex for asymmetric catalysis, **30** was treated with (*S*,*S*)-DIOP {(*S*,*S*)-4,5-[bis(diphenylphosphanyl)methyl]-2,2-dimethyl-1,3-dioxolane}. Unfortunately, dinuclear $[Cr(N\mathit{t}Bu)Cl_3]_2$\{μ-(*S*,*S*)-DIOP\} was isolated rather than mononuclear (*S*,*S*)-DIOP complex.[66] Recently, Sundermeyer and co-workers prepared a chiral Mo^{VI} complex with a C_2-symmetric bidentate diimido ligand $[TADDAMINat]^{4-}$ [TADDAMIN = (4*S*,5*S*)-2,2-dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-diylbis(methanamine)]. $[Mo(TADDAMINat)Cl_2(DME)]$ (**53**, Figure 6) has been used as a catalyst for the kinetic resolution of styrene oxide with Me_3SiN_3 and the asymmetric trimethylsilylcyanation of benzaldehyde. The enantioselectivities for the two reactions were 30 and 20% *ee*, respectively.[67]

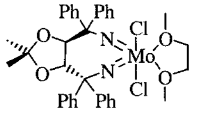


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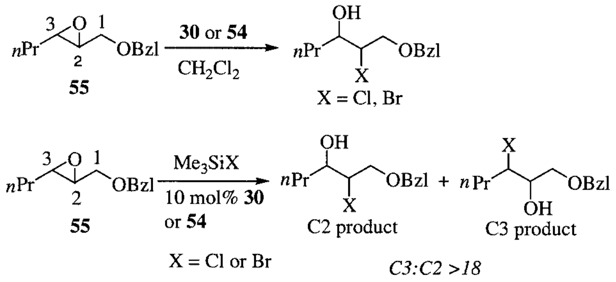
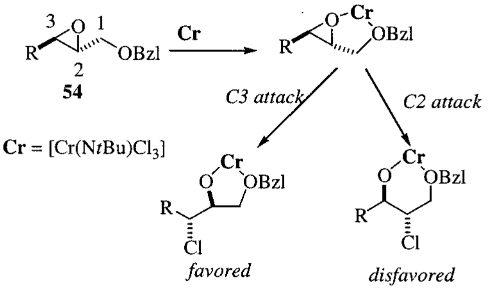
Figure 6. Structure of $[Mo(TADDAMINat)Cl_2(DME)]$

Because of the high affinities of (imido)Cr^V complexes for O-donor ligands, **30** and $[Cr(N\mathit{t}Bu)Br_3(DME)]$ (**54**) were used to study the regioselectivity of ring-opening of disubstituted epoxides containing benzyloxy groups. Thus, treatment of **30** or **54** with disubstituted epoxide **55** afforded the corresponding 3-halohydrins in good yield and with good selectivity (C-3/C-2 > 49:1). The imido complexes **30** and **54** were also capable of catalyzing regioselective ring-opening of disubstituted epoxides with trimethylsilyl halide. Thus, treatment of epoxide **55** with trimethylsilyl halide in the presence of a catalytic amount of **30** or **54** afforded the halohydrins with good C-3 selectivity (C-3/C-2 > 18, Scheme 19).[68]



Scheme 19. Cr-mediated regioselective ring-opening of benzyloxy epoxides

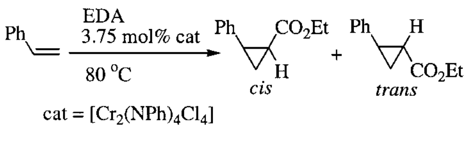
The observed C-3 selectivity for the ring-opening of **55** has been explained in terms of Cr chelation (Scheme 20). Nucleophilic attack at C-3 is preferred because of the higher stability of the five-membered metallacycle intermediate relative to the six-membered analogue.[68]



Scheme 20. Proposed mechanism for Cr-catalyzed regioselective ring-opening of disubstituted epoxides

6.3. Cyclopropanation of Olefins

Bis(imido)Cr^{VI} complexes $[Cr(\mu\text{-}NPh)(NPh)Cl_2]_2$ and $[Cr(NAr)_2Cl_2]$ (Ar = 2,6-$Cl_2C_6H_3$ or 2,6-$Br_2C_6H_3$) were found to catalyze cyclopropanation of substituted styrene on treatment with ethyl diazoacetate (EDA, Scheme 21). For example, treatment of styrene with EDA in the presence of ca. 4 mol % of $[Cr(\mu\text{-}NPh)(NPh)Cl_2]_2$ afforded the cyclopropane product in 90% yield with a *cis*/*trans* ratio of 0.65. Treatment of ethyl acrylate with EDA in the presence of the (imido)Cr catalyst afforded both cyclopropane and vinyl C−H insertion products.



Scheme 21. Cyclopropanation of styrene catalyzed by (imido)Cr complexes

The active intermediate for the Cr-catalyzed cyclopropanation was believed to be a Cr imido carbene species, possibly $[Cr(NPh)_2Cl_2(CHCO_2Et)]$. A competition experiment for the Cr-mediated carbene transfer showed that ethyl acrylate was consumed in preference to styrene, indicative of the nucleophilic character of the (carbene)Cr intermediate.[69]

7. Concluding Remarks

The successes obtained in isolation of stable (imido)Cr^{VI} and -Cr^{V} complexes and their organometallic derivatives demonstrate the significance of organoimido groups as stabilizing spectator ligands for organometallic compounds with highly oxidizing metal centers. In addition, owing to the steric bulk of organoimido ligands, coordinatively unsaturated $M(NR)_2$ and M(NR) complexes that are reactive toward unsaturated organic substrates can readily be synthesized. For example, d^0 Group-6 M(NR) and $M(NR)_2$ complexes have been found to be well-defined catalysts for olefin metathesis and polymerization, and have been used as Lewis acid catalysts for organic transformations. Recently, the imido chemistry has been extended to the right-hand side of the first transition series.[70−74] Notably, a new family of stable imido complexes of Mn in oxidation states VII−V has been synthesized by Danopoulos et al.[52,70] It may therefore be anticipated that compounds of Fe in less common oxidation states, such as Fe^{IV} and Fe^{V}, should be accessible if stabilized by organoimido ligands[72] and would exhibit novel organometallic chemistry.

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