Novel Chromium(III) Complexes Containing Imidazole-Based Chelate Ligands with Varying Donor Sets: Synthesis and Reactivity

Thomas Rüther,*,† Nathalie Braussaud,† and Kingsley J. Cavell*,‡

*School of Chemistry, University of Tasmania, GPO Box 252-75, Hobart,
Tasmania 7001, Australia, and Department of Chemistry, Cardiff University, P.O. Box 912,
Cardiff, CF1 3TB, U.K.*

*Summary: Reaction of (THF)₃RCrCl₂ (R = Cl, Me) with tri- and bidentate bis(N-methylimidazole-2-yl) ligands gave the new Cr(III) complexes [Cr(N∧N∧Y)Cl₃] (**3a**–**c**), [Cr(N∧N)Cl₃]₂ (**4a**–**c**), and [Cr(Me)(N∧N∧Y)Cl₂] (**5a**,**b**) in ≥ 90% yield. Toluene solutions of **3,4**/MMAO convert ethylene into linear 1-alkenes with selectivities of up to 79%.*

The synthesis of transition metal complexes containing nitrogen-based chelates has received much attention in recent years.[1] Most notably with the discoveries by Brookhart and Gibson of new Ni, Pd[2], Co, and Fe[3] catalyst systems incorporating bidentate α-diimine and tridentate bisiminopyridine environments. These systems were found to be highly active catalysts for olefin polymerization. With these discoveries it became evident that a broad spectrum of rather simple coordination compounds may find application in the conversion of α-olefins into higher molecular weight products. These studies on coordination chemistry and catalysis have since been extended to include catalysts based on new chromium complexes.[4] Despite the industrial importance of chromium-based catalysts for the production of ethylene oligomers[5] (e.g., 1-hexene) and polymers,[6] well-defined homogeneous model systems are scarce and have been prepared only recently.[4,7] Both cyclopenta-

diene-based and noncyclopentadiene Cr complexes containing N∧N and N∧O ligand environments were investigated by Theopold,[4a,7a,b] Gibson,[4b,c] and Jolly et al.[7c] From the desire to contribute to this relatively unexplored field we recently became interested in the synthesis and properties of transition metal complexes bearing chelating ligands derived from the heteroaromatic imidazole unit.[8] In this note we report the synthesis of a number of novel chromium(III) complexes in which the metal resides in chelate environments bearing *N*-methylimidazole-based components linked to varying donor sets. We demonstrate how changes within the ligand system control the reactivity of the complexes in the catalytic oligomerization of ethylene.

The ligands described herein and depicted in Scheme 1 all consist of a bridged bisimidazole framework, which in the case of compounds **1a**–**c** and **2b**,**c** carries additional P, N, or O donor centers. **1a**[9] and **2a**,**c**[10] were prepared according to modified literature procedures. Compound **2a** proved to be a versatile building block for the synthesis of the new mixed donor ligands **1b**,**c** and **2b**. Details of the ligand syntheses will be published elsewhere. Despite their obvious ligating properties, chelating imidazoles have mainly been studied as structural models to mimic binding sites in metalloenzymes.[9,11] No Cr(III) complexes containing chelating imidazole-based ligands have previously been reported.[12]

Chromium(III) complexes with chelating bisimidazole ligands were prepared by adding the respective ligand to a solution of (THF)₃CrCl₃ in CH₂Cl₂. The products precipitate as air/moisture sensitive green or gray-green solids and were isolated in ≥90% yield. The complexes are moderately soluble in CH₃CN and hot methanol. For the complex **4c** coordination of the keto-bridged ligand

† University of Tasmania.
‡ Cardiff University.
(1) (a) Togni, A.; Venanzi, L. M. *Angew. Chem.* **1994,** *106*, 517; *Angew. Chem., Int. Ed. Engl.* **1994,** *33*, 497. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999,** *111*, 448–468; *Angew. Chem., Int. Ed.* **1999,** *38*, 429–447. (c) Gade, L. H. *J. Chem. Soc., Chem. Commun.* **2000,** 173–181.
(2) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995,** *117*, 6414–6415. (b) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997,** *16*, 2005–2007.
(3) (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberly, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998,** 849–850. (b) Small, B. L.; Brookhart, M.; Bennet, A. M. A. *J. Am. Chem. Soc.* **1998,** *120*, 4049–4050. (c) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998,** *120*, 7143–7144.
(4) (a) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998,** *17,* 4541–4543. (b) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998,** 1651–1652. (c) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999,** 827–829. (d) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. J. *Chem. Commun.* **1995,** 1709–1711.
(5) (a) Reagen, W. K.; Pettijohn, T. M., Freeman, J. W.; Benham, E. A. US-A 5,451,645, 1995. (b) Briggs, J. R. *Chem. Commun.* **1989,** 674–675. (c) Wu, F.-J. US-A 5,550,305, 1996.
(6) (a) Hogan, J. P.; Banks, R. L. (Phillips Petroleum Co.) US-A 2,-825, 721, 1958 [*Chem. Abstr.* **1958,** *52*, 8621h]. (b) Hogan, J. P. *J. Polym. Sci.* **1970,** *8*, 2637–2652. (c) Karol, F. J.; Karapinaka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972,** *10*, 2621–2637.

(7) (a) Theopold, K. H. *CHEMTECH* **1997,** October, 26–32. (b) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998,** 15–24. (c) Emmerich, R.; Heinemann, O.; Jolly, P. W.; Krueger, C.; Verhovnik, G. P. J. *Organometallics* **1997,** *16*, 1511–1513.
(8) Done, M. C.; Rüther, T.; Cavell, K. J.; Kilner, M.; Peacock, E. J.; Braussaud, N.; Skelton, B. W.; White, A. *J. Organomet. Chem.* **2000,** *607*, 78–92.
(9) Sorrell, T. N.; Borovik, A. S. *J. Am. Chem. Soc.* **1987,** *109*, 4255–4260.
(10) (a) Elgafi, S.; Field, L. D.; Messerle, B. A.; Hambley, T. W.; Turner, P. *J. Chem. Soc., Dalton Trans.* **1997,** 2341–2345. (b) Burling, S.; Field, L. D.; Messerle, B. A. *Organometallics* **2000,** *19*, 87–90.
(11) For recent examples and further references see: (a) Place, C.; Zimmermann, J.-L.; Mulliez, E.; Guillot, G.; Bois, C.; Chottard, J.-C. *Inorg. Chem.* **1998,** *37*, 4030–4039. (b) Sorrell, T. N.; Allen, W. E.; White, P. S. *Inorg. Chem.* **1995,** 34, 952–960.
(12) (a) Sanchez, M.; Losada, J. *J. Therm. Anal.* **1983,** *28*, 381–394. (b) Gonzales Garmendia, M. J.; Losada, J.; Moran, M. *J. Inorg. Nucl. Chem.* **1981,** *43*, 2269–2271.

Scheme 1. Synthesis of the Complexes 3a−c, 4a−c, and 5a,b
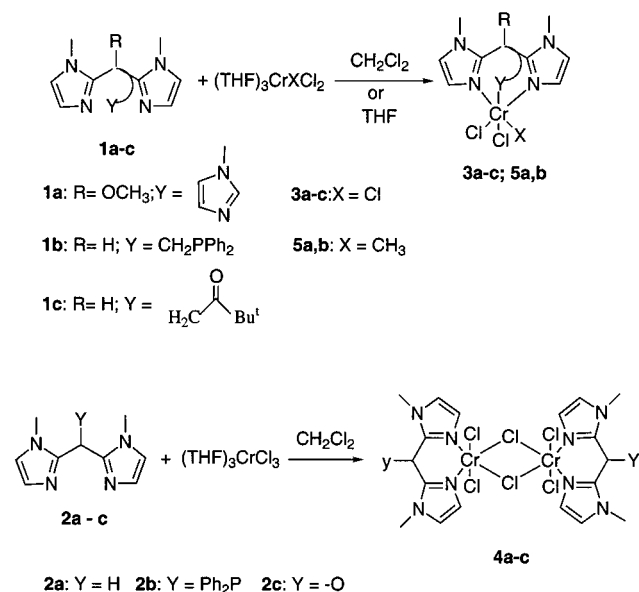
may occur in either an N−N or N−O fashion. Comparison of the IR spectra of the free ligand **2c** ($\nu(C=O) =$ 1632 cm^{-1}) and its complex **4c** ($\nu(C=O) = 1651$ cm^{-1}) suggests N−N coordination since a shift of the C=O absorption to lower wavenumbers is expected for N−O coordination. The electronic spectra of complexes **3** and **4** show two of the three expected absorptions (ν_1, 14420−16650 cm^{-1}; ν_2, 21370−23200 cm^{-1}) for chromium(III) in an octahedral field. The third d−d transition is obscured by CT bands, a common feature observed in many chromium(III) complexes. Good elemental analyses data were difficult to obtain for several of these complexes due to high moisture sensitivity. It was clear during the collection of data that variable partial absorption of water and in some cases hydrolysis occur. By deliberately exposing the complexes to moist air, up to 6 equiv of water could be absorbed in a short time.

The first example of an alkyl Cr(III) complex with this ligand type was prepared by reacting (THF)$_3$CrCl$_2$Me with **1b** in THF. **5b** precipitated from THF solution as a green solid and was characterized by MS and elemental analysis. When the ligand **1a** was employed in the same reaction, a green solid (**5a**) precipitated and, as observed for **5b**, a monomer fragment at *m/e* 408 (M$^+$ − CH$_3$) was recorded in the MS. However, a satisfactory elemental analysis could not be obtained for **5a**, which appears to be less stable at room temperature than **5b**. The air/moisture sensitive alkyl complexes are partially soluble in CH$_2$Cl$_2$, but decompose in methanol. Attempts were made to generate a cationic complex from the methyl complex **5b** via halide abstraction with AgBF$_4$ or Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] in coordinating solvents such as THF and CH$_3$CN. Halogen abstraction occurs at −30 °C, as indicated by a color change from green to brown with formation of a grayish solid and the dissolution of the insoluble starting product. On warming to ambient temperature, the slightly turbid solution becomes turquoise and gas evolution is observed. After workup, elemental analysis of the resulting turquoise solid indicated the possible formation of an oligomeric de-

composition product. Similar observations were reported for [Cp*Cr(THF)$_2$Me]PF$_6$.[7b,13]

The complexes **4a−c**, which contain bidentate ligands, appear to be dimers with bridging and terminal chlorides placing each chromium in an octahedral ligand environment. Accordingly, the mass spectrum shows dinuclear pentachloro molecular ions, albeit of low intensity. Further evidence for a dinuclear structure arises from their effective magnetical moments (3.0 μ_B per Cr, **4a,c**). This value is significantly reduced from that expected (3.87 μ_B) for a mononuclear Cr(III) complex and from the values found for **3a,b** (see below). A possible explanation for the low effective moments is antiferromagnetic coupling. A similar observation was made for bridged CpCr(III) complexes,[14] and a structurally characterized dimeric chloro bridged complex was prepared by Gibson et al. from (THF)$_3$CrCl$_3$ and a metalated β-diimine.[4b] The complexes **3a−c**, which contain tripodal ligand systems, appear to be monomeric according to their magnetical moments (**3a**, 3.53 μ_B; **3b**, 3.76 μ_B) and mass spectra. Mononuclear structures with coordination through all three donor centers have been established for other tripodal ligands linked to the CrCl$_3$ unit.[15] Considering **1a−c** as neutral 6e donors, analogous to Cp$^-$, complexes **3a−c** are unique isoelectronic metal complexes.[16] The variation of the third donor atom in **1a−c** provides a valuable opportunity for studying the reactivity of complexes in which the metal center is placed in slightly differing electronic and steric environments generated from one donor moiety only.

While a number of homogeneous model systems for chromium-based olefin polymerization and oligomerization catalysts, based on CpCr complexes, were reported by Theopold et al. and Jolly et al.,[7] examples of chromium catalysts containing hard donor ligands are scarce.[4,17] Cr complexes with β-diiminato,[4a,b] pyrrole-pyridine,[4b] reduced Schiff-base,[4c] and bis(imido)[4d] ligands have been reported by Gibson and Theopold et al. Due to the hardness of the donor atoms of the imidazole framework, complexes **3** and **4** may serve as model systems for hard donor environments present in the Phillips catalysts (CrO$_3$/SiO$_2$;[6a,b] CrX$_3$/pyrrole, X = halogen, carboxylate[5a]). In this context, exposure of toluene solutions of **3,4**/MMAO to 40 bar of ethylene resulted in the formation of linear 1-alkenes in the range of C$_4$−C$_{30}$ (maximum at C$_8$; GC−MS analysis) with selectivities of up to 79% (Table 1). Some branched 1-alkenes are also formed. The occurrence of homologous alkanes, an unexpected byproduct of this reaction, is dependent on the MMAO concentration (entries 2/3 and 5/6) and is possibly also associated with the decomposition characteristics of chromium alkyls.

(13) Thomas, B. J.; Mitchell, J. F.; Theopold, K. H.; Leary, J. A. *J. Organomet. Chem.* **1988**, *348*, 333.

(14) (a) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738−745. (b) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570−2577.

(15) (a) Koehn, R. D.; Kociok-Koehn, G. *Angew. Chem.* **1994**, *106*, 1958; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1877−1878. (b) Arif, A. M.; Hefner, J. G.; Jones, R. A.; Whittlesey, B. R. *Inorg. Chem.* **1986**, *25*, 1080−1084.

(16) (a) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45−53. (b) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169−3170.

(17) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 2341−2345.

Table 1. Ethylene Oligomerization in Toluene[a]

entry	catalyst/ (mmol)	MMAO (equiv)[b]	activity[c]	1-alkenes	isoalkenes	alkanes[d]	isoalkanes	solid (wt %)
1	**3a**/0.11	400	208	79	9	12		3.4
2	**3b**/0.1	400	108	65	10	21	4	9
3	**3b**/0.12	182	90	77	11	12		3.3
4	**3c**/0.1	400	120	65	13	20	2	15
5	**4a**/0.09	400	56	50	16	25	9	1.7
6	**4a**/0.06	170	55	70	15	15		2.1
7	**4b**/0.04	408	90	60	20	18	2	2.6
8	**4c**/0.06	414	60	57	17	24	2	5.5

[a] 50 mL; $P(CH_2=CH_2)$ 40 bar, $T = 100$ °C. [b] Per [Cr]. [c] In g product mmol^{-1} catalyst h^{-1} per [Cr]. [d] Determined by GC−MS.

From the series of complexes investigated a trend becomes evident that marks the strong impact of the precatalyst structures on catalyst behavior. Catalyst activities and 1-alkene selectivities differ significantly across the various complex types studied. The highest activities and 1-alkene selectivities were found for monomeric complexes bearing a tripodal ligand. This study is particularly pertinent, as it is only recently that complexes with tridentate ligands have received increased attention in the field of ethylene polymerization[3] and systems in which the tridentate ligand binds in a trigonal arrangement are less well known.[1b,c,15,18] α-Olefins rather than polyethylene are generated by catalysts formed from **3** and **4** since the ligands employed create a relatively unencumbered environment at the metal center, leading to enhanced rates of chain transfer and thus to the formation of ethylene oligomers. Interestingly catalysts based on **3b** and **3c** produce considerable amounts of polyethylene, indicating that this class of complexes has the potential to be further developed into polymerization catalysts.

Our preliminary results demonstrate that hard donor bi- and tridentate imidazole ligand frameworks, carrying additional donor groups to tune the electronic properties of the ligands, react with appropriate chromium(III) chloro and alkyl precursors, forming stable complexes in high yields. The novel complexes described herein contribute to the relatively unexplored field of chromium imidazole complexes and to the limited number of well-defined, homogeneous, non-cyclopentadiene chromium-based catalysts for ethylene conversion. In addition, the metal center in these complexes resides in a ligand environment that until now has not found application in this type of reaction. Once activated with MMAO, the complexes represent a new class of catalysts for the generation of linear 1-alkenes from ethylene with selectivities of up to approximately 80%.

Experimental Section

General Comments. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox (Innovative Technology Inc.). All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. IR spectra were recorded for each complex, and electronic spectra were recorded for complexes **3** and **4**. Elemental analysis, MS, and GC−MS were carried out by the Central Science Laboratory (CSL), University of Tasmania.

General Procedure for Chromium Chloro Complexes. A 1.03 equiv sample of the respective ligand dissolved in CH_2-

(18) Jaffart, J.; Nayral, C.; Choukroun, R.; Mathieu, R.; Etienne, M. *Eur. J. Inorg. Chem.* **1998**, *532*, 425−428.

Cl_2 was added to a CH_2Cl_2 solution of $(THF)_3CrCl_3$. The products started to precipitate within minutes. After stirring for 12 h the solvent was separated and the crude product stirred again in CH_2Cl_2 overnight. Removal of the CH_2Cl_2 followed by washing with CH_2Cl_2 and three portions of hexanes and drying in vacuo gave the respective complexes as green solids in ≥90% yield.

General Procedure for the Synthesis of Chromium Mono Methyl Complexes. One equivalent of the respective ligand dissolved in THF was added to a THF solution of $(THF)_3CrMeCl_2$ (**5a**, at −20 °C). The green products started to precipitate within minutes. After stirring for 4 h (**5a**, at −15 to −10 °C) the THF phase was separated and the crude product washed twice with THF and hexanes. Drying in vacuo at −5 °C gave the respective complexes as green solids in ≥90% yield. Despite the care in preparing and handling complex **5a**, its reactivity toward air and moisture precluded obtaining a satisfactory microanalysis.

[Cr{tris(*N*-methylimidazol-2-yl)methoxymethane}-Cl₃] (3a). Anal. Calcd for $C_{14}H_{18}N_6OCl_3Cr$: C, 37.81; H, 4.09; N, 18.90. Found: C, 38.02; H, 5.06; N 18.26. MS (FAB): m/z (correct isotope patterns) 408, [M − Cl]$^+$ (80%); 373, [M − 2Cl]$^+$ (20%); 255, [L − OCH$_3$]$^+$, (100%). IR (KBr): 1539, 1507, 1478 cm^{-1} ($\nu_{imidazole\ ring}$).

[Cr{2-[2-(diphenylphosphino)-1-(*N*-methylimidazol-2-yl)ethyl]-*N*-methylimidazole}Cl₃] (3b). Anal. Calcd for $C_{22}H_{23}N_4Cl_3Cr$: C, 49.59; H, 4.36; N, 10.51. Found: C, 49.59; H, 4.60; N 10.35. MS (FAB): m/z (correct isotope patterns) 496, [M − Cl]$^+$ (100%); 461, [M − 2Cl]$^+$ (31%); 267, [LH − P−C$_6$H$_5$]$^+$, (80%). IR (KBr): 1550, 1508, 1486 cm^{-1} ($\nu_{imidazole\ ring}$); 1434 cm^{-1} ($\nu_{P-phenyl}$); 739, 698 cm^{-1} (δ_{arom}).

[Cr{4,4-dimethyl-1,1-bis(*N*-methylimidazol-2-yl)pentan-3-one}Cl₃] (3c). Anal. Calcd for $C_{15}H_{22}N_4OCl_3Cr$: C, 41.62; H, 5.13; N, 12.95. Found: C, 41.13; H, 5.41; N 12.53. MS (FAB): m/z (correct isotope patterns) 396, [M − Cl]$^+$ (100%); 361, [M − 2Cl]$^+$ (38%); 275, [LH]$^+$, (42%). IR (KBr): 1667 cm^{-1} (ν_{CO}); 1551, 1511, 1461 cm^{-1} ($\nu_{imidazole\ ring}$).

[Cr{bis(*N*-methylimidazol-2-yl)methane}Cl₃]₂ (4a). Anal. Calcd for $C_{18}H_{24}N_8Cl_6Cr_2$: C, 32.31; H, 3.62; N, 16.75. Found: C, 31.86; H, 4.75; N, 14.87. MS (FAB): m/z (correct isotope patterns) 633, [M H$_2$ − Cl]$^+$ (7%); 598, [M H$_2$ − 2Cl]$^+$ (6%); 561 [M − 3Cl]$^+$ (4%); 298, [LCrCl$_2$]$^+$ (59%); 263, [LCrCl]$^+$ (80%); 177 [LH]$^+$, (100%). IR (KBr): 1552, 1513, 1456 cm^{-1} ($\nu_{imidazole\ ring}$).

[Cr{2-[(diphenylphosphino)(*N*-methylimidazol-2-yl)-methyl]-*N*-methylimidazole}Cl₃]₂ (4b). Anal. Calcd for $C_{42}H_{42}N_8Cl_6P_2Cr_2$: C, 48.62; H, 4.09; N 10.79. Found: C, 47.90; H, 4.35; N, 10.03. MS (electrospray in CH$_3$CN): m/z (correct isotope patterns) 1001, [MH$_2$ − Cl]$^+$ (98%); 523 [LCrCl$_2$ + CH$_3$-CN]$^+$ (100%). IR (KBr): 1544, 1505, 1462 cm^{-1} ($\nu_{imidazole\ ring}$), 1435 cm^{-1} ($\nu_{P-phenyl}$); 743, 696 cm^{-1} (δ_{arom}).

[Cr{bis(*N*-methylimidazol-2-yl)ketone}Cl₃]₂ (4c). Anal. Calcd for $C_{18}H_{20}N_8O_2Cl_6Cr_2$: C, 31.01; H, 2.90; N, 16.08. Found: C, 31.04; H 2.80; N, 16.19. MS (FAB): m/z (correct isotope patterns): 661, [MH$_2$ − Cl]$^+$ (12%); 626, [MH$_2$ − 2Cl]$^+$ (7%); 589, [M H$_2$ − 3Cl]$^+$ (4%); 312, [LCrCl$_2$]$^+$ (95%); 277,

[LCrCl]$^+$ (100%); 191 [LH]$^+$, (17%). IR (KBr): 1651 cm^{-1} (ν_{CO}); 1490, 1425 ($\nu_{imidazole\ ring}$).

[Cr(Me){tris(N-methylimidazol-2-yl)methoxymethane}-Cl₂]5a. MS (FAB): m/z (correct isotope patterns) 408, [M − CH$_3$]$^+$ (57%); 373, [M − Cl, − CH$_3$]$^+$ (22%); 255, [L − OCH$_3$], (100%). IR (KBr): 1511, 1505, 1455 cm^{-1} ($\nu_{imidazole\ ring}$).

[Cr(Me){2-[2-(diphenylphosphino)-1-(N-methylimidazol-2-yl)ethyl]-N-methylimidazole}Cl₂] (5b). Anal. Calcd for C$_{23}$H$_{26}$N$_4$Cl$_2$PCr: C, 53.91; H, 5.12; N, 10.94. Found: C, 53.20; H, 4.34; N, 10.22. MS (FAB): m/z (correct isotope patterns) 512, [MH −CH$_3$]$^+$ (12%); 496, [M − CH$_3$]$^+$ (55%); 477, [MH − Cl]$^+$ (41%); 461, [M − CH$_3$, − Cl]$^+$ (55%); 442, [MH − 2Cl]$^+$ (44%). IR (KBr): 1549, 1509, 1484 cm^{-1} ($\nu_{imidazole\ ring}$); 1434 cm^{-1} ($\nu_{P-phenyl}$); 741, 697 cm^{-1} (δ_{arom}).

General Procedure for the Catalysis. MMAO (1.82 M in heptane) was added slowly with stirring to a suspension of the selected complex in 5 mL of toluene. A 300 mL autoclave (dried at 100 °C, cooled to RT under vacuum, and back-filled with nitrogen) was charged with toluene and the catalyst solution added via a syringe. The reactor was immersed into a preheated oil bath and pressurized with ethylene. The reactions were terminated by cooling the reactor in an ice salt bath, venting of excess ethylene, and slow addition of a few milliliters of MeOH followed by dilute HCl. The solid material was collected on a frit, washed with MeOH, diluted HCl, and MeOH, and dried in a high vacuum at 60 °C. The filtrate was dried over Na$_2$SO$_4$ and analyzed by GC−MS.

OM000846B