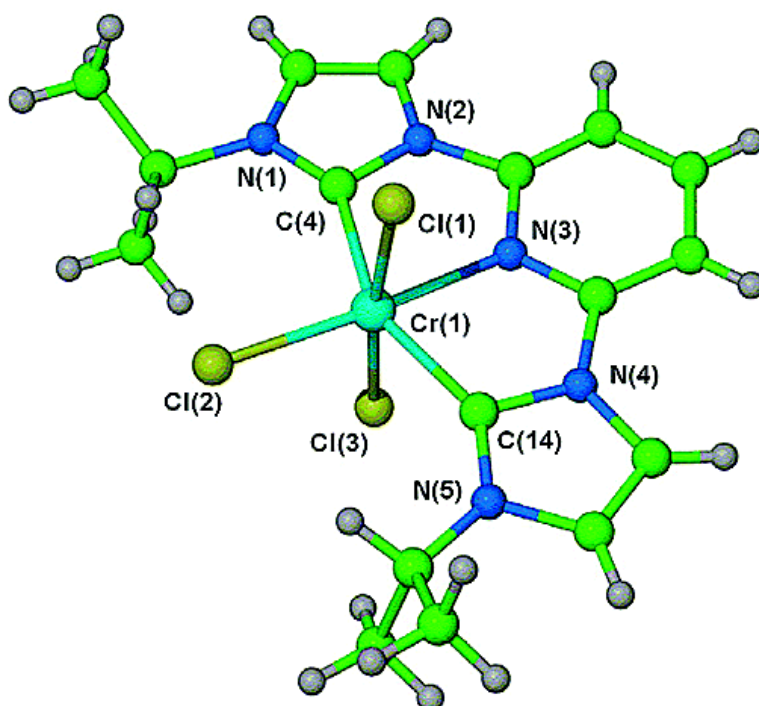


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J. Am. Chem. Soc., **2003**, 125 (42), 12716-12717 • DOI: 10.1021/ja037217o • Publication Date (Web): 30 September 2003

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Bis(carbene)pyridine Complexes of Cr(III): Exceptionally Active Catalysts for the Oligomerization of Ethylene

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One of the more active areas of chemical research over the past decade has been the discovery and development of new molecular catalysts for the oligomerization and polymerization of olefins (ethylene, α -olefins), particularly the search for "non-metallocene" polymerization catalysts,¹ and for new catalysts for the production of linear α -olefins from ethylene.² Olefins in the C₆–C₂₀ range are produced on a large global scale as comonomers for polyethylene, for surfactant production, and for synthetic lubricants,³ predominantly through the use of aluminum alkyls or Ni-based catalysts (SHOP).⁴ Heterogeneous polymerization catalysts based on Cr are well established in the form of the Phillips and Union Carbide systems (Cr/SiO₂), and much interest in Cr-based polymerization catalysts has arisen from these technologies.⁵ In particular, the development of homogeneous models for these systems has been explored.⁶ Research in this area frequently involves the design of new ancillary ligands to support and activate the metal center toward polymerization. In this respect, over the past decade there has been much interest in the application of heterocyclic carbene ligands over a broad range of catalytic reactions. For example, Pd-based catalysts for C–C coupling reactions,⁷ and highly active catalysts for ring-opening metathesis polymerization based on Ru-carbene complexes,⁸ have been developed. Interestingly, however, the use of these ligands in conventional olefin oligomerization and polymerization catalysts has yet to be exploited, and their application in these reactions has been very limited. Although half-sandwich chromium carbene adducts have been evaluated for ethylene polymerization,⁹ and imine-functionalized carbene complexes of several transition metals have been disclosed in the patent literature,¹⁰ their activities have proved disappointingly low. Simple carbene adducts of the group 4 metals were found to give low to moderate activity for the polymerization of ethylene,¹¹ while carbene complexes of Ni(II) were found to be very active for α -olefin dimerization, but only when stabilized by an ionic liquid solvent, which limits decomposition of the complexes via reductive elimination of alkyl-imidazolium cations.¹²

Very recently, CNC-pincer ligands of the form 2,6-(1-alkylimidazol-2-ylidene)pyridine have been prepared and complexed to late transition metals, and these complexes have been applied to a number of catalytic reactions.¹³ To date, these tridentate ligands have not been complexed to early transition metals, nor have complexes of them been evaluated for olefin polymerization. It is notable that this ligand bears structural similarities to the bis(imino)pyridine ligands that have been employed to stabilize highly active oligomerization/polymerization catalysts based on Fe and Co.^{2b,c} This, along with the lack of representation of heterocyclic carbene ligands in olefin oligomerization/polymerization systems, prompted

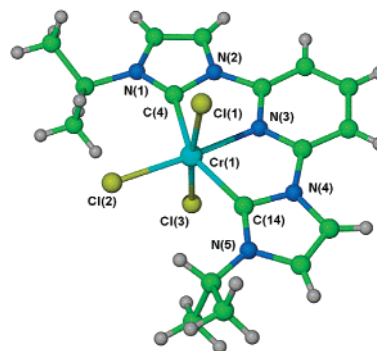
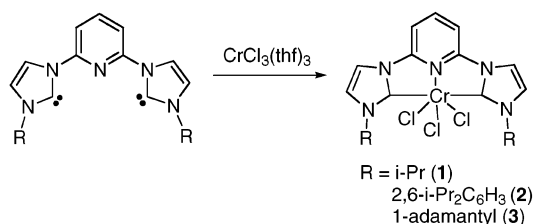


Figure 1. Molecular structure of **1**. Selected bond distances (Å) and angles (deg): Cr(1)–C(4) 2.120(6), Cr(1)–C(14) 2.087(6), Cr(1)–N(3) 2.049(4), N(3)–Cr(1)–C(14) 76.3(2), N(3)–Cr(1)–C(4) 75.68(9), C(14)–Cr(1)–C(4) 154.9(2).

Scheme 1



us to evaluate complexes of CNC-pincer carbene ligands as catalysts for this reaction. Herein, we report new Cr(III) complexes of these ligands which, in combination with MAO, give exceptionally active catalysts for ethylene oligomerization.

The green Cr(III) complexes **1–3**, with differing degrees of steric hindrance on the carbene donor, were prepared in good (>80%) yield via the reaction of the corresponding bis(carbene)pyridine with CrCl₃(THF)₃ in tetrahydrofuran at room temperature (Scheme 1).¹⁴

Crystals of complex **1** suitable for an X-ray diffraction study were grown by diffusion of dichloromethane into a DMSO solution of the complex. The molecular structure of **1**,¹⁵ which shows a slightly distorted octahedral geometry, along with selected bond distances and angles is shown in Figure 1. To our knowledge, this represents the first structural characterization of a Cr(III) heterocyclic carbene complex. The Cr–C distances [2.087(6), 2.120(6) Å] are similar to those in Cr(II) carbene complexes [2.1232(13), 2.127(5) Å],¹⁶ while the chelate bite angles of the CNC ligand [76.3(2)°, 75.68(9)°] are similar to those in bis(imino)pyridine Cr(III) complexes (77–78°).¹⁷

The results of ethylene oligomerization tests using **1–3**, along with MAO cocatalyst, are collected in Table 1. Other cocatalysts, such as diethylaluminum chloride and triisobutyl aluminum/trityl-B(C₆F₅)₃, were also tested and found to be inferior to MAO. In the

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Table 1. Ethylene Oligomerization Results Using **1**–**3**^a

entry	catalyst	P_{ethylene} (bar)	T_{max}^b	activity ^c	prod. ^d	K	α -Ol %
1	1	5	44	727	1817	0.48	93
2	1	1	33	1394	697	0.46	92
3	2	5	70	2263	5657	0.78	93
4	2	2.5	60	2623	3279	0.78	90
5	2	1	46	5490	2745	0.78	89
6	2	1	25 ^e	12 065	6032	0.75	80
7	3	5	25	15	37		
8	3	1	23	73	37		
9	2 ^f	1	25 ^e	27 100	13 550	0.78	80
10	2 ^g	1	25 ^e	40 440	20 220	0.80	86

^a [Cr] = 20 μ M, toluene, 500 MAO, 30 min. ^b Temperature reached due to exotherm. ^c g(product) mmol(Cr)⁻¹ bar⁻¹ h⁻¹. ^d Overall productivity g(product)/mmol(Cr). ^e Temperature held constant throughout run. ^f 10 μ M [Cr], 1000 MAO, 1000 Al(ⁱBu)₃ scavenger. ^g 4.5 μ M [Cr], 1000 MAO, 3000 Al(ⁱBu)₃ scavenger.

case of **1** and **2**, an immediate exotherm is observed with no induction period. There is a remarkable effect of ligand structure on activity. While **1**, and particularly **2**, are very highly active, complex **3**, which contains adamantyl substituents, shows only moderate activity, giving mainly polymer with trace oligomers.

Complexes **1** and **2** give rise in each case to a Schulz–Flory distribution of α -olefins, characterized by the K value¹⁸ (see Table 1). The K value for the ligand bearing the 2,6-diisopropylphenyl group is larger than that for the ligand bearing isopropyl groups, as might be expected on the basis of literature precedents which show increasing K values with increasing steric bulk.^{2c,19} The K values are independent of ethylene pressure, indicating that chain transfer is first order in ethylene. It is notable that the K values obtained with **2** are within the industrially desirable range of 0.75–0.80.⁴ The selectivity toward α -olefins ranges from 80% to 93%.

For both **1** and **2**, the catalytic activity decreases over a 30 min run, as noted by a decrease in ethylene consumption. This deactivation is dependent upon temperature, and above 50 °C a very rapid deactivation is observed. The catalyst benefits from a longer lifetime at lower temperatures, although expectedly the rate of ethylene conversion also decreases at lower temperature.

At 25 °C, low catalyst concentration, and through the use of triisobutyl aluminum as scavenger, exceptionally high activities can be achieved with complex **2** (entries 9, 10). The activities obtained (ca. 40 000 g mmol⁻¹ bar⁻¹ h⁻¹) compare favorably to the most active ethylene oligomerization systems, such as those based on bis(imino)pyridine iron complexes.^{2b,c}

In summary, we have described a new class of exceptionally active Cr(III) complexes for the production of α -olefins, based on tridentate ligands containing heterocyclic carbene donors. While the rapid development of catalysts based on heterocyclic carbene ligands has been ongoing for over a decade, these results represent the first time this ligand class has been employed to produce highly active catalysts for olefin oligomerization/polymerization reactions. These results extend the usefulness of this versatile ligand class,

and the potential for them to act as ancillary ligands for early transition metal olefin polymerization seems promising.

Acknowledgment. The Ramsay Memorial Fellowship Trust and BP are gratefully acknowledged for financial support in the form of a Ramsay Fellowship to D.S.M.

Supporting Information Available: Crystallographic data, in CIF format, for structure **1**. Procedure for ethylene oligomerization, preparation of **1**–**3**, and crystallographic data for **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- 1**: C₁₇H₂₁N₃CrCl₃ calcd. (found) C 45.00 (44.90), H 4.66 (4.79), N 15.43 (15.32). MS (FAB) m/z 452 [M]⁺, 417 [M – Cl]⁺, 382 [M – 2Cl]⁺. μ_{eff} (NMR, BM); 3.88. **2**: C₂₅H₄₁N₅CrCl₃ calcd. (found) C 60.92 (60.73), H 5.99 (5.97), N 10.15 (10.04). MS (FAB) m/z 653 [M – Cl]⁺, 618 [M – 2Cl]⁺, 532 [LH]⁺. μ_{eff} (NMR, BM) 3.97. **3**: C₃₁H₃₇N₅CrCl₃ calcd. (found) C 58.36 (58.31), H 5.86 (5.95), N 10.98 (10.94). MS (FAB) m/z 601 [M – Cl]⁺, 566 [M – 2Cl]⁺, 480 [LH]⁺. μ_{eff} (NMR, BM) 4.00.
- Crystal data for **1**: C₁₈H₂₃Cl₃CrN₅, $M = 538.66$, yellow/green plate, 0.40 × 0.40 × 0.10 mm³, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.6464(4)$, $b = 12.0047(4)$, $c = 15.3782(6)$ Å, $\beta = 94.7420(10)^\circ$, $V = 2326.67(14)$ Å³, $Z = 4$, $D_c = 1.538$ g/cm³, $F_{000} = 1100$, Nonius KappaCCD, Mo K α radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{\text{max}} = 50.0^\circ$, 6440 reflections collected, 3749 unique ($R_{\text{int}} = 0.0682$). The structure was solved and refined using the programs SHELXS-97 and SHELXL-97, respectively. The program X-Seed was used as an interface to the SHELX programs and to prepare the figures. Final GOF = 1.025, $R_1 = 0.0632$, $wR_2 = 0.1506$, R indices based on 2271 reflections with $I > 2\sigma(I)$ (refinement on F^2), 264 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.081$ mm⁻¹.
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JA037217O