

Chromium(III) and chromium(IV) bis(trimethylsilyl)amido complexes as ethylene polymerisation catalysts†

Katherine H. D. Ballem,^a Vidhath Shetty,^a Nola Etkin‡, ^{*,a} Brian O. Patrick^b and Kevin M. Smith^{*,a}^a Department of Chemistry, University of Prince Edward Island, 550 University Avenue, Charlottetown, PE, Canada C1A 4P3. E-mail: kmsmith@upei.ca; Fax: +902 566 0632; Tel: +902 566 0375^b Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

Received 16th August 2004, Accepted 24th September 2004

First published as an Advance Article on the web 8th October 2004

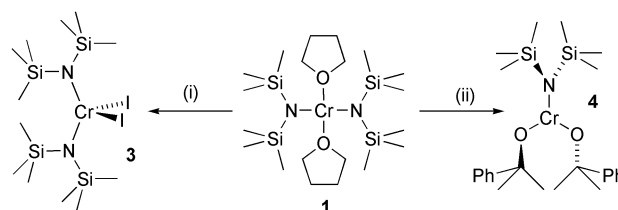
Oxidation of Cr[N(SiMe₃)₂](THF)₂ with iodine and dicumyl peroxide results in tetrahedral Cr(IV) Cr[N(SiMe₃)₂]₂I₂ and trigonal planar Cr(III) Cr[N(SiMe₃)₂](OCMe₂Ph)₂, respectively; both complexes have been characterised by single-crystal X-ray diffraction, and both are active for ethylene polymerisation with alkylaluminium co-catalysts.

While examples of *homoleptic* tetrahedral Cr(IV) d² CrX₄ compounds (X = OR, NR₂, R) have been known for many years,^{1–4} there has been recent interest in *mixed-ligand* Cr(IV) complexes. Initially motivated by the polymerisation activity of silica-supported Cr(IV) organometallic complexes,⁵ recent computational studies have predicted that cationic Cr(IV) bis(amido) alkyl species should be highly active olefin polymerisation catalysts.⁶ A very recent computational study has also proposed that cationic Cr(IV) metallacycles are important intermediates for the Cr-catalysed trimerisation of ethylene to 1-hexene.⁷ We would like to report the synthesis, X-ray crystal structures, and olefin polymerisation activities of Cr[N(SiMe₃)₂]₂I₂ and Cr[N(SiMe₃)₂](OCMe₂Ph)₂.

The bis(trimethylsilyl)amido ligand played a pre-eminent role in the initial exploration of metal amido compounds.⁸ Since this pioneering work it has been almost entirely superseded, in part due to advances in ligand design and synthesis in contemporary transition metal amido chemistry, and in part due to the notorious propensity of the N(SiMe₃)₂ group to decompose *via* N–Si and C–H bond cleavage reactions.⁹ Despite its perceived obsolescence as an ancillary ligand, we found the bis(trimethylsilyl)amido group to be attractive for the investigation of mixed-ligand Cr(IV) compounds for several reasons. Both Cr[N(SiMe₃)₂]₂(THF)₂ **1** and Cr[N(SiMe₃)₂]₂ **2** are well-known, beautifully crystalline compounds that are readily prepared in multigram quantities from commercially available starting materials.¹⁰ The equivalence and relatively unhindered rotation of the methyl groups are expected to simplify the ¹H NMR spectra of paramagnetic Cr[N(SiMe₃)₂]_nX_m species. Well-defined, stable Cr(II) and Cr(III) complexes with multidentate amido ligands containing NSiMe₂R structural units have been previously prepared.¹¹ Most significantly, Filippou and co-workers have demonstrated that the Me₃Si-substituted triamido amine ligand can stabilize a range of Cr[N(CH₂CH₂NSiMe₃)₃]X Cr(IV) complexes.¹²

In 1998, Cummins and co-workers prepared Cr(NRAr_F)₂I₂ by reaction of Cr(NRAr_F)₃ with iodine (R = C(CD₃)₂CH₃, Ar_F = 2,5-C₆H₃FMe).¹³ Our initial attempt to extend this reaction to the N(SiMe₃)₂ system using the analogous Cr(III) tris(amido) complex was unsuccessful: no new chromium species were detected by ¹H NMR after treatment of **2** with I₂ in Et₂O at room temperature for several days. However,

the Cr(II) bis(amido) **1** reacted readily with I₂ in Et₂O to give Cr[N(SiMe₃)₂]₂I₂ **3** in 80% yield as thick black plates, as shown in Scheme 1. The Cr(IV) bis(iodo) complex exhibits a broad singlet in its ¹H NMR spectrum (C₆D₆, 300.1 MHz, 6.38 ppm, *v*_{1/2} = 100 Hz) for the equivalent N(SiMe₃)₂ methyl groups, distinct from the corresponding signals for **1** (30.5 ppm, *v*_{1/2} = 800 Hz) and **2** (25.9 ppm, *v*_{1/2} = 1040 Hz). The recently reported Cr(IV) Cr[N(CH₂CH₂NSiMe₃)₃]X complexes also display SiMe₃ signals in the region 5.88 to 3.28 ppm with *v*_{1/2} values of between 150 and 250 Hz.¹²



Scheme 1 Synthesis of **3** and **4**. Reagents and conditions: i, I₂, Et₂O; ii, dicumyl peroxide, pentane.

Compound **3** was also characterized by X-ray diffraction (Fig. 1).§ The complex adopts a distorted tetrahedral structure, and possesses a crystallographic C₂ axis bisecting the N–Cr–N and I–Cr–I angles.

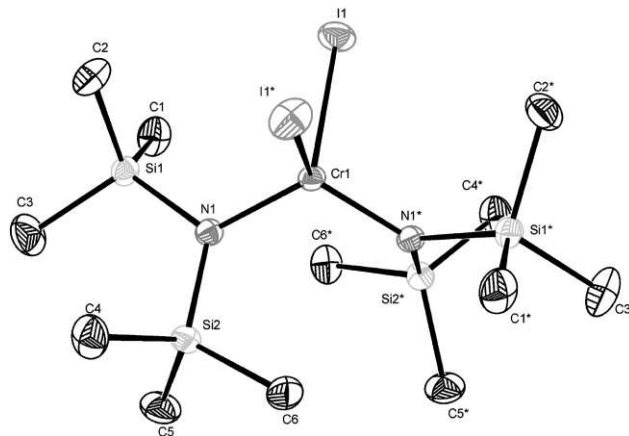


Fig. 1 The molecular structure of **3**. Selected bond lengths (Å) and angles (°): Cr1–N1 1.8355(14), Cr1–I1 2.5610(3), N1–Si1 1.8036(15), N1–Si2 1.7918(15), N1–Cr1–N1* 116.90(9), N1–Cr1–I1 116.44(4), N1–Cr1–I1* 103.42, I1–Cr1–I1* 99.322(14).

Homoleptic Cr(OR)₄ complexes are useful synthetic precursors to CrR₄ species, as an alternative to the oxidation of Cr(III) [CrR₄][–] “ate” complexes obtained by alkylating CrCl₃.⁴ Inspired by the synthesis of Cr(OCMe₃)₄ by treatment of Cr(C₆H₆)₂ with di-*tert*-butylperoxide,¹ we attempted to prepare a mixed ligand Cr(IV) bis(amido) complex by reacting **1** with PhMe₂COOCMe₂Ph. As illustrated in Scheme 1, the

† Electronic supplementary information (ESI) available: Experimental details. See <http://www.rsc.org/suppdata/dt/b4/b412584c/>

‡ Correspondence regarding polymerisation studies (netkin@upei.ca)

Table 1 Results of ethylene polymerisation runs using pre-catalysts **1–4**^a

Run	Pre-catalyst/ mmol	Activator ^{b/} mmol (equiv)	Time/min	Yield PE ^c /g	Activity/g mmol ⁻¹ h ⁻¹ bar ⁻¹
1	3 (0.017)	MAO (3.0/180)	5	0.068	48
2	3 (0.017)	DEAC (0.52/31)	5	0.010	7
3	3 (0.018)	MAO (3.2/180)	30	0.384	43
4	3 (0.016)	DEAC (0.54/34)	30	0.401	50
5	3 (0.017)	MAO (3.0/180)	60	0.508	30
6	3 (0.018)	DEAC (0.54/30)	60	0.754	42
7	2 (0.018)	DEAC (0.54/30)	60	0.027	1
8	4 (0.019)	DEAC (0.54/28)	60	0.683	36
9	1 (0.017)	DEAC (0.54/32)	60	0.703	41

^aGeneral conditions: Schlenk tests carried out at 1 bar ethylene in toluene (40 mL) at ambient temperature, reaction quenched at indicated time with HCl in methanol, solid PE washed with methanol and water (50 mL each) and dried in a 50 °C vacuum oven. ^bMAO = methylaluminoxane, DEAC = diethylaluminium chloride. ^cSolid polyethylene.

reaction unexpectedly gave a Cr(III) mono(amido) complex, Cr[N(SiMe₃)₂](OCMe₂Ph)₂ **4** in 25% yield as blue crystals. The ¹H NMR spectrum of **4** (C₆D₆, 300.1 MHz) displays broad peaks at 53.6 ppm ($\nu_{1/2}$ = 1360 Hz) and 21.2 ppm ($\nu_{1/2}$ = 1090 Hz), assigned to the SiMe₃ and CMe₂ groups of **4**, respectively, based on their relative integration. The molecular structure of **4** was determined by X-ray diffraction and is shown in Fig. 2. Like **3**, **4** also possesses a C₂ axis bisecting the O–Cr–O angle. While trigonal planar CrX₃ tris(amido) complexes are known,⁸ we are aware of only one previously reported example of a Cr(III) trigonal planar complex bearing alkoxide ligands.¹⁴

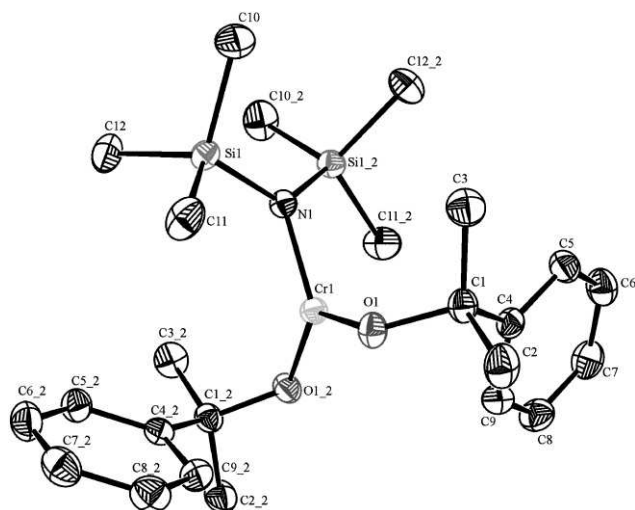


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Cr1–N1 1.8639(14), Cr1–O1 1.8048(8), N1–Si1 1.7522(7), O1–C1 1.4444(14), N1–Cr1–O1 117.91(3), Cr1–N1–Si1 116.43(4), Si1–N1–Si1 2 127.15(8), O1–Cr1–O1 2 124.17(6), Cr1–O1–C1 126.22(7).

Although well-defined, homogeneous Cr(II) and Cr(III) complexes are known ethylene polymerisation pre-catalysts,¹⁵ the few studies that have used Cr(IV) precursors are almost all heterogeneous.^{5,16} As shown in Table 1, **3** displays moderate activity¹⁵ with alkylaluminium co-catalysts, with higher activity at longer reaction times observed using AlEt₂Cl (DEAC)¹⁷ rather than methylaluminoxane (MAO). Under our conditions, the activity of the Cr(III) tris(amido) **2** with DEAC is significantly lower than that of **3**, although higher activity for **2**/MAO was recently reported by Monoi, Yasuda and co-workers.¹⁶ Interestingly, under the same activating conditions, the activities of pre-catalysts **3**, **4**, and **1** (runs 6, 8 and 9, respectively) are all remarkably similar despite the range in pre-catalyst oxidation state (Cr(IV), Cr(III) and Cr(II), respectively). Such similarities between alkylaluminium activated chromium pre-catalysts of differing oxidation states have been noted previously,^{15,17} most recently for neutral tridentate pyridine-based ligands coordinated to CrCl₂ or CrCl₃.¹⁸

Computational studies have identified Cr(IV) [Cr(NR₂)₂(CH₂R')]⁺ species as potentially useful catalysts for ethylene

polymerisation.⁶ Oxidation of Cr(II) and Cr(III) amido compounds^{10,11} provides access to Cr(IV) mixed-ligand amido complexes amenable to further synthetic elaboration.^{12,13} Further studies of the properties of the polyethylene generated by DEAC-activated **1**, **3**, and **4**, and the synthesis and reactivity of well-defined Cr(IV) complexes derived from **3** are currently under investigation.

This work was supported by UPEI and the Natural Sciences and Engineering Research Council of Canada (NSERC).

Notes and references

§ Crystal data for C₁₇H₃₀CrI₂N₂Si₄ **3**: *M* = 626.59, monoclinic, space group = *C2/c*, *a* = 16.9513(9), *b* = 8.7479(3), *c* = 18.2601(9) Å, β = 111.51(1)°, *V* = 111.510(10) Å³, *T* = 173 K, *Z* = 4, μ(Mo-Kα) = 30.93 cm⁻¹, 20227 reflections measured, 3015 unique, 102 variable parameters (*R*_{int} = 0.029), final residuals *R*1 = 0.019 [for 2904 reflections with *I* > 2σ(*I*)], *wR*2 = 0.051 [all data]. Crystal data for C₂₄H₄₀CrNO₂Si₂ **4**: *M* = 482.75, monoclinic, space group = *C2/c*, *a* = 18.480(3), *b* = 9.380(1), *c* = 17.280(3) Å, β = 116.135(5)°, *V* = 2689.0(7) Å³, *T* = 173 K, *Z* = 4, μ(Mo-Kα) = 5.33 cm⁻¹, 38321 reflections measured, 3175 unique, 142 variable parameters (*R*_{int} = 0.023), final residuals *R*1 = 0.026 [for 2911 reflections with *I* > 2σ(*I*)], *wR*2 = 0.073 [all data]. CCDC reference numbers 247651 and 247652. See <http://www.rsc.org/suppdata/dt/b4/b412584c/> for crystallographic data in CIF or other electronic format.

- N. Hagihara and H. Yamazaki, *J. Am. Chem. Soc.*, 1959, **81**, 3160–3161.
- G. Drykacz and J. Roček, *J. Am. Chem. Soc.*, 1973, **95**, 4756; M. Bochmann, G. Wilkinson, G. B. Young, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 1863–1871.
- J. S. Basi, D. C. Bradley and M. H. Chisholm, *J. Chem. Soc. A*, 1971, 1433–1436.
- W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 533–542; W. Mowat, A. J. Shortland, N. J. Hill and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 770–778; W. Seidel and G. Kreisel, *Z. Anorg. Allg. Chem.*, 1976, **426**, 150–154; W. Seidel and I. Bürger, *Z. Anorg. Allg. Chem.*, 1976, **426**, 155–158; P. J. Alonso, J. Forniés, M. A. García-Monforte, A. Martín, B. Menjón and C. Rillo, *Chem. Eur. J.*, 2002, **8**, 4056–4065; C. Schulzke, D. Enright, H. Sugiyama, G. LeBlanc, S. Gambarotta, G. P. A. Yap, L. K. Thompson, D. R. Wilson and R. Duchateau, *Organometallics*, 2002, **21**, 3810–3816.
- J. Amor Nait Ajjou and S. L. Scott, *Organometallics*, 1997, **16**, 86–92; J. Amor Nait Ajjou and S. L. Scott, *J. Am. Chem. Soc.*, 2000, **122**, 8968–8976; S. L. Scott and J. Amor Nait Ajjou, *Chem. Eng. Sci.*, 2001, **56**, 4155–4168; M. C. Beaudoin, O. Womiloju, A. Fu, J. Amor Nait Ajjou, G. L. Rice and S. L. Scott, *J. Mol. Catal. A*, 2002, **190**, 159–169.
- R. Schmid and T. Ziegler, *Organometallics*, 2000, **19**, 2756–2765; R. Schmid and T. Ziegler, *Can. J. Chem.*, 2000, **78**, 265–269; T. K. Firman and T. Ziegler, *J. Organomet. Chem.*, 2001, **635**, 153–164.
- W. Janse van Rensburg, C. Grové, J. P. Steynberg, K. B. Stark, J. J. Huyser and P. J. Steynberg, *Organometallics*, 2004, **23**, 1207–1222.
- D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, 1976, **9**, 273–280; P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, *Coord. Chem. Rev.*, 1977, **24**, 1–95; C. C. Cummins, *Prog. Inorg. Chem.*, 1998, **47**, 685–836.
- P. Berno, R. Minhas, S. Hao and S. Gambarotta, *Organometallics*, 1994, **13**, 1052–1054; C. E. Laplaza, M. J. A. Johnson, J. C. Peters,

- A. L. Odom, E. Kim, C. C. Cummins, G. N. George and I. J. Pickering, *J. Am. Chem. Soc.*, 1996, **118**, 8623–8638; R. Messere, M.-R. Spirlet, D. Jan, A. Demonceau and A. F. Noels, *Eur. J. Inorg. Chem.*, 2000, 1151–1153.
- 10 H. Bürger and U. Wannagat, *Monatsh. Chem.*, 1964, **95**, 1099–1102; D. C. Bradley, M. B. Hursthouse, C. W. Newing and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1972, 567–568; D. C. Bradley and R. G. Copperthwaite, *Inorg. Synth.*, 1978, **18**, 112–120; A. Kayal and S. Lee, *Inorg. Chem.*, 2002, **41**, 321–330.
- 11 C. C. Cummins, J. Lee, R. R. Schrock and W. D. Davis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1501–1503; M. D. Fryzuk, D. B. Leznoff and S. J. Rettig, *Organometallics*, 1995, **14**, 5193–5202; H. Ikeda, T. Monoi, Y. Nakayama and H. Yasuda, *J. Organomet. Chem.*, 2002, **642**, 156–162.
- 12 S. Schneider and A. C. Filippou, *Inorg. Chem.*, 2001, **40**, 4674–4677; A. C. Filippou, S. Schneider and B. Ziemer, *Eur. J. Inorg. Chem.*, 2002, 2928–2935; A. C. Filippou and S. Schneider, *Organometallics*, 2003, **22**, 3010–3012; A. C. Filippou, S. Schneider and G. Schnakenburg, *Angew. Chem., Int. Ed.*, 2003, **42**, 4486–4489.
- 13 D. J. Mindiola and C. C. Cummins, *Angew. Chem., Int. Ed.*, 1998, **37**, 945–947.
- 14 H. Blanchard, M. B. Hursthouse and A. C. Sullivan, *J. Organomet. Chem.*, 1988, **341**, 367–371.
- 15 K. H. Theopold, *Eur. J. Inorg. Chem.*, 1998, 15–24; G. J. B. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428–447; V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283–315; N. J. Robertson, M. J. Carney and J. A. Halfen, *Inorg. Chem.*, 2003, **42**, 6876–6885.
- 16 H. Ikeda, T. Monoi, K. Ogata and H. Yasuda, *Macromol. Chem. Phys.*, 2001, **202**, 1806–1811.
- 17 V. C. Gibson, P. J. Maddox, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 1651–1652; V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1999, 827–829; V. C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 1969–1971; V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Eur. J. Inorg. Chem.*, 2001, 1895–1903; V. C. Gibson, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2002, 4017–4023.
- 18 B. L. Small, M. J. Carney, D. M. Holman, C. E. O'Rourke and J. A. Halfen, *Macromolecules*, 2004, **37**, 4375–4386.