

# Isolation of a Chromium Hydride Single-Component Ethylene Polymerization Catalyst

Khalid Albahily,<sup>†</sup> Danya Al-Baldawi,<sup>†</sup> Sandro Gambarotta,<sup>\*,†</sup> Ece Koç,<sup>‡</sup> and Robbert Duchateau<sup>\*,‡</sup>

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, and Department of Chemistry and Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, Eindhoven 5600 MB, The Netherlands

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Reaction of the divalent complex  $[(t\text{-Bu})\text{NPN}(t\text{-Bu})_2\text{Cr}$  (**1**) with different stoichiometric ratios of  $\text{Al}(i\text{-Bu})_3$  afforded  $\{\mu\text{-}[(t\text{-Bu})\text{NP}(i\text{-Bu})\text{N}(t\text{-Bu})\text{Al}(i\text{-Bu})_2]\}_2\text{Cr}$  (**2**) and  $[\{(i\text{-Bu})\text{P}\{\mu\text{-N}(t\text{-Bu})\}_2\text{Al}(i\text{-Bu})_2\}\text{Cr}(\mu\text{-H})_2]$  (**3**) as part of the same reaction sequence. Complex **2** arises from association of alane and the two ligands via alkylation of the P atom and retention of the  $\text{AlR}_2$  unit. Complex **3** appears to be generated from subsequent dissociation of one alkylated ligand and possible transfer of an *i*-Bu group to Cr followed by  $\beta\text{-H}$  elimination or transfer of a hydride originating from isobutyl elimination of the aluminum-containing residue. Both species are potent ethylene polymerization catalysts with no need for further activation. It is assumed that **2** is transformed in situ into **3** under the influence of ethylene. Reactions with ethylene carried out in the presence of excess of  $\text{Al}(i\text{-Bu})_3$  switch the selectivity completely toward selective trimerization.

## Introduction

Homogeneous catalytic systems for ethylene oligomerization and polymerization generally comprise two components: a catalyst precursor and an activator.<sup>1</sup> At least in the case of polymerization, reasonably precise information is available about the requisites of the catalytically active species which, instead, remains more elusive in the case of selective oligomerization. This is in spite of the fact that from a formal point of view the two processes are closely related.<sup>2</sup> Obviously, isolating catalytically active species from the catalytic cycles would be the best source of information to get insight into the mechanism of the C–C forming reaction and oxidation state of the metal center. Isolable active species are, however, relatively rare. Most well-known examples are lanthanoid single-component ethylene polymerization catalysts,<sup>3</sup> the borate-stabilized cationic group 4 metal catalysts,<sup>3f</sup> and borate-free transition-metal single-component catalysts.<sup>4</sup> To the best of our knowledge, active species performing ethylene trimerization have never been

reported. Attempting the isolation of such species may not only lead to more active and efficient processes but may also improve our understanding of the mechanistic cycle.

With this aim, we have recently embarked on a research project targeting the isolation of catalytically active intermediates of new or established catalytic systems for both selective oligomerization and polymerization. Chromium provides an ideal element for this research, since it has produced both potent

\* To whom correspondence should be addressed. S.G.: tel, (613) 562-5199; fax, (613) 562-5170; e-mail, Sgambaro@uottawa.ca.

<sup>†</sup> University of Ottawa.

<sup>‡</sup> Eindhoven University of Technology.

(1) For selected examples in chromium chemistry see: (a) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2005**, *127*, 1082. (b) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, *15*. (c) Bhandari, G.; Kim, Y.; McFarland, J. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1995**, *14*, 738. (d) Dohring, A.; Gohre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhovnik, G. P. *J. Organometallics* **2000**, *19*, 388. (e) Rogers, J. S.; Bu, X. H.; Bazan, G. C. *Organometallics* **2000**, *19*, 3948. (f) Enders, M.; Fernandez, P.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 5005. (g) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 1651. (h) MacAdams, L. A.; Kim, W. K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952. (i) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2000**, 1969.

(2) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451. (b) Cossee, P. *J. Catal.* **1964**, *3*, 80. (c) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

(3) For example, see: (a) Desurmont, G.; Li, Y.; Yasuda, H.; Maruo, T.; Kanehisa, N.; Kai, Y. *Organometallics* **2000**, *19*, 1811. (b) Shapiro, P. J.; Bunel, E. E.; Schafer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867. (c) Evans, W. J.; Forrester, K. J.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 774. (d) Evans, W. J.; De Coster, D. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929. (e) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507. (f) See for example: Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 9660, and references cited therein.

(4) For example see: (a) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236, and references cited therein. (b) Qihui, C.; Jing, Y.; Jiling, H. *Organometallics* **2007**, *26*, 617. (c) Strauch, J. W.; Erker, G.; Kehr, G.; Frohlich, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2543. (d) Brookhart, M. J.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378. (e) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (f) Götter-Schnetmann, I.; Wehrmann, P.; Röhr, C.; Mecking, S. *Organometallics* **2007**, *26*, 2348. (g) Johnson, L. K.; Killian, C. M.; Brookhart, M. J. *Am. Chem. Soc.* **1995**, *117*, 6414. (h) Keim, W.; Kowaldt, F. H.; Goddard, R.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (i) Ostojka Starzewski, K. A.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599. (j) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123. (k) Kuhn, P.; Semeril, D.; Jeunesse, C.; Matt, D.; Neuburger, M.; Mota, A. *Chem. Eur. J.* **2006**, *12*, 5210. (l) Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217. (m) Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836. (n) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2003**, *22*, 4699. (o) Diamanti, S. J.; Ghosh, P.; Shimizu, F.; Bazan, G. C. *Macromolecules* **2003**, *36*, 9731. (p) Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 250. (q) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *24*, 3533. (r) Jenkins, J. C.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 5827. (s) Götter-Schnetmann, I.; Korthals, B.; Mecking, S. *J. Am. Chem. Soc.* **2006**, *128*, 7708. (t) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473. (u) Wehrmann, P.; Mecking, S. *Organometallics* **2008**, *27*, 1399. (v) Jabri, A.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 6119.

polymerization<sup>1,5</sup> and oligomerization catalysts,<sup>6</sup> including selective trimerization<sup>7</sup> and tetramerization systems.<sup>8</sup> The main issue for all these chromium-catalyzed C–C forming reactions consists of the chromium oxidation state in the catalytically active species, which remains debatable for all these processes. In the course of our mechanistic studies on some of the most established selective oligomerization systems, our results led us to conclude that reduction of the commonly used trivalent precursor to its corresponding divalent derivative is a step toward generating the catalytically active species.<sup>9</sup> Since polymerization invariably accompanies selective tri- and tetramerization to variable extents, questions arise about which metal oxidation state is responsible for each of these mechanistically distinct processes. Divalent chromium complexes may provide high activity but often lack selectivity.<sup>6</sup> On the other hand, we observed at least in one case that reoxidation to the trivalent state via disproportionation might in fact be the key to selective trimerization.<sup>10</sup> Recently, we have reported preliminary results on the versatile system [(*t*-Bu)NPN(*t*-Bu)]<sub>2</sub>Cr (**1**), which switches selectivity from statistical oligomerization to selective trimerization (99.9% 1-hexene) and even to polymerization just

**Table 1. Crystal Data and Structure Analysis Results.**

	2	3
formula	C <sub>40</sub> H <sub>90</sub> Al <sub>2</sub> CrN <sub>4</sub> P <sub>2</sub>	C <sub>40</sub> H <sub>92</sub> Al <sub>2</sub> Cr <sub>2</sub> N <sub>4</sub> P <sub>2</sub>
mw	795.06	849.08
space group	monoclinic, <i>P</i> <sub>2</sub> /n	triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	12.604(3)	9.702(4)
<i>b</i> (Å)	13.740(3)	10.454(4)
<i>c</i> (Å)	14.445(4)	14.135(8)
$\alpha$ (deg)		107.554(6)
$\beta$ (deg)	97.494(4)	95.139(9)
$\gamma$ (deg)		101.520(6)
<i>V</i> (Å <sup>3</sup> )	2480.2(11)	1322.0(11)
<i>Z</i>	2	1
radiation (Å)	0.710 73	0.710 73
<i>T</i> (K)	202(2)	202(2)
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.065	1.066
$\mu$ <sub>calcd</sub> (mm <sup>-1</sup> )	0.359	0.532
<i>F</i> <sub>000</sub>	876	464
R1, wR2 <sup>a</sup>	0.0537, 0.1292	0.0679, 0.1809
GO <sub>F</sub>	1.055	1.021

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|, wR2 = [\sum (|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}.$$

**Table 2. Selected Bond Distances (Å) and Angles (deg)**

	2	3
Cr(1)–N(2)	2.129(3)	Cr(1)···Cr(1a) 2.6142(16)
Cr(1)–P(1)	2.3989(10)	Cr(1)–N(1) 2.156(3)
Cr(1)–N(2a)	2.129(3)	Cr(1)–N(2) 2.141(3)
N(1)–Al(1)	1.898(3)	Cr(1)–P(1) 2.6178(15)
N(2)–Al(1)	1.988(3)	N(1)–Al(1) 1.953(3)
P(1)–Cr(1)–P(1a)	180.0	N(2)–Al(1) 1.956(3)
N(2)–Cr(1)–N(2a)	180.0	N(1)–Cr(1)–N(2) 65.20(11)
P(1)–Cr(1)–N(2)	44.51(7)	N(1)–Cr(1)–P(1) 41.88(8)
		N(2)–Cr(1)–P(1) 42.27(8)

depending on the nature of the alane activator.<sup>11</sup> This behavior makes this system ideal to study the factors determining the selectivity toward polymerization versus oligomerization. The nonspectator behavior of the ligand in this particular system<sup>11</sup> is most likely a crucial feature of the system's peculiar conduct. Herein, we describe the results of a further study aiming at clarifying this important behavior and resulting in the isolation of two novel single-component polymerization catalysts, including a rare case of a divalent chromium hydride.<sup>12</sup>

## Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Molecular weights and molecular weight distributions of the resulting polymers were determined by means of gel permeation chromatography on a PL-GPC210 equipped with an RI and viscosity detector and a 3 × PLgel 10 μm MIXED-B column set at 135 °C using 1,2,4-trichlorobenzene as solvent. The molecular weight of the polyethylenes was referenced to polystyrene standards. The liquid product mixtures were analyzed by using a CP 9000

(11) Albahily, K.; Koç, E.; Al-Baldawi, D.; Savard, D.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5816.

(12) (a) Barron, A. R.; Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1986**, *5*, 1833. (b) Heintz, R. A.; Haggerty, B. S.; Wan, H.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1077. (c) Heintz, R. A.; Koetzle, T. F.; Ostrander, R. L.; Rheingold, A. L.; Theopold, K. H.; Wu, P. *Nature* **1995**, *378*, 359. (d) Heintz, R. A.; Ostrander, R. L.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 11387. (e) Filippou, A. C.; Schneider, S.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4486. (f) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J.; Thompson, R. C. *Inorg. Chem.* **1994**, *33*, 5528. (g) Monillas, W. H.; Yap, G. P. A.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 6692. (h) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Golen, J. A.; Rheingold, A. L.; Theopold, K. H. *Chem. Commun.* **2003**, 1164. (i) Thaler, E.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 374. (j) Girolami, G. S.; Salt, J. E.; Wilkinson, G. *J. Am. Chem. Soc.* **1983**, *105*, 5954.

(5) (a) Theopold, K. H. *Eur. J. Inorg. Chem.* **1998**, 15. (b) Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (d) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *1*, 283. (e) Jutz, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 6, 663. (f) Emrich, R.; Heinemann, O.; Jolly, P. W.; Kruger, C.; Verhovnik, G. P. *J. Organometallics* **1997**, *16*, 1511. (g) Dohring, A.; Gohre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhovnik, G. P. *J. Organometallics* **2000**, *4*, 388. (h) Jensen, V. R.; Angermund, K.; Jolly, P. W.; Børve, K. J. *Organometallics* **2000**, *19*, 403. (i) Dohring, A.; Jensen, V. R.; Jolly, P. W.; Thiel, W.; Weber, J. C. *Organometallics* **2001**, *11*, 2234. (j) Kotov, V. V.; Avtomonov, E. V.; Sundermeyer, J.; Aitola, E.; Repo, T.; Lemenovskii, D. A. *J. Organomet. Chem.* **2001**, *640*, 21. (k) Enders, M.; Fernandez, P.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *24*, 5005. (l) Enders, M.; Fernandez, P.; Mihan, S.; Pritzkow, H. *J. Organomet. Chem.* **2003**, *687*, 125. (m) Enders, M.; Kohl, G.; Pritzkow, H. *Organometallics* **2004**, *23*, 3832. (n) Enders, M. *Macromol. Symp.* **2006**, *236*, 38. (o) Fernandez, P.; Pritzkow, H.; Carbo, J. J.; Hofmann, P.; Enders, M. *Organometallics* **2007**, *26*, 4402. (p) Zhang, H.; Ma, J.; Qian, Y. L.; Huang, J. L. *Organometallics* **2004**, *24*, 5681. (q) Ogata, K.; Nakayama, Y.; Yasuda, H. *J. Polym. Sci., Part A* **2002**, *40*, 2759. (r) Ikeda, H.; Monoi, T.; Ogata, K.; Yasuda, H. *Macromol. Chem. Phys.* **2001**, *202*, 1806. (s) Bazan, G. C.; Rogers, J. S.; Fang, C. C. *Organometallics* **2001**, *20*, 2059.

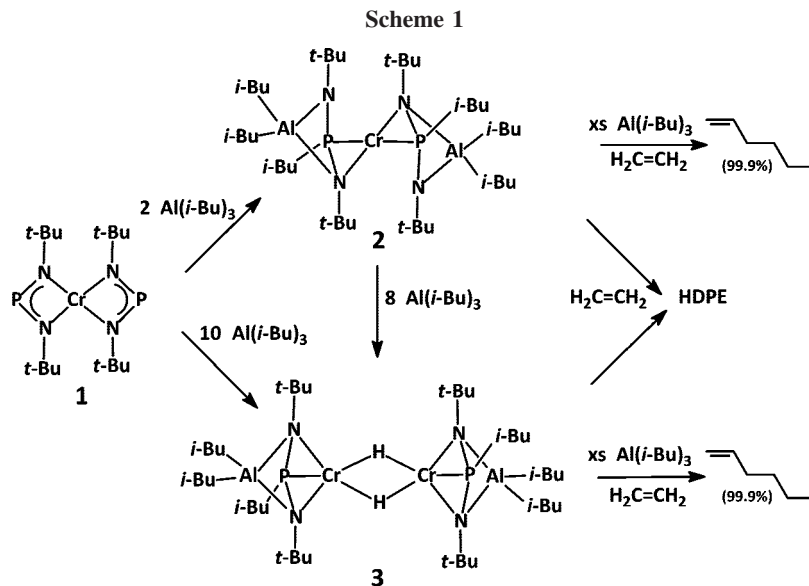
(6) For example see: Crewdson, P.; Gambarotta, S.; Djoman, M.-C.; Korobkov, I.; Duchateau, R. *Organometallics* **2005**, *24*, 5214.

(7) (a) Reagan, W. K. (Phillips Petroleum Company) EP 0417477, 1991. (b) Mimura, H.; Aoyama, T.; Yamamoto, T.; Oguri, M.; Koie, Y. (Tosoh Corporation) JP 09268133, 1997. (c) Mohamed, H.; Bollmann, A.; Dixon, J.; Gokul, V.; Griesel, L.; Grove, C.; Hess, F.; Maumela, H.; Pepler, L. *Appl. Catal., A* **2003**, *255*, 355. (d) Grove, J. J. C.; Mohamed, H. A.; Griesel, L. (Sasol Technology (Pty) Ltd) WO 03/004158, 2002. (e) Yoshida, T.; Yamamoto, T.; Okada, H.; Murakita, H. (Tosoh Corporation) U.S. Patent 2002/0035029, 2002. (f) Wass, D. F. (BP Chemicals Ltd) WO 02/04119, 2002. (g) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858. (h) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D. H.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F. M.; Englert, U. *J. Am. Chem. Soc.* **2003**, *125*, 5272. (i) Dixon, J. T.; Wasserscheid, P.; McGuinness, D. S.; Hess, F. M.; Maumela, H.; Morgan, D. H.; Bollmann, A. WO 03053890 (Sasol Technology (Pty) Ltd), 2001. (j) Agapie, T.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2733. (k) Schofer, S. J.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2743.

(8) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *J. Am. Chem. Soc.* **2004**, *126*, 14712.

(9) (a) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *J. Am. Chem. Soc.* **2006**, *128*, 9238. (b) Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* **2006**, *25*, 715. (c) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. *J. Chem. Commun.* **2005**, 620.

(10) Temple, C.; Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angew. Chem., Int. Ed.* **2006**, *118*, 7208.



gas chromatograph (GC) equipped with a 30 m  $\times$  0.32 mm i.d. capillary CP volamine column and an FID detector. All single-point experiments were performed in duplicate. The total yield was determined by  $^1\text{H}$  NMR spectroscopy (Varian Mercury 400 MHz spectrometer) by integrating the olefinic peaks against the toluene solvent Me group peak. The relative percentages of oligomers were obtained by GC. Samples for magnetic susceptibility were preweighed inside a dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Complex **1** was prepared according to a published procedure.<sup>11</sup>  $\text{Al}(i\text{-Bu})_3$  (Strem 95%) was used as received. Samples for magnetic susceptibility measurements at room temperature were preweighed inside a drybox equipped with an analytical balance and flame-sealed into calibrated 5 mm o.d. quartz tubes. Magnetic measurements were carried out using a Johnson Matthey magnetic balance. Background corrections for the sample holder were included in the magnetic calculations. Standard corrections for the underlying diamagnetism were applied to the data.

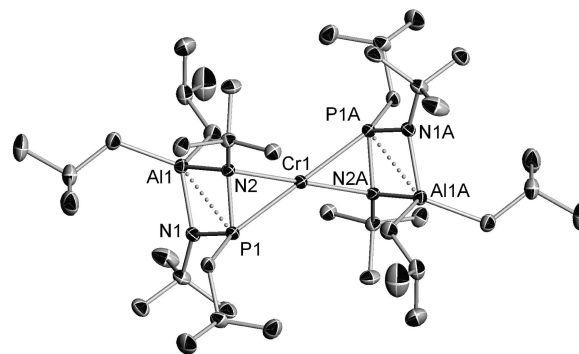
**Preparation of  $\{\mu\text{-}[(i\text{-Bu})\text{NP}(i\text{-Bu})\text{N}(t\text{-Bu})\text{Al}(i\text{-Bu})_2]_2\text{Cr}\}$  (**2**).** Neat  $\text{Al}(i\text{-Bu})_3$  (0.79 g, 4.0 mmol) was added at  $-30\text{ }^\circ\text{C}$  to a solution of  $[(t\text{-Bu})\text{NPN}(t\text{-Bu})]_2\text{Cr}$  (**1**; 0.83 g, 2.1 mmol) in toluene (10 mL) and the mixture stirred for 15 min at room temperature. The solvent was removed in vacuo and the residue redissolved in hexane (10 mL). Crystals of **2** separated from the resulting solution upon standing at  $-30\text{ }^\circ\text{C}$  for 3 days. The brown crystals were filtered and washed with cold hexanes (10 mL) and dried in vacuo (0.96 g, 1.2 mmol, 57%)  $\mu_{\text{eff}} = 4.74\ \mu_{\text{B}}$ . Anal. Calcd (found) for  $\text{C}_{40}\text{H}_{90}\text{Al}_2\text{CrN}_4\text{P}_2$ : C, 60.43 (60.41); H, 11.41 (11.39); N, 7.05 (7.00).

**Preparation of  $\{\mu\text{-}[(i\text{-Bu})\text{P}[\text{N}(t\text{-Bu})]_2\text{Al}(i\text{-Bu})_2]\text{Cr}(\mu\text{-H})_2\}$  (**3**).** Neat  $\text{Al}(i\text{-Bu})_3$  (3.96 g, 20.0 mmol) was added at  $-30\text{ }^\circ\text{C}$  to a solution of  $[(t\text{-Bu})\text{NPN}(t\text{-Bu})]_2\text{Cr}$  (**1**; 0.80 g, 2.0 mmol) in toluene (10 mL) and the mixture stirred for 15 min at room temperature. The solvent and excess  $\text{Al}(i\text{-Bu})_3$  were removed in vacuo, and the resulting solid residue was redissolved in hexane (10 mL). The solution was stored in a  $-30\text{ }^\circ\text{C}$  freezer for 3 days. Red-purple crystals of **3** separated which were filtered, washed with cold hexanes (10 mL), and dried in vacuo (0.75 g, 0.9 mmol, 90%).  $\mu_{\text{eff}} = 1.63\ \mu_{\text{B}}$ . Anal. Calcd (found) for  $\text{C}_{40}\text{H}_{92}\text{Al}_2\text{Cr}_2\text{N}_4\text{P}_2$ : C, 56.58 (56.55); H, 10.92 (10.88); N, 6.60 (6.54).

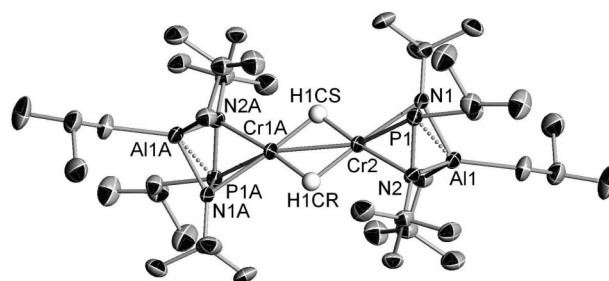
**Polymerization and Oligomerization Results.** Polymerizations were carried out in either 200 mL high pressure Büchi reactors containing a heating/cooling jacket or at a high-throughput platform

available at the Eindhoven University of Technology (developed by DSM Research and BP Chemicals), consisting of eight independently operated 125 mL Premex reactors. A preweighed amount of catalyst (**2** and **3** or **2** and **3** plus 1000 equiv of  $\text{Al}(i\text{-Bu})_3$ ) was dissolved in toluene (100 mL for Büchi reactors, 50 mL for the HTE platform) under  $\text{N}_2$  prior to loading the reaction vessel. Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. Polymerizations were quenched by release of the pressure and addition of EtOH and HCl. The polymers obtained were isolated by filtration, sonicated with a solution of HCl, rinsed, and thoroughly dried prior to measuring the mass. The reaction mixtures of the oligomerization runs were cooled to  $0\text{ }^\circ\text{C}$  prior to releasing the overpressure and quenching with EtOH and HCl.

**X-ray Crystallography.** Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data



**Figure 1.** Thermal ellipsoid plot of **2** with ellipsoids drawn at the 50% probability level.



**Figure 2.** Thermal ellipsoid plot of **3** with ellipsoids drawn at the 50% probability level.



**Table 3. Oligomerization and Polymerization Results for Complexes 1–3 with and without Cocatalysts<sup>a</sup>**

cat.	amt of TIBA (equiv)	activity <sup>c</sup>	amt of PE (g)	amt of 1-hexene (mL)	mol wt	PDI
<b>1</b>	500	415 <sup>b</sup>	trace	4		
<b>1</b>	1000	801 <sup>b</sup>	1.5	8		
<b>2</b>		820 <sup>c</sup>	8.2		1 300 000	3.2
<b>2</b>	500	402 <sup>b</sup>	0.5	4		
<b>2</b>	1000	807 <sup>b</sup>	0.2	8		
<b>3</b>		1450 <sup>c</sup>	14.5	2	1 400 000	3.0
<b>3</b>	500	399 <sup>b</sup>	2.0	4		
<b>3</b>	1000	800 <sup>b</sup>	0.8	8		

<sup>a</sup> Conditions: 20  $\mu$ mol, 50  $^{\circ}$ C, 35 bar, 30 min. <sup>b</sup> In units of mL of  $C_6^2/(mol\ of\ Cr)\ h$ . <sup>c</sup> In units of g of PE/(mmol of Cr) h.

collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. Data collection was performed with three batch runs at  $\psi = 0.00^{\circ}$  (600 frames), at  $\psi = 120.00^{\circ}$  (600 frames), and at  $\psi = 240.00^{\circ}$  (600 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on  $F^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions, with the exception of the hydride in **3**, whose position was yielded by the difference Fourier maps. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library. Relevant crystal data and bond distances and angles are given in Tables 1 and 2, respectively.

## Results and Discussion

In a previous paper<sup>11</sup> we described that  $[(t\text{-Bu})\text{NPN}(t\text{-Bu})_2]\text{Cr}$  (**1**) affords 1-hexene upon activation with  $\text{Al}(i\text{-Bu})_3$  along with a small amount of polymer. In an attempt to isolate this trimerization catalyst, we have reacted **1** on a preparative scale with 2 equiv of  $\text{Al}(i\text{-Bu})_3$  in toluene. The reaction afforded the new paramagnetic species  $\{\mu\text{-}[(t\text{-Bu})\text{NP}(i\text{-Bu})\text{N}(t\text{-Bu})]\text{Al}(i\text{-Bu})_2\}_2\text{Cr}$  (**2**) as dark brown crystals ( $\mu_{\text{eff}} = 4.74\ \mu_{\text{B}}$ ) (Scheme 1).

The crystal structure of **2** (Figure 1) revealed the connectivity as consisting of a divalent chromium atom in a square-planar coordination environment. Both NPN ligands have undergone the same addition of  $i\text{-Bu}$  and  $\text{Al}(i\text{-Bu})_2$  residues across the  $\text{N}=\text{P}$  formal double bond. As a result, the P atom was alkylated, the ligand acquired a second negative charge, and the  $\text{Al}(i\text{-Bu})_2$  cationic residue was retained through coordination to the two N atoms.

Treatment of **2** with 8 equiv of  $\text{Al}(i\text{-Bu})_3$  or a convenient one-pot synthesis via reaction of **1** with 10 equiv afforded the dinuclear hydride-bridged  $\{\mu\text{-}[(i\text{-Bu})\text{P}[\text{N}(t\text{-Bu})_2]\text{Al}(i\text{-Bu})_2]\text{Cr}(\mu\text{-H})_2\}_2$  (**3**) as dark purple crystals. Complex **3** is paramagnetic ( $\mu_{\text{eff}} = 1.63\ \mu_{\text{B}}$ ) with the magnetic moment expected on the basis of the presence of a fairly short Cr–Cr distance ( $\text{Cr}(1)\cdots\text{Cr}(1a) = 2.6142\ \text{\AA}$ ) and two bridging hydrides.<sup>12</sup> The  $^1\text{H}$  NMR spectrum showed only broad and overlapping features in the range  $-20$  to  $+20$  ppm which could not be conclusively assigned (see the Supporting Information).

The salient features of the crystal structure of **3** (Figure 2) are the replacement of one alkylated ligand system by one hydride, which bridges an identical unit by forming a  $\text{Cr}_2\text{H}_2$  core. Different from the case for **2**, the ligand adopted a

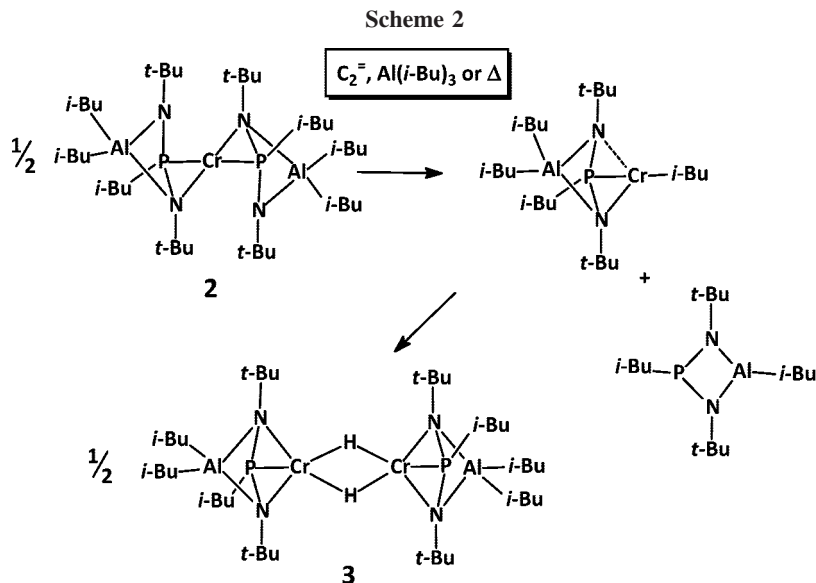
“tridentate” facial type of bonding mode in the sense that both nitrogen and phosphorus coordinate the chromium center. This is of course in the event that we consider the short Cr–P contact ( $\text{Cr}\text{--}\text{P} = 2.6178(15)\ \text{\AA}$ ) as a genuine bond. Depending on this, the coordination geometry can be considered as either square planar or distorted square pyramidal. This difference is most likely the result of the release of steric compression and increased Lewis acidity of the metal as arising from the loss of one ligand system. The position of the two bridging hydrogen atoms was yielded by the difference Fourier maps. The intermetallic distance is consistent with that observed in the other very few existing divalent chromium hydrides.<sup>12</sup>

Given the structure of **3**, it is reasonable to propose that the role of the excess of  $\text{Al}(i\text{-Bu})_3$  during its formation from either **1** or **2** is 2-fold: (1) abstracting one ligand system and (2) producing an unstable  $i\text{-Bu}\text{--}\text{Cr}$  group which, upon H-elimination reaction, generates the hydride. Conversely, other possibilities such as isobutene elimination of  $(i\text{-Bu})_3\text{Al}$  affording  $(i\text{-Bu})_2\text{Al}(\mu\text{-H})_2\text{Al}(i\text{-Bu})_2$  as a possible source of hydride cannot be conclusively ruled out. However, attempts to more directly obtain **3** via reaction of **1** with  $(i\text{-Bu})_2\text{Al}(\mu\text{-H})_2\text{Al}(i\text{-Bu})_2$  afforded complete decomposition to metallic chromium. Well-characterized chromium hydrides are rare.<sup>12</sup> Divalent chromium hydrides are exclusively limited to one cubane structure of the  $\text{Cp}^*\text{Cr}$  moiety,<sup>12b–d</sup> one dinuclear structure with a  $\text{Cr}_2\text{H}_2$  core similar to that of **3**,<sup>12f</sup> two cases of the NaCNac ligand system,<sup>12g,h</sup> and two terminally bonded phosphine complexes.<sup>12a,i,j</sup> In the present case, it is the first time that a chromium hydride is actually active as a single-component polymerization catalyst (Table 3). The single-component catalytic behavior of **3** can be easily explained by assuming dimer-to-monomer dissociation, ethylene coordination, and insertion into the Cr–H bond. It is interesting to observe that the complex contains Cr in its divalent state. Thus, assuming that reaction with ethylene does not result in an oxidation of the metal center, neutral, divalent chromium is responsible for ethylene polymerization.

Complex **2**, which does not have a preformed Cr–C bond, is also active as a single-component polymerization catalyst. The single-component character of **2** is most likely due to a spontaneous conversion of **2** into **3** under the polymerization conditions (Scheme 2), given that both **2** and **3** produce polyethylenes with basically identical activities, molecular weights, and polydispersities. It is tempting to speculate that a similar formation of chromium hydrides might be responsible for the ubiquitous presence of polyethylene in variable amounts during the oligomerization processes. The catalytic activity of the single component **3** is of the same order of magnitude as for the most active chromium catalyst precursors.<sup>5d,13</sup>

Upon activation with a large excess of  $\text{Al}(i\text{-Bu})_3$ , both **2** and **3** show a switching of selectivity from ethylene polymerization to selective trimerization. Given that also complex **1** affords a selective ethylene trimerization catalyst upon treatment with an excess of  $\text{Al}(i\text{-Bu})_3$ , it is reasonable to assume that the same active species is generated regardless which of the three complexes has been used as a precursor. This is also affirmed by the nearly identical catalytic activities observed for the three species. It is most unfortunate that the actual active trimerization catalyst has so far escaped crystallographic characterization. At this stage we can only reiterate that it is the *large excess* of  $\text{Al}(i\text{-Bu})_3$  that triggers this further transformation toward the selective trimerization catalyst. Oxidation to the trivalent state via a disproportionation,<sup>10</sup> similar to the case of the Sasol “SNS”

(13) For example see: Randoll, S.; Jones, P. G.; Tamm, M. *Organometallics* **2008**, *27*, 3232, and references cited therein.



catalyst, is certainly a possibility. Alternatively, the formation of the coordinatively unsaturated Cr(I) species  $\{\mu-[(t\text{-Bu})\text{NP}(i\text{-Bu})\text{N}(t\text{-Bu})]\text{Al}(i\text{-Bu})_2\}\text{Cr}$ , possibly with the formation of a toluene complex,<sup>14</sup> is another realistic possibility. Further attempts to clarify the nature of this compound and its oxidation state are in progress at the moment.

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(14) (a) La Macchia, G.; Gagliardi, L.; Power, P. P.; Brynda, M. *J. Am. Chem. Soc.* **2008**, *130*, 5104. (b) Kreisel, K. A.; Yap, G. P. A.; Dmitrenko, O.; Landis, C. R.; Theopold, K. H. *J. Am. Chem. Soc.* **2007**, *129*, 14162.

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**Supporting Information Available:** CIF files and tables giving complete crystallographic data for the complexes reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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