

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 January 2009 (15.01.2009)

PCT

(10) International Publication Number
WO 2009/006979 A3

(51) International Patent Classification:

B01J 31/18 (2006.01) *C07C 2/36* (2006.01)
B01J 31/14 (2006.01) *C07F 9/46* (2006.01)

(21) International Application Number:

PCT/EP2008/004815

(22) International Filing Date: 16 June 2008 (16.06.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

07013543.9 11 July 2007 (11.07.2007) EP

(71) Applicants (for all designated States except US): **LINDE AG** [DE/DE]; Leopoldstrasse 252, 80807 Munich (DE). **SAUDI BASIC INDUSTRIES CORPORATION** [SA/SA]; P.O. Box 5101, Riyadh 11422 (SA).

(71) Applicant and

(72) Inventor: **MÜLLER, Bernd, H.** [DE/DE]; Gellertstr. 7, 18057 Rostock (DE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **FRITZ, Peter, M.** [DE/DE]; Truderinger Strasse 21, 82008 Unterhaching (DE). **BÖLT, Heinz** [DE/DE]; Schiessstättstrasse 12b, 85515 Wolfratshausen (DE). **WÖHL, Anina**

[DE/DE]; Wolfratshausener Str. 86a, 82049 Pullach (DE). **MÜLLER, Wolfgang** [DE/DE]; Jasperallee 36, 81245 Munich (DE). **WINKLER, Florian** [DE/DE]; Holzstr. 49, 80469 Munich (DE). **WELLENHOFER, Anton** [DE/DE]; Torriweg 33, 81247 München (DE). **ROSENTHAL, Uwe** [DE/DE]; Hahnenkamp 9, 18069 Lambrechtshagen (DE). **HAPKE, Marko** [DE/DE]; Thomas-Müntzer-Platz 13, 18057 Rostock (DE). **PEULECKE, Normen** [DE/DE]; Buhnenweg 3, 23968 Wismar (DE). **AL-HAZMI, Mohammed, Hassan** [SA/SA]; c/o Saudi Basic Industries Corporation, P.O. Box 5101, 11422 Riyadh (SA). **ALIYEV, Vugar, O** [SA/SA]; SABIC R & T Complex, P.O. Box 42503, 11551 Riyadh (SA). **MOSA, Fuad, Mohammed** [SA/SA]; c/o Saudi Basic Industries Corporation, P.O. Box 42503, 11551 Riyadh (SA).

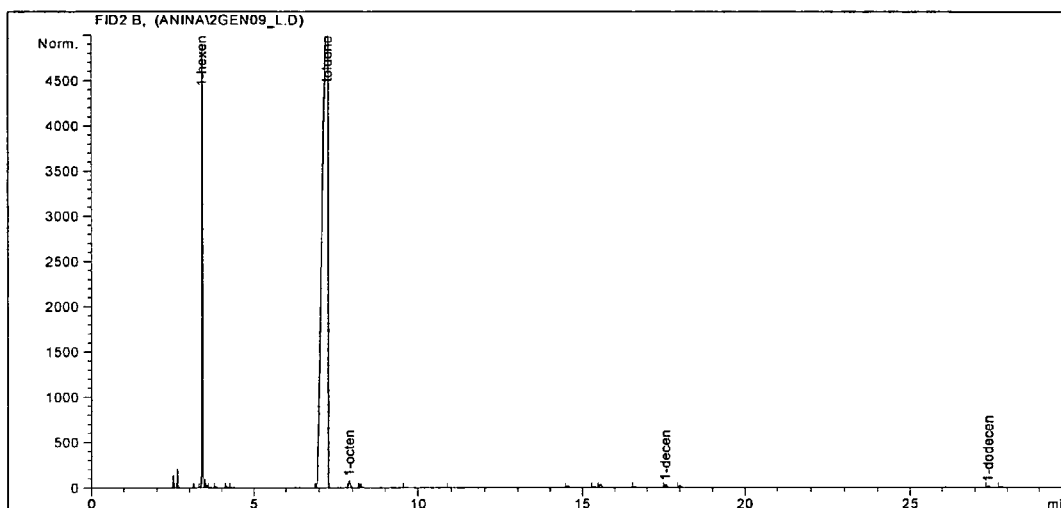
(74) Agent: **BOEHMERT & BOEHMERT**; Volker Scholz, Hollerallee 32, 28209 Bremen (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN,

[Continued on next page]

(54) Title: CATALYST COMPOSITION AND PROCESS FOR DI-, TRI- AND/OR TETRAMERIZATION OF ETHYLENE

Fig. 1: GC/FID analysis of the liquid phase. Experimental conditions according to example 2.



(57) Abstract: The present invention relates to a catalyst composition and a process for di-, tri- and/or tetramerization of ethylene, wherein the catalyst composition comprises a chromium compound, a ligand of the general structure (A) $R_1R_2P-N(R_3)-P(R_4)-N(R_5)-H$ or (B) $R_1R_2P-N(R_3)-P(R_4)-N(R_5)-PR_6R_7$, or any cyclic derivatives of (A) and (B), wherein at least one of the P or N atoms of the PNP-unit or PNPNP-unit is member of a ring system, the ring system being formed from one or more constituent compounds of structures (A) or (B) by substitution and a co-catalyst or activator.

WO 2009/006979 A3



MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) Date of publication of the international search report:
26 March 2009

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/004815

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J31/18 B01J31/14 C07C2/36 C07F9/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C07C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/057458 A (SHELL INT RESEARCH [NL]; DE BOER ERIC JOHANNES MARIA [NL]; VAN DER HEI) 24 May 2007 (2007-05-24) page 8, line 17 - page 9, line 5 page 16, line 22 - page 17, line 6 claims	1-17
A	WO 02/04119 A (BP CHEM INT LTD [GB]; WASS DUNCAN FRANK [GB]) 17 January 2002 (2002-01-17) page 3, line 28 - page 4, line 2 page 4, lines 13-18; claims 7,9,10,17,19,26,27,29-37,43,44 ----- -/--	1-17

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

30 January 2009

Date of mailing of the international search report

09/02/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

Goebel, Matthias

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/004815

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DIXON J T ET AL: "Advances in selective ethylene trimerisation - a critical overview" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 689, no. 23, 15 November 2004 (2004-11-15), pages 3641-3668, XP004629409 ISSN: 0022-328X cited in the application the whole document</p>	1-17
A	<p>MCGUINNESS DAVID S ET AL: "Cocatalyst Influence in Selective Oligomerization: Effect on Activity, Catalyst Stability, and 1-Hexene/1-Octene Selectivity in the Ethylene Trimerization and Tetramerization Reaction" ORGANOMETALLICS, ACS, WASHINGTON, DC, US, vol. 26, no. 10, 10 April 2007 (2007-04-10), pages 2561-2569, XP002443443 ISSN: 0276-7333 the whole document</p>	1-17
A	<p>WO 97/37765 A (BP CHEM INT LTD [GB]; DOSSETT STEPHEN JOHN [GB]) 16 October 1997 (1997-10-16) claims 3,13,20; examples 5,9</p>	1,12
A	<p>WO 01/10876 A (BP CHEM INT LTD [GB]; WASS DUNCAN FRANK [GB]) 15 February 2001 (2001-02-15) claim 13</p>	1,12
A	<p>WRACKMEYER, BERND ET AL: "The first 1,3,2-diazaphospha-[3]ferrocenophanes" INORGANIC CHEMISTRY COMMUNICATIONS, 7(7), 884-888 CODEN: ICCOFP; ISSN: 1387-7003, 8 June 2004 (2004-06-08), XP002464832 pages 884-885; figure 1; compound 4B</p>	1,12
A	<p>KEAT R ET AL: "Preparation of bis-(N-alkyl-N-diphenylphosphinoamino)phenylphosphines and their reactions with sulphur and methyl iodide" JOURNAL OF THE CHEMICAL SOCIETY A, 1970, pages 2715-2719, XP009094476 the whole document</p>	1,12

-/--

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/004815

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BURFORD, NEIL ET AL: "Sequential dehydrochloride coupling of trichlorophosphine with 2,6-di-isopropylaniline: aminophosphine precursors to phosphetidines" CANADIAN JOURNAL OF CHEMISTRY , 80(11), 1404-1409 CODEN: CJCHAG; ISSN: 0008-4042, 7 October 2002 (2002-10-07), XP002464833 page 1404 - page 1407; figures 1,2; compounds 5, 7	1,12
A	SCHERER, OTTO J. ET AL: "Synthesis and isolation of cis- and trans-1,3,2.lambda.3,4.lambda.3-diazadiphosphetidine" ANGEWANDTE CHEMIE INT. ED. ENGL., vol. 15, no. 12, 1976, pages 772-772, XP002464834 the whole document	1,12
A	KATZ, STEPHANIE A. ET AL: "Diastereoselectivity in the Formation of Skeletally Stabilized Phosphazanes" INORGANIC CHEMISTRY , 33(9), 1762-9 CODEN: INOCAJ; ISSN: 0020-1669, 1994, XP002464835 page 1762 - page 1765; compounds 2, 5, 11-13	1,12
A	HELM, MONTE L. ET AL: "Synthesis, Characterization, and Solution Properties of Skeletally Stabilized Triphosphazanes" INORGANIC CHEMISTRY , 38(13), 3167-3172 CODEN: INOCAJ; ISSN: 0020-1669, 8 June 1999 (1999-06-08), XP002464836 abstract page 3167 - page 3170; compounds 5, 6, 8	1,12
A	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MOSKVA, V. V. ET AL: "N,N'-Diphosphorylated 1,3,2-diazaphospholanes" XP002464838 retrieved from STN Database accession no. 1985:523606 abstract & ZHURNAL OBSHCHEI KHIMII , 55(4), 935-6 CODEN: ZOKHA4; ISSN: 0044-460X, 1985,	1,12

-/--

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/004815

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>MUNDT, CORNELIA ET AL: "N-Phosphorylated 1,3,2-oxaza- and 1,3,2-diazaphospholanes and phosphorinanes"</p> <p>PHOSPHORUS, SULFUR AND SILICON AND THE RELATED ELEMENTS , 88(1-4), 75-81 CODEN: PSSLEC; ISSN: 1042-6507, 1994, XP009094587 pages 79-80</p> <p>pages 75-77; compounds 3, 4, 7, 9</p> <p>-----</p>	1,12
A	<p>WANNAGAT, U. ET AL: "Novel inorganic ring systems. XXIV. Attempts at preparation of phosphorus nitrogen-silicon containing ring systems"</p> <p>ZEITSCHRIFT FUER ANORGANISCHE UND ALLGEMEINE CHEMIE , 420(2), 119-31 CODEN: ZAACAB; ISSN: 0044-2313, 1976, XP002464837 pages 126-127; compound VIII</p> <p>-----</p>	1,12
A	<p>GUDAT, DIETRICH ET AL: "Synthesis, structure, and chemical reactivity of a stable pentamethylcyclopentadienyl-substituted phosphanylium ion: (pentamethylcyclopentadienyl)(tert-butylamino)phosphanylium tetrachloroaluminate"</p> <p>JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS: INORGANIC CHEMISTRY (1972-1999) , (4), 693-700 CODEN: JCDTBI; ISSN: 0300-9246, 1989, XP009094571 the whole document</p> <p>-----</p>	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/004815

Patent document cited in search report		Publication date	Patent family member(s)	Publication date			
WO 2007057458	A	24-05-2007	AU 2006314445 A1	24-05-2007			
			CA 2629889 A1	24-05-2007			
			CN 101351424 A	21-01-2009			
			EP 1951645 A1	06-08-2008			
			KR 20080080570 A	04-09-2008			
			US 2007185357 A1	09-08-2007			
			WO 0204119	A	17-01-2002	AR 028795 A1	21-05-2003
AU 6774301 A	21-01-2002						
BG 107539 A	30-09-2003						
BR 0112470 A	29-07-2003						
CA 2412990 A1	17-01-2002						
CN 1630554 A	22-06-2005						
EG 22912 A	30-10-2003						
EP 1299189 A1	09-04-2003						
HU 0400497 A2	28-05-2004						
JP 2004502527 T	29-01-2004						
MX PA03000301 A	05-04-2004						
NO 20030108 A	13-02-2003						
PL 358746 A1	23-08-2004						
RU 2299096 C2	20-05-2007						
SK 172003 A3	11-09-2003						
TW 562696 B	21-11-2003						
US 2003166456 A1	04-09-2003						
ZA 200210392 A	05-11-2003						
WO 9737765	A	16-10-1997				AU 2302797 A	29-10-1997
						DE 69727460 D1	11-03-2004
			DE 69727460 T2	01-07-2004			
			EP 0850105 A1	01-07-1998			
			ES 2216137 T3	16-10-2004			
			JP 4027423 B2	26-12-2007			
			JP 11506981 T	22-06-1999			
			US 6018016 A	25-01-2000			
WO 0110876	A	15-02-2001	AU 6000100 A	05-03-2001			
			DE 60034795 T2	20-09-2007			
			EP 1208108 A1	29-05-2002			
			US 2003018141 A1	23-01-2003			