

METHOD FOR PURIFYING A CRUDE PNPNH COMPOUND

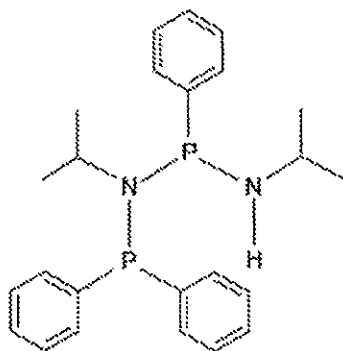
BACKGROUND

[0001] The present invention relates to a purification method for a crude PNPNH-compound.

[0002] Compounds having the general structure PNPNH are well known ligand systems which can be successfully used in a catalyst for the oligomerization of ethylene. Here, they function as ligands to be reacted with, preferably, chromium catalysts. Together with a suitable cocatalyst such a system is effective in the di-, tri- and/or tetramerization of ethylene.

[0003] For example, EP 2 239 056 B1 describes a catalyst composition and a process for the di-, tri- and/or tetramerization of ethylene. The catalyst composition comprises a chromium compound, a ligand of the general structure $R_1R_2P-N(R_3)-P(R_4)-N(R_5)-H$ and a co-catalyst acting as activator. The ligand's substituents R_1 , R_2 , R_3 , R_4 , and R_5 are independently selected from a number of functional groups, comprising (among others) C_1 - C_{10} -alkyl, aryl and substituted aryl. The chromium source is $CrCl_3(THF)_3$, $Cr(III)$ acetyl acetonate, $Cr(III)$ octanoate, Cr -hexacarbonyl, $Cr(III)$ -2-ethylhexanoate or (benzene)tricarbonyl-chromium (wherein THF is tetrahydrofuran). The co-catalyst or activator is trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, ethylaluminumsesquichloride, diethylaluminum chloride, ethylaluminum dichloride, methylaluminoxane, or a combination comprising at least one of the foregoing.

[0004] A preferred choice of catalyst constituents comprises $CrCl_3(THF)_3$ as chromium source, triethylaluminum as activator, and $(Ph)_2P-N(i-Pr)-P(Ph)-N(i-Pr)-H$ as ligand for the catalytically active complex as shown below



where Ph is a phenyl group and i-Pr is an isopropyl group. This ligand features the typical PNP-N-H-backbone, which is why this class of compounds, regardless of the precise nature of its substituents, is often referred to as a “PNPNH-ligand”.

[0005] WO 2009/006979 A2 describes essentially modified catalyst systems of the general type already disclosed in EP 2 239 056 B1. These modified systems take advantage from the same PNP-NH – type ligands. However, now a “modifier” is added to the system, (but not limited to) ammonium or phosphonium salts of the type $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$ or $[ER_4]X$ (with E = N or P, X = Cl, Br or I and R = alkyl, cycloalkyl, acyl, aryl, alkenyl, alkynyl etc.).

[0006] Preferred embodiments of the invention disclosed in WO 2009/006979 A2 involve, for instance, modifiers such as tetraphenylphosphonium chloride, tetraethylammonium chloride – monohydrate, triethylamine – hydrochloride etc. Also, as a “type $[ER_4]X$ ” – modifier, dodecyltrimethylammonium chloride can advantageously be used, due to its low price, abundant supply and good solubility in the reaction solution.

[0007] In fact, the specifically designed coordination behaviour of the PNP-NH ligands is largely the origin of the high selectivities of the catalytically active chromium complexes. Clearly, the high product selectivities are of great importance for the economic viability of the technical process.

[0008] Of course, a high selectivity directly results in a minimization of undesired side products in the technical oligomerization process. It is therefore evident that the “key ingredients” of the catalyst have to be produced on technical scale with the highest possible quality.

[0009] The laboratory procedure for the preparation of the PNP-NH ligand, as demonstrated in Example 1 below, gives a material of good quality. Hexane is assumed to be a good recrystallization solvent due to its non-polar properties.

[0010] Using the ligand from the laboratory bench-scale synthesis in standardized catalytic tests of the ethylene trimerization to 1-hexene, it is easily possible to obtain overall 1-hexene yields of 91-93 weight percent at 1-hexene purities of 99.0-99.3 % with hardly any detectable wax/polymer formation.

[0011] While being transferred to technical scale, however, this laboratory procedure regularly needs some modifications so as to meet the requirements imposed by boundary conditions in a technical environment. For example, in order to avoid hot spots in the reaction mass, it might be advisable to change the dosing sequence and/or dosing speed of some of the ingredients. Furthermore, reaction temperatures as low as -40°C will, most likely, turn out to

be unfavourable or even not feasible on technical scale. Moreover, solvents may have to be recycled.

[0012] Even after optimization of the ligand's production process on technical scale, it does not seem to be possible to reach a ligand quality, i.e., purity, comparable to the product synthesized using the laboratory procedure.

[0013] One of the most severe problems in all known technical-scale oligomerization processes is the formation of long-chain by-products such as waxes and polyethylene. Clearly, this leads to frequent fouling of equipment such as reactor inner surfaces, heat exchangers, etc. Moreover, wax or polymer formation can lead to plugging of tubing, valves, pumps, and other equipment, making frequent plant shut downs for purging/cleaning and maintenance of equipment necessary.

[0014] The measured formation rate of waxes/polymers has to be considered in the design of a commercial ethylene oligomerization plant. Adequate minimization measures and handling procedures for these undesired by-products are inevitable in order to allow for commercially successful plant operation.

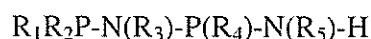
[0015] Having in mind that, as already pointed out above, a high selectivity results directly in a minimization of undesired side products in this technical process, the "key ingredients," i.e. especially the ligand, has to be produced on technical scale with the highest possible quality.

[0016] The attempt to purify crude PNPNH compound by vacuum distillation using a thin-film evaporator turned out to be rather unsuccessful, since there was hardly any separation effect between the ligand and the impurities.

[0017] There accordingly remains a need in the art for a method for purifying a crude PNPNH compound (ligand). Preferably the method is easy to perform with only few process steps.

SUMMARY

[0018] A method for purifying a crude PNPNH compound of the general structure



wherein R_1 , R_2 , R_3 , R_4 and R_5 are independently halogen, amino, trimethylsilyl, C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, C_6 - C_{20} -aryl and substituted C_6 - C_{20} -aryl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution,

comprising the steps:

A.

- a) dissolving the crude PNPNH-compound in a C₁-C₁₀ alcohol or mixture thereof under heating;
- b) cooling the solution obtained in step a),
- c) precipitating the PNPNH compound, separating and optionally drying, or

B.

- (i) washing the crude PNPNH compound with C₁-C₁₀ alcohol or a mixture thereof,
- (ii) separating the PNPNH compound and optionally drying thereof.

DETAILED DESCRIPTION

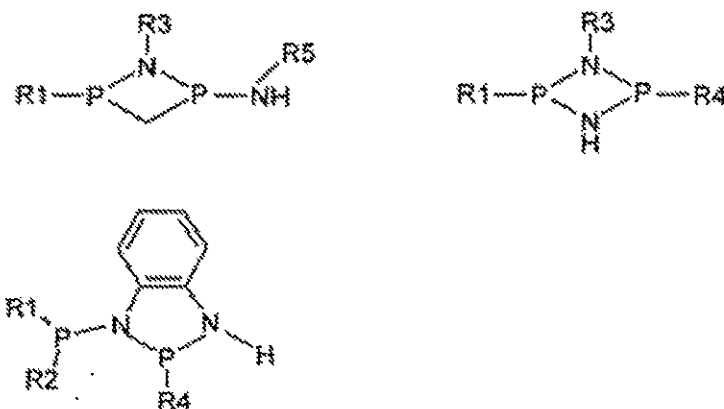
[0019] As used herein, the term PNPNH is to be understood to represent the general structure R₁R₂P-N(R₃)-P(R₄)-N(R₅)-H.

[0020] The present invention is related to the purification of a crude PNPNH compound. As the term “crude” might be somewhat open and unclear, the method of the present invention is to be understood that the PNPNH compound obtained after being processed in the inventive method has higher purity than the starting material. That means, the extent of purity of the “crude” starting material is not relevant, as long as the final product obtained has a higher purity than the starting material.

[0021] As is to be understood, any cyclic derivative of the PNPNH compound can be utilized, wherein at least one of the P or N atoms of the PNPN-unit is a ring member, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, i.e., .e., by formally eliminating per constituent compound either two whole groups R₁-R₅ (as defined above) or H, one atom from each of two groups R₁-R₅ (as defined above) or a whole group R₁-R₅ (as defined above) or H and an atom from another group R₁-R₅ (as defined above), and joining the formally so created valence-unsaturated sites by one covalent bond per constituent compound to provide the same valence as initially present at a given site. In an embodiment, the ring is formed by substitution of one or more, preferably two of the constituents of one PNPNH molecule. In other words, the cyclic derivative can include a ring system formed by removal of two of groups R₁-R₅ (as defined above) or H from one PNPNH molecule, with formation of a covalent bond in place of the groups. The cyclic derivative can include a ring system formed

by removal of an atom from two of the groups R_1 - R_5 (as defined above) or H from one PNPNH molecule, with formation of covalent bond in place of the atoms. Alternatively, the cyclic derivative can be formed by removal of one of the groups R_1 - R_5 (as defined above) or H from one PNPNH molecule, and an atom from one of the groups R_1 - R_5 (as defined above) or H from the same PNPNH molecule, with formation of a covalent bond in place of the removed group and the atom.

[0022] Suitable cyclic derivatives can be as follows:



[0023] A preferred solvent for dissolving the crude PNPNH compound in step a) can be toluene, n-hexane, cyclohexane, 1-hexene, or mixtures thereof, preferably toluene.

[0024] The separation in step c) can be preferably achieved by filtration or centrifugation. The optional washing can be done with pure solvent.

[0025] Preferably, the crude PNPNH compound is dissolved in step a) in or is washed in step (i) with C_1 - C_5 alcohol, preferably ethanol.

[0026] More preferably, the ethanol/ligand weight ratio is from 5.0-0.1, preferably 1.0-0.3.

[0027] Even preferred, heating in step a) is to a temperature of about 50-100°C.

[0028] More preferred, the solution in step b) is cooled to temperature between -20 - +20°C, preferably 0-10°C.

[0029] More preferred, PNPNH seed crystals are added before or in step b) and/or c).

[0030] In one preferred embodiment, the precipitate obtained in step c) is washed with C_1 - C_5 alcohol, preferably at a temperature of 0-25°C, and is then dried at 10-50°C, preferably 15-25°C, in vacuum of 5.0-500 millibar, preferably 10-100 millibar.

[0031] Preferably, washing in step i) is at a temperature of about 0-25°C, more preferably 15-25°C

[0032] Finally preferred, the C₁-C₁₀ alcohol is removed in step ii) by drying at 10-50°C, preferably 15-25°C, in vacuum of 5.0-500 mbar, preferably 10-100 mbar.

[0033] The inventive method yields a white crystalline powder with a melting point of 56°C and a purity in excess of 99.0 weight percent. The purified ligand can be directly used in a selective ethylene-oligomerization process.

[0034] It was surprisingly found that it is the quality/purity of the ligand system in a process for oligomerization of ethylene which is essential for avoiding wax/polyethylene formation. PE/wax formations of less than 0.30 weight percent, based on the total amount of oligomers/polymers obtained in such a process, can be achieved, while ligand systems prepared according to the art resulted in PE/wax formation of significantly higher amounts.

[0035] It was further surprisingly found that the crude ligand material can be successfully recrystallized from C₁-C₁₀ alcohols, especially ethanol. Ethanol can be regarded as an "R-substituted water" (R = ethyl) and it is known that the ligand is not totally stable against hydrolysis, especially in the presence of traces of acids. Nevertheless, it was found that, preferably under proper re-crystallization conditions and through careful kinetic control, the hydrolysis-analogous alcoholysis can be slowed down to an extent more than sufficient to effort a very satisfactory purification effect.

[0036] Utilizing the purified PNPNH ligand obtained according to the present method in the oligomerization of ethylene provides strong reduction of side-product wax and polyethylene formation, extension of oligomerization equipment's time on stream, less frequent shutdowns for purging, cleaning and maintenance, mitigation of equipment fouling, lower chances of operational upset conditions due to plugged equipment and, in summary, improvement of the plant operability in general.

[0037] As a further surprising fact, it was found that none of other possible candidates for the "key factors," i.e. key factors influencing a wax/polyethylene formation, showed any significant or discernable effect on polymer formation. Such further key factors can be, e.g., intrinsic mechanistic reasons linked to the metallocycle mechanism that is considered the origin of the high selectivity towards preferred oligomers, metallic impurities introduced as trace amounts of Fe, Ni, Ti, Zr, etc., along with the catalyst components, surface-induced heterogeneous reactions on the reactor's inner surface, chromium hydride species, radical polymerisation mechanisms or unfavourable oxidation states of chromium.

[0038] As starting point for an effective purification method for the PNPNH compound, considerable effort was put into the investigation of the chemical nature of the

impurities. The structure of some of these impurities, as identified in the crude material after synthesis by ^{31}P -NMR and/or mass spectroscopy, are shown in Example 1 below.

[0039] These impurities were detected and characterized during a scale-up of the laboratory method to technical scale (approximately 20-100 kg per batch) using ^{31}P -NMR and/or mass spectrometry. The amount of each impurity in the crude ligand material varies, according to the crude ligand sample's history. Some of the impurities originate from the synthesis itself, others are reaction products with trace amounts of oxygen or water. The fact that the ligand is susceptible to water and air/oxygen is also important for the purification procedure as any contact with water and oxygen has to be preferably avoided.

[0040] Additional advantages and features of the method are now illustrated in the following example section.

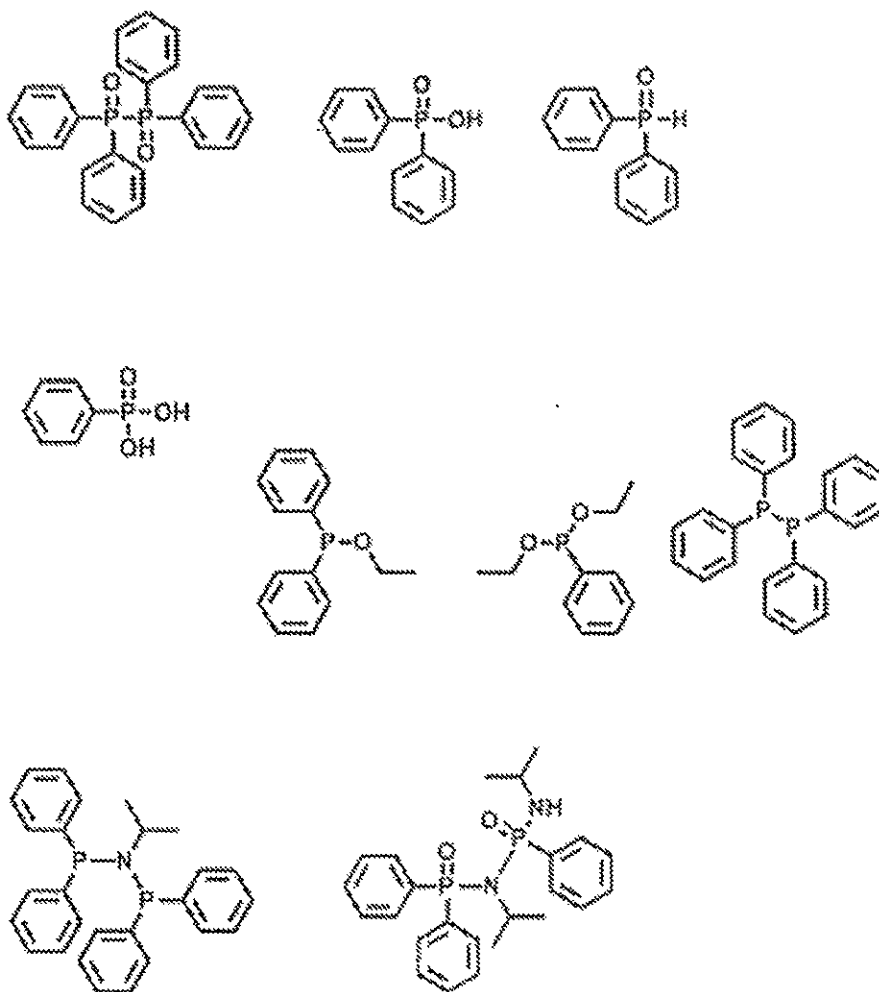
EXAMPLES

Example 1: Ligand Preparation, laboratory scale

Preparation of Bis(isopropyl-amino-)phenylphosphine (NPN)

[0041] To a stirred solution of isopropylamine (30 ml, 352 mmol) in diethyl ether (250 ml), dichlorophenylphosphine (9.63 ml, 71 mmol, dissolved in 50 ml diethylether) was added at 0°C over a period of 30 min. After stirring for a total of 72 hrs the solution was filtered. The residue was washed with diethylether and the solvent was removed in vacuum. The remaining oil was distilled at 0.2 Torr/76-78°C to give a colorless liquid with 33% yield (5.3 g). $^{31}\text{P}\{\text{H}\}$ NMR: 49.0 ppm.

[0042] Some impurities found in the crude $\text{Ph}_2\text{P-N(i-Pr)-P(Ph)-N(i-Pr)-H}$ -ligand after synthesis are shown below.



Preparation of $(\text{Ph})_2\text{PN}(\text{i-Pr})\text{P}(\text{Ph})\text{NH}(\text{i-Pr})$ (PNPN-H)

[0043] A solution of the NPN-species (2.4 g, 10.7 mmol) in tetrahydrofuran (10 ml) was added dropwise to a stirred solution of triethylamine (6 ml) and chlorodiphenylphosphine (2.36 g, 10.7 mmol) in THF (40 ml) at -40°C . After additional stirring for 24 hrs at room temperature the triethylammonium salt was filtered off and the residue was dissolved in n-hexane, filtered again, and the solution was kept at -30°C for crystallisation. Yield 52% (2.3 g, 5.6 mmol). $^{31}\text{P}\{\text{H}\}$ NMR: 41.2, 68.4 (broad).

Example 2:

Recrystallization from ethanol

[0044] For the re-crystallization the crude ligand material of 75 – 80 wt% purity is mixed with ethanol in an ethanol / ligand weight ratio of 5.0 – 0.1, preferentially 1.0 – 0.3 at ambient temperature and then heated under stirring until a clear solution without any solids is

obtained. Subsequently, the solution is rapidly cooled down to temperatures between -20 and +20°C, preferentially to 0 – 10°C, accelerating the precipitation by contacting the solution with PNPN-H seed crystals if necessary. The solid is then separated by filtration or centrifugation and washed with ethanol at 0 – 25°C.

[0045] Finally, the ethanol is removed by drying at 10-50°C, preferentially 15-25°C in vacuum 5.0-500 mbar, preferentially 10-100 mbar.

Example 3:

Washing with ethanol

[0046] Alternatively, a washing procedure with ethanol can be applied. According to that procedure, the crude material is mixed with ethanol in an ethanol / ligand weight ratio of 5.0 – 0.1, preferentially 1.0 – 0.3 at ambient temperature (20°C). The slurry is then agitated by means of a stirrer or kneader.

[0047] Subsequently, the solid PNPN-H ligand is separated by filtration or centrifugation and dried under the same conditions as in the recrystallization procedure.

Example 4:

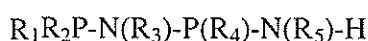
[0048] A standard ethylene oligomerization (trimerization to 1-hexene) was carried out and ligands prepared by different purification techniques were utilized. The PE/wax formation was measured. The results are given in Table 1. Table 1 shows the correlation between (Ph)₂P-N(i-Pr)-P(Ph)-N(i-Pr)-H – ligand purity and polyethylene / wax formation during ethylene trimerization to 1-hexene, measured in a standard performance test. Standard reaction conditions are: $p_{\text{ethylene}} = 30 \text{ bar}$, $T = 50^\circ\text{C}$, co-catalyst = triethylaluminum, modifier = dodecyltrimethylammonium chloride, residence time = 60 min, $[\text{Cr}] = 0.3 \text{ mmol/l}$, $[\text{Ligand}]/[\text{Cr}] = 1.75$, $[\text{Al}]/[\text{Cr}] = 25$, $[\text{Cl}]/[\text{Cr}] = 8$ (all ratios in molar units).

Table 1.

	Ligand purification technique	Appearance	Purity (³¹ P-NMR, GC), wt%*	PE/wax formation during catalytic ethylene trimerization (standard reaction conditions), wt%*
1	Crude PNPN-H directly from synthesis on technical scale	Yellow, high-viscosity liquid ("honey-like")	75 – 80	1.0 – 1.5
2	Distilled PNPN-H (low pressure thin-film evaporator)	Yellow, high-viscosity liquid ("honey-like")	86 – 87	0.8 – 1.0
3	Recrystallization of PNPN-H from hexane – solution	White crystalline powder	98.6	< 0.55
4	Recrystallization of PNPN-H from ethanol - solution	White crystalline powder, m.p. 56°C	99.2	< 0.25

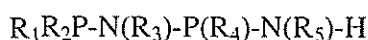
*wt%, based on total amounts of oligomers/polymers obtained

[0049] In summary, in an embodiment, a method for purifying a crude PNPNH compound of the general structure



wherein R_1 , R_2 , R_3 , R_4 and R_5 are independently halogen, amino, trimethylsilyl, C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, C_6 - C_{20} -aryl and substituted C_6 - C_{20} -aryl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, the method comprising the steps: (a) dissolving the crude PNPNH-compound in a C_1 - C_{10} alcohol or mixture thereof, preferably a C_1 - C_5 alcohol, more preferably ethanol, and preferably wherein the alcohol or ethanol/ligand weight ratio is from 5.0-0.1, preferably 1.0-0.3, under heating preferably to a temperature of about 50-100°C; (b) cooling the solution obtained in step a), preferably cooled to temperature between -20 - +20°C, more preferably 0-10°C; and (c) isolating the PNPNH compound, preferably by precipitating the PNPNH compound from the solution, separating the PNPNH compound from the solution and optionally drying the PNPNH compound, preferably wherein PNPNH seed crystals are added before or during step b) and/or c), and preferably wherein the precipitate obtained in step c) is washed with C_1 - C_5 alcohol, preferably at a temperature of 0-25°C, and is then dried at 10-50°C, preferably 15-25°C, in vacuum of 5.0-500 millibar, preferably 10-100 millibar.

[0050] In another embodiment, a method for purifying a crude PNPNH compound of the general structure



wherein R₁, R₂, R₃, R₄ and R₅ are independently halogen, amino, trimethylsilyl, C₁-C₁₀-alkyl, substituted C₁-C₁₀-alkyl, C₆-C₂₀-aryl and substituted C₆-C₂₀-aryl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPNH structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, the method comprising (i) washing the crude PNPNH compound with C₁-C₁₀ alcohol or a mixture thereof, preferably a C₁-C₅ alcohol, more preferably ethanol and preferably wherein the alcohol or ethanol/ligand weight ratio is from 5.0-0.1, preferably 1.0-0.3, preferably wherein the washing is at a temperature of about 0-25°C, preferably 15-25°C; and (ii) separating the washed PNPNH compound from the washing liquid; and optionally drying thereof, wherein the C₁-C₁₀ alcohol is removed in step ii) by drying at 10-50°C, preferably 15-25°C, in vacuum of 5.0-500 millibar, preferably 10-100 millibar.

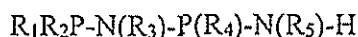
[0051] The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. “Or” means “and/or.” Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0052] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0053] The features disclosed in the foregoing description, in the claims and in the drawings may, both separately and in any combination thereof, be material for realizing the invention in diverse forms thereof.

CLAIMS

1. A method for purifying a crude PNPNH compound comprising a ligand of the general structure



wherein R_1 , R_2 , R_3 , R_4 and R_5 are independently halogen, amino, trimethylsilyl, C_1 - C_{10} -alkyl, substituted C_1 - C_{10} -alkyl, C_6 - C_{20} -aryl and substituted C_6 - C_{20} -aryl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPNH structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, wherein the substitution is by formally eliminating per constituent compound either two whole groups R_1 - R_5 or H, one atom from each of two groups R_1 - R_5 or a whole group R_1 - R_5 or H and an atom from another group R_1 - R_5 , and joining the formally so created valence-unsaturated sites by one covalent bond per constituent compound to provide the same valence as initially present at a given site,

the method comprising:

A.

- a) dissolving the crude PNPNH-compound in a C_1 - C_{10} alcohol or mixture thereof under heating, wherein an alcohol/ligand weight ratio is from 1.0-0.3;
- b) cooling the solution obtained in step a); and
- c) isolating the PNPNH compound; or

B.

- (i) washing the crude PNPNH compound with C_1 - C_{10} alcohol or a mixture thereof;
- (ii) separating the PNPNH compound; and optionally drying thereof.

2. The method according to claim 1, wherein the crude PNPNH compound is dissolved in step a) in or is washed in step (i) with a C_1 - C_5 alcohol.

3. The method according to claim 1, wherein an alcohol/ligand weight ratio in step B. (i) is from 5.0-0.1.

4. The method according to claim 1, wherein the heating in step A. a) is to a temperature of about 50-100°C.
5. The method according to claim 1, wherein the solution in step A. b) is cooled to temperature between -20 to +20°C.
6. The method according to claim 1, wherein PNPNH seed crystals are added before or during step A. b) and/or A. c).
7. The method according to claim 1, wherein a precipitate obtained in step A. c) is washed with C₁-C₅ alcohol, and is then dried at 10-50°C, in a vacuum of 5.0-500 millibar.
8. The method according to claim 1, wherein the washing in step B. (i) is at a temperature of about 0-25°C.
9. The method according to claim 1, wherein the C₁-C₁₀ alcohol is removed in step B. (ii) by drying at 10-50°C, in a vacuum of 5.0-500 millibar.
10. The method according to claim 1, wherein the crude PNPNH compound comprises an impurity comprising ligand synthesis products, ligand reaction products with oxygen and/or water, or a combination thereof.