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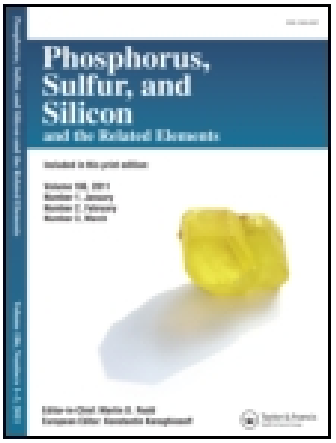

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Synthesis of Differently Substituted N- and P-Aminodiphosphinoamine PNPN-H Ligands

Marc Gongoll [a] , Bernd H. Müller [a] , Stephan Peitz [a] , Bhaskar R. Aluri [a] , Normen Peulecke [a] , Anke Spannenberg [a] , Uwe Rosenthal [a] , Mohammed H. Al-Hazmi [b] , Anina Wöhl [c] & Wolfgang Müller [c]

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SYNTHESIS OF DIFFERENTLY SUBSTITUTED N- AND P-AMINODIPHOSPHINOAMINE PNPN-H LIGANDS

Marc Gongoll,[1] Bernd H. Müller,[1] Stephan Peitz,[1] Bhaskar R. Aluri,[1] Normen Peulecke,[1] Anke Spannenberg,[1] Uwe Rosenthal,[1,*] Mohammed H. Al-Hazmi,[2] Anina Wöhl,[3] and Wolfgang Müller[3,*]

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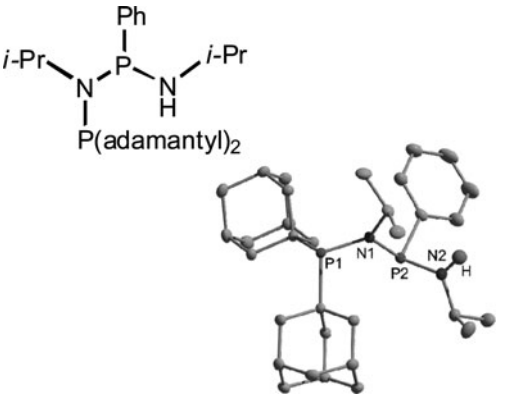
GRAPHICAL ABSTRACT



Abstract *On the basis of the known aminodiphosphinoamine ligand $Ph_2PN(i\text{-}Pr)P(Ph)N(i\text{-}Pr)\text{-}H$ (**3a**), differently substituted aminodiphosphinoamine PNPN-H ligands (**3**) were prepared. By using different synthetic methods, the N-substituted ligands $Ph_2PN(i\text{-}Pr)P(Ph)N(c\text{-}Hex)\text{-}H$ (**3b**), $Ph_2PN(c\text{-}Hex)P(Ph)N(i\text{-}Pr)\text{-}H$ (**3g**), and $Ph_2PN(i\text{-}Pr)P(Ph)N[(CH_2)_3Si(OEt)_3]\text{-}H$ (**3c**), in addition to the formerly described $Ph_2PN(n\text{-}Hex)P(Ph)N$*

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Address correspondence to Uwe Rosenthal, Leibniz-Institut für Katalyse, an der Universität Rostock e.V., Albert-Einstein-Str. 29 A, D-18059 Rostock, Germany 1 or Wolfgang Müller, Linde AG, Linde Engineering Division, Dr.-Carl-von-Linde-Str. 6-14, D-82049 Pullach, Germany. E-mail: uwe.rosenthal@catalysis.de

*(i-Pr)-H (**3h**), Ph_2PN(i-Pr)P(Ph)N(Et)-H (**3d**), Ph_2PN(i-Pr)P(Ph)N(Me)-H (**3e**), and Ph_2PN(c-Hex)P(Ph)N(c-Hex)-H (**3f**), were obtained. In addition, Ph_2PN(i-Pr)P(Me)N(i-Pr)-H (**3i**), $(cyclopentyl)_2PN$(i-Pr)P(Ph)N(i-Pr)-H (**3j**), (-O-CH_2-CH_2-O-)PN(i-Pr)P(Ph)N(i-Pr)-H (**3k**), and $(1\text{-Ad})_2PN$(i-Pr)P(Ph)N(i-Pr)-H (**3l**) were prepared with different P-substitutions. All compounds were characterized and the molecular structures of the intermediates Ph_2PN(i-Pr)P(Ph)Cl (**1a**) and $(cyclopentyl)_2PN$(i-Pr)P(Ph)Cl (**1e**) and the ligand $(1\text{-Ad})_2PN$(i-Pr)P(Ph)N(i-Pr)-H (**3l**) were investigated by single-crystal X-ray diffraction.*

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Keywords Synthesis; ligand design; N,P ligands; substituent effects

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INTRODUCTION

Mixed P and N donor ligand systems were developed and successfully applied for a variety of catalytic reactions, mostly in the field of olefin oligomerization.[1–5] Earlier, we have shown the utilization of novel PNPN-H donor ligands in homogeneous chromium-based selective trimerization reaction for 1-hexene. In particular for the Ph_2PN(*i*-Pr)P(Ph)N(*i*-Pr)-H (**3a**) ligand as the best example, we published detailed kinetic experiments and modeling.[6–10,12–15] Also, the coordination behavior of this ligand and some organometallic chemistry with relevance toward the activation and deactivation of the catalyst were investigated.[7] Now, it is interesting to synthesize such compounds with varying substituents at phosphorus and nitrogen and characterize them by using different analytical techniques including single-crystal X-ray diffraction.

The obtained compounds are interesting ligands for many purposes. In this context, a fine-tuning of electronic and steric properties by introducing different substituents is inevitable for the optimization of the performance of the respective metal complexes.

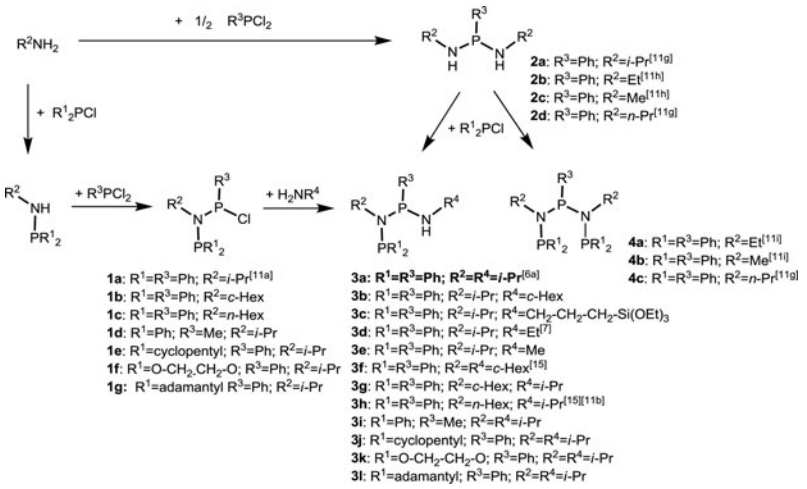
RESULTS AND DISCUSSION

The synthesis of the PNPN-H ligand can be carried out following two different routes (Scheme 1). The synthesis of Ph_2PN(*i*-Pr)P(Ph)Cl (**1a**),[11a] Ph_2PN(*i*-Pr)P(Ph)N(*i*-Pr)H (**3a**),[6] Ph_2PN(*c*-Hex)P(Ph)N(*c*-Hex)H (**3f**),[15] Ph_2PN(*c*-Hex)H (**3h**),[11b] Ph_2PN(*n*-Hex)P(Ph)N(*i*-Pr)H (**3f**),[15] Ph_2PN(*i*-Pr)P(Ph)N(Et)H,[7] Ph_2PN(*i*-Pr)H (**3d**),[11c] and $(1\text{-Ad})_2PCl$[11d,e] was described earlier. Additionally, it is worth mentioning that Ph_2PN(*i*-Pr)P(Ph)Cl (**1a**) and **3c** were useful in immobilization of the ligand.[11f]

Following a two-step process, dichlorophenylphosphine reacts with an excess of a primary amine to the diaminophenylphosphine (**2**).[11g,h] Further reaction with chlorodiphenylphosphine results in the formation of **3** or **4** depending on the substituent at the nitrogen R^2. Compounds **2b**, **2c**, and **2d** could be transformed to the *N*,*N*′-bis(diphenylphosphino)diaminophenylphosphines **4a**, **4b,** and **4c**.[11g,i] In contrast, the reaction of bis(isopropylamino)phenylphosphine (**2a**) yields Ph_2PN(*i*-Pr)P(Ph)N(*i*-Pr)-H (**3a**), even if a 10-fold excess of chlorodiphenylphosphine was used.[11g]

The formation either of **3** or **4** depends on the incorporated substituents. In some cases, the transformation of the PNPN-H ligand **3** into a PNPN-P ligand **4** seems possible.[1–5]

The two-step approach to the desired ligand type **3** (upper pathway, Scheme 1) is limited to the availability of the starting material **2**. Only compounds with equal substituents



Scheme 1 Different methods for synthesizing $R^1{}_2PN(R^2)P(R^3)N(R^4)H$ (**3**)[6].

at the nitrogen are accessible. To overcome these limitations, a three-step process was applied. Starting from a primary amine, the reaction with a chlorophosphine $R^1{}_2PCl$ produces $R^1{}_2PN(R^2)H$. Further reaction with a dichlorophosphine R^3PCl_2 results in the intermediates $R^1{}_2PN(R^2)P(R^3)Cl$ **1a–1g**, which yield the title compounds $R^1{}_2PN(R^2)P(R^3)N(R^4)H$ (**3**) by aminolysis with a primary amine (lower pathway, Scheme 1). The ligands **3a** and **3k** were proven to be accessible by both methods.

The ^{31}P NMR data of **3a–3l** at room temperature are presented in Table 1. Only the aminodiphosphino-amine PNPN-H ligands **3g** ($R^2 = c$-Hex), **3h** ($R^2 = n$-Hex), and **3l** ($R^2 = i$-Pr) show the expected pattern of two sets of sharp doublets. The ligands (**3a–3e**, **3j**, **3k**) ($R^2 = i$-Pr) give spectra with two rather broad singlets. Variable temperature ^{31}P NMR spectroscopy was performed in the case of **3a**.[11g] Different conformers of **3a**, which interconvert on the NMR time scale at room temperature, were postulated. Restricted rotation about the P−N bonds caused by the bulkiness of the *i*-Pr group is given as reason for this observation.

The $^2J_{PP}$ coupling constants presented in Table 1 show some interesting features as they cover a broad range from 14 Hz to 280 Hz. Not all are observable due to line broadening, which indicates dynamic behavior. For the NPNP compound **3a**, this has been evaluated by dynamic ^{31}P NMR spectroscopy and several conformational isomers were found that differ with respect to this $^2J_{PP}$ coupling constant.[11g] Restricted rotation about the P−N bond was made responsible for this observation. Moreover, Keat and co-workers[11a] reported strongly differing coupling constants for triphosphazanes $(Ph_2PNR)_2PPh$ (25.1 Hz for R = Et, **4a**; 280 Hz for R = Et, **4b**) and also for diphosphinoamines Ph_2P-NR-PPhCl (−35 Hz to +334 Hz, depending on the alkyl substituent R). They discussed steric factors (bulkiness of R) and the resulting different conformations about the P−N bonds as the reason. In line with these observations, we may assume that the observed variations in $^2J_{PP}$ reflect the differences in population of the possible conformational isomers, which naturally depend on the substituents.

It is worth mentioning that the ^{31}P chemical shifts for the ligands **3h**, **3i**, **3k,** and **3l** without phenyl substituents at the phosphorus atoms differ expectedly more from the other

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Table 1 ^{31}P NMR data of intermediates and compounds **1**–**4**. Solvent: C_6D_6, exceptions: [a] CD_2Cl_2, [b] $CDCl_3$, and [c] toluene-d_8

1		2		3	
1a	42.1 d; 132.0 d $^2J_{PP} = 29$ Hz[5]	**2a**	57[11h,j,k]	**3a**	41.4 br; 68.7 br
1b	48.2 br; 135.1 br	**2b**	[11k]	**3b**	40.6 br; 69.3 br
1c	66.0 d; 139.4 d $^2J_{PP} = 147$ Hz	**2c**	69[11h,j,k]	**3c**[b]	40.6 br; 72.4 br
1d	44.2 br; 144.6 d $^2J_{PP} = 23$ Hz			**3d**	41.0 br; 72.6 br
1e	58.0 d; 133.5 d $^2J_{PP} = 35$ Hz			**3e**	40.5 br; 76.6 br
1f	121.9 br; 144.5 br			**3f**	42.1 d; 68.2 br $^2J_{PP} = 18$ Hz
1g[b]	84.3; 143.1 $^2J_{PP} = 40$ Hz			**3g**	42.1 d; 68.2 d $^2J_{PP} = 18$ Hz
		4a[a]	52.8 d; 104.3 t[11a] $^2J_{PP} = 25$ Hz	**3h**	49.6 d; 80.4 d $^2J_{PP} = 60$ Hz
		4b[a]	62.3 d; 119.5 t[11a] $^2J_{PP} = 280$ Hz	**3i**	34.1 d; 58.8 br $^2J_{PP} = 14$ Hz
				3j	51.3 br; 70.7 br
				3k	61.1 br; 147.7br
				3l[c]	77.95 d, 87.7 d $^2J_{PP} = 35.0$ Hz

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examples with phenyl substituents at P1 and P2. A detailed prediction of the relevance of these spectroscopic data with respect to the general reactivity of the PNPN-H compounds is highly desirable. For example, in catalytic oligomerization of ethylene, a deprotonation of N-H occurs during catalysis.[7–10]

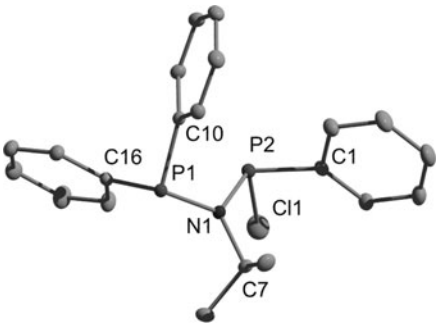

Figure 1 Molecular structure of $Ph_2PN(i\text{-}Pr)P(Ph)Cl$ (**1a**) in the crystal with thermal ellipsoids set at 30% probability level. All hydrogen atoms have been omitted for clarity. Selected atom distances [Å] and bond angles [°]: P1−N1 1.7246(9), P2−N1 1.6843(10), P2−Cl1 2.1052(10), N1−P1−C16 105.4(1), N1−P1−C10 103.0(1), C16−P1−C10 102.5(1), N1−P2−C1 101.4(1), N1−P2−Cl1 102.0(1), C1−P2−Cl1 99.1(1), C7−N1−P2 122.2(1), C7−N1−P1 116.4(1), P2−N1−P1 121.0(1). (Color figure available online).

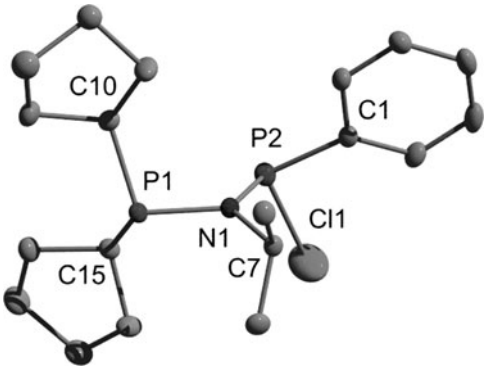

Figure 2 Molecular structure of (cyclopentyl)$_2$PN(*i*-Pr)P(Ph)Cl (**1e**) in the crystal with thermal ellipsoids set at 30% probability level. All hydrogen atoms have been omitted for clarity. Selected atom distances [Å] and bond angles [°]: P1−N1 1.7534(13), P2−N1 1.6663(12), P2−Cl1 2.1284(6), N1−P1−C15 102.7(1), N1−P1−C10 103.7(1), C15−P1−C10 100.7(1), C7−N1−P2 122.0(1), C7−N1−P1 116.7(1), P2−N1−P1 120.4(1), N1−P2−C1 102.8(1), N1−P2−Cl1 104.3(1), C1−P2−Cl1 97.7(1). (Color figure available online).

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The molecular structures of the intermediates Ph$_2$PN(*i*-Pr)P(Ph)Cl (**1a**) (Figure 1) and (cyclopentyl)$_2$PN(*i*-Pr)P(Ph)Cl (**1e**) (Figure 2) and of the ligand (1-Ad)$_2$PN(*i*-Pr)P(Ph)N(*i*-Pr)-H (**3l**) (Figure 3) were determined by singly-crystal X-ray diffraction.

The molecular structures of other PNPN-H ligands like Ph$_2$PN(^{i}Pr)P(Ph)N(^{i}Pr)-H (**3a**)[6a] and Ph$_2$PN(*i*-Pr)P(Ph)N(Et)-H (**3d**)[7] were published before so that a comparison of all structural data of the intermediates and the ligands is now possible (Table 2).

The atoms N1 are in a distorted trigonal planar environment, whereas the atoms P1 and P2 with their substituents are in a distorted trigonal pyramidal shape. The structural

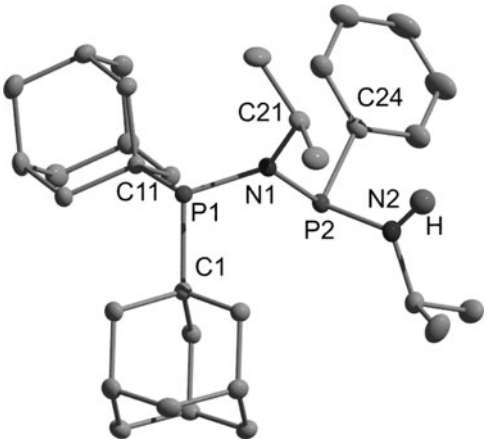


Figure 3 Molecular structure of (1-Ad)$_2$PN(*i*-Pr)P(Ph)N(*i*-Pr)-H (**3l**) in the crystal with thermal ellipsoids set at 30% probability level. All hydrogen atoms (except of hydrogen attached to nitrogen) have been omitted for clarity. Selected atom distances [Å] and angles [°]: P1−N1 1.7380(13), N1−P2 1.7168(13), P2−N2 1.6785(14), N1−P1−C11 103.8(1), N1−P1−C1 108.4(1), C11−P1−C1 109.4(1), C21−N1−P2 117.7(1), C21−N1−P1 117.5(1), P2−N1−P1 123.4(1), N2−P2−N1 108.1(1), N2−P2−C24 99.6(1), N1−P2−C24 103.0(1). (Color figure available online).

Table 2 Comparison of structural data for $Ph_2PN(i\text{-}Pr)P(Ph)Cl$ (**1a**), $(cyclopentyl)_2PN(i\text{-}Pr)P(Ph)Cl$ (**1e**), $(1\text{-}Ad)_2PN(i\text{-}Pr)P(Ph)N(i\text{-}Pr)$-H (**3l**), $Ph_2PN(^iPr)P(Ph)N(^iPr)$-H (**3a**),[6a] and $Ph_2PN(i\text{-}Pr)P(Ph)N(Et)$-H (**3d**).[7]

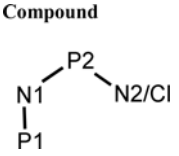
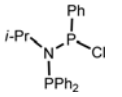
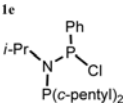
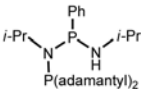
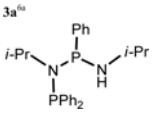
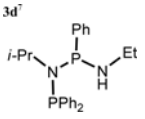
Compound		**1a** 	**1e** 	**3l** 	**3a**[6a] 	**3d**[7] 
Atom distances [Å]						
P1−N1		1.7246(9)	1.7554(13)	1.7380(13)	1.708(2)	1.7092(15)
N1−P2		1.6843(10)	1.6663(12)	1.7168(13)	1.720(2)	1.7155(14)
P2−Cl		2.1052(10)	2.1284(6)			
P2−N2				1.6785(14)	1.666(2)	1.678(2)
Angles [°]						
P1−N1−P2		121.0(1)	120.4(1)	123.4(1)	121.5(1)	123.1(1)
N1−P2−Cl		102.0(1)	104.3(1)			
N1−P2−N2				108.1(1)	106.8(1)	107.7(1)
Torsion angles [°]						
(P1−N1)−(P2−Cl)		−132.0(1)	−108.6(1)			
(P1−N1)−(P2−N2)				−122.8(1)	136.9(1)	−125.5(1)

Table 3 Crystal structure and data refinement parameters

Compound	**1a**	**1e**	**3l**
Empirical Formula	$C_{21}H_{22}ClNP_2$	$C_{19}H_{30}ClNP_2$	$C_{39}H_{58}N_2P_2$
Formula Weight	385.79	369.83	616.81
Crystal System/Space Group	*P*-1 Triclinic	*P*-1 Triclinic	*P*-1 Triclinic
a/Å	10.118(2)	10.2037(5)	10.7235(4)
b/Å	10.153(2)	10.2286(5)	11.0167(4)
c/Å	11.622(2)	11.3823(6)	15.0329(6)
α/°	73.97(3)	67.053(4)	82.176(3)
β/°	65.70(3)	67.230(4)	82.062(3)
γ/°	65.83(3)	76.754(4)	84.878(3)
V/Å^3	984.5(3)	982.40(0)	1738.06(11)
Z	2	2	2
D_{calc} (g/cm^3)	1.301	1.250	1.179
μ (mm^{-1})	0.360	0.357	0.155
Crystal size (mm)	0.50 × 0.48 × 0.45	0.60 × 0.50 × 0.22	0.45 × 0.42 × 0.19
Color/Shape	Colorless	Colorless prism	Colorless plate
Temp (K)	150(2)	150(2)	200(2)
Theta range for collection	13, 13, 15	13, 14, 15	13, 14, 19
Reflections collected	16327	18881	28888
Independent reflections	4521	5292	7989
Restraints/parameters	0/228	12/209	10/366
Goodness of fit on F^2	1.046	1.041	0.873
Final *R* indices [$I > 2\sigma(I)$]	0.0298	0.0391	0.0398
R indices (all data)	0.0736	0.1015	0.0976
Largest difference peak/hole	0.390/−0.230	0.669/−0.512	0.648/−0.340

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parameters of ligand **3l** are in the expected usual range as found in the earlier reported examples **3a** and **3d**. Only a significantly longer P1–N1 distance of 1.7380(13) compared to the phenyl analogues **3a** and **3d** is observed, caused by the steric and electronic influence of the two adamantyl substituents.

CONCLUSIONS

Synthesis of a series of aminodiphosphinoamine PNPN-H (3) compounds with varying substituents on phosphorus and nitrogen atoms is possible by using two different synthetic methods. Following a two-step process, dichlorophenylphosphine reacts with an excess of a primary amine to give diaminophenyl-phosphines H-PNPN-H (2). Depending on the used substituent at the nitrogen atom in the further reaction with chlorodiphenylphosphine either the aminodiphosphinoamines PNPN-H (3) or the *N*,*N*′-bis(diphenylphosphino)diaminophenylphosphines PNPNP (4) are formed.

The alternative three-step process consists of the reaction of a primary amine with chlorophosphines R_2PCl to give the corresponding aminophosphines, which give in reactions with dichlorophosphines $RPCl_2$ the compounds PNP-Cl (1) as intermediates and by further aminolysis with a primary amine the title compounds PNPN-H (3). General possibilities of synthesis and yields for the considered compounds and single steps strongly depend on the substituents used and the intermediates, which are described in detail. The described compounds are very potent ligands for various catalytic applications, including ethylene oligomerization.

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EXPERIMENTAL

General

All operations were carried out under argon with standard Schlenk techniques or in a glove box. Prior to use, nonhalogenated solvents (including benzene-d_6) were freshly distilled from sodium tetraethylaluminate and stored under argon. All other chemical reagents and solvents were obtained from commercial sources and used without further purification. The following spectrometers were used: NMR spectra: Bruker AV 300, AV 400, and AMX 400 (Sigma-Aldrich Co. LLC., St. Louis, Missouri, USA). Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of the used solvent: benzene-d_6 ($\delta_H = 7.16$, $\delta_C = 128.0$). Chemical shifts for ^{31}P are given relative to 85% H_3PO_4. The spectra were assigned with the help of DEPT. —Melting points: sealed capillaries, Büchi 535 apparatus. — Elemental analyses: Leco CHNS-932 elemental analyzer. Mass spectra were obtained with a MAT 95XP (Thermo) instrument at an ionizing voltage of 70 eV or for ESI mass spectrometry with an ESI-TOF-MS 6210 (Agilent). A general synthesis of aminophosphines as educts, the synthesis of the PNP-Cl intermediate **1**, and the synthesis of ligand **3** are given here. Detailed procedures of the individual compounds along with their analytical data can be found in the Supplemental Materials (available online).

Crystallographic Details

Diffraction data for compounds **1a**, **1e**, and **3l** were collected with a STOE-IPDS II diffractometer using graphite-monochromated Mo-Kα radiation. The structures were

solved by direct methods (SHELXS-97[16]) and refined by full-matrix least-squares procedures on F^2 (SHELXL-97[16]). DIAMOND was used for graphical representations.[17] The data collection and refinement parameters are given collected in Table 1 of the supplemental Materials. CCDC 912129 (**1a**), CCDC 912129 (**1e**), and CCDC 912131 (**3l**) contain supplementary crystallographic data (available online) for the structures presented in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, B2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

General Synthesis of Compounds 3 and 4

***Aminophosphines as Educts for the Synthesis of Compounds* 1a, 1d, 1e, 1f, *and* 1g.** Chlorophosphine R_2PCl was added slowly to an excess amount of isopropylamine, dissolved either in toluene or in THF at −78°C. The reaction mixture was stirred overnight while bringing it slowly from −78°C to room temperature to give a pale yellow–white suspension. Excess amine was removed under reduced pressure, the solid was filtered off, and the solvent was removed from the solution till dryness. If necessary, the product was washed with *n*-hexane or alternatively crystallized from *n*-hexane at −78°C to afford a colorless oil or powder.

***Aminophosphines as Educts for the Synthesis of Compounds* 1b *and* 1c.** Triethylamine and the required amine were dissolved either in toluene or in THF and cooled to −78°C. An equimolar (with respect to the amine) amount of diphenylchlorophosphine was added slowly to the solution and the reaction mixture was stirred overnight warming from −78°C to room temperature to give a pale yellow–white suspension. The workup was as described earlier for the educts for **1a**, **1d**, **1e**, **1f**, and **1g**.

***Synthesis of PNP-Cl Intermediates* 1a–1g.** The aminophosphine products as discussed earlier were dissolved in a mixture of toluene with triethylamine and cooled to −78°C. An equimolar amount of dichlorophenylphosphine or dichloromethylphosphine was added dropwise with stirring. The suspension was allowed to warm up to room temperature overnight. The excess of unreacted amine was removed under reduced pressure, the suspension was filtrated, and the toluene was removed till dryness. Pale-yellow oil was obtained and crystallization from *n*-hexane gave the pure product.

***Synthesis of Ligands* 3a–3l.** The PNP-Cl intermediates (**1a–1g**) were dissolved in a mixture of toluene with triethylamine and cooled to −78°C. The equimolar amount of the required amine was added slowly to the solution and the reaction mixture was stirred overnight warming from −78°C to room temperature giving a pale yellow–white suspension. The unreacted amine was removed under reduced pressure and the suspension was filtrated. Toluene was removed till dryness to yield the pure product after washing with *n*-hexane at −78°C.

***Synthesis of the NPN Intermediate 2a for the Alternative Synthesis of* 3a *and* 3k.** An excess of isopropylamine was dissolved in toluene and cooled to −78°C. Dichlorophenylphosphine was added slowly to the solution and the reaction mixture was stirred overnight warming from −78°C to room temperature to give a pale yellow–white suspension. The unreacted amine was removed under reduced pressure, the suspension was filtered, and the toluene was removed till dryness. If necessary, the product was washed with *n*-hexane at −78°C to yield the pure product.

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***Synthesis of the Ligands* 3a *and* 3k *from* 2a.** Compound **2a** was dissolved in toluene and triethylamine, the solution was cooled to −78°C, and an equimolar amount of the chlorophosphine R_2PCl was added slowly to the solution. After stirring overnight and warming from −78°C to room temperature, a pale yellow–white suspension was obtained. Triethylamine was removed under reduced pressure, the suspension was filtered off, and the toluene was removed till dryness. Washing the product with *n*-hexane at −78°C yielded the pure products.

Compounds **3a,**[6a] **3d,**[7] **3f,**[15] and **3h,**[15] were prepared according to published literature procedures.

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