

First Diphosphinoamine Ligand Bearing a Polymerizable Side Chain: Complexation with Copper(I)

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ABSTRACT: A diphosphinoamine ligand with a polymerizable side chain, $(\text{PPh}_2)_2\text{N}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$ (vbzpnP or **1**), was synthesized. The ligand could be polymerized by anionic polymerization with *n*-butyllithium as the initiator. PolyvbzpnP was soluble in tetrahydrofuran and chloroform but was insoluble in methanol and was characterized with NMR, IR, and gel permeation chromatography. The number-average and weight-average molecular weights were 40,050 and 55,690, respectively, and the polydispersity index was 1.39. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ formed a bischelated complex with the monomer and produced $[\text{Cu}(\text{1})_2]\text{ClO}_4$ (**2**), and CuCl formed a tetramer, $\text{Cu}_4(\text{1})_2\text{Cl}_4$ (**3**). All the compounds (**1**, **2**, and **3**) were characterized with single-crystal-structure determination, NMR, and IR spectroscopy. The addition of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ to polyvbzpnP resulted in an insoluble crosslinked polymer, which was characterized with solid-state ^{31}P $\{^1\text{H}\}$ magic-angle-spinning NMR. The copolymerization of styrene and **1** produced a styrene–vbzpnP copolymer that was found to be soluble in common organic solvents.

Keywords: anionic polymerization; copper(I); crosslinking; diphosphinoamine; gel permeation chromatography (GPC)

INTRODUCTION

The immobilization of homogeneous catalysts on a support is one of the possible ways of preparing analogous, well-defined heterogeneous catalytic systems. The development of insoluble-polymer-bound metal catalysts and reagents that maintain high activity and selectivity has attracted immense interest.^{1–3} In an ideal case, these insoluble supported complexes can be recovered by simple filtration and recycled.

There are, however, a number of disadvantages, including metal leaching during the course of the reaction, that lead to nonrecyclability. Another strategy that has been gaining attention is the use of soluble polymeric supports instead of their insoluble counterparts. In practice, the separations are achieved with several methods. The easiest process is dilution with an appropriate solvent that induces precipitation and crystallization.^{4,5} Other techniques, such as dialysis through semipermeable membranes,⁶ centrifugation methods, gel permeation chromatography (GPC),⁷ and adsorption chromatography,^{8,9} have also been demonstrated.

The number and diversity of transition-metal phosphine complexes are very large, and a wide range of catalysts is available for synthetic organic transformations. Therefore, it comes as little surprise that the preparation of polymer-

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supported metal phosphine complexes and the assessment of their metal complexes for catalysis have attracted much attention.^{10–13} Although polymeric ligands with a P–C–P framework were prepared and shown by Bianchini and co-workers^{14,15} to be useful, analogous diphosphinoamine ligands with a P–N–P framework have not been linked to polymeric systems. The most attractive features of diphosphinoamines are the ease with which a variety of ligands can be synthesized by the alteration of the substituents on nitrogen and phosphorus^{16–19} and their use in transition-metal-catalyzed hydrogenation,^{20–22} hydroformylation,²³ copolymerization,^{23,24} Pauson Khand reactions,²⁵ olefin polymerization,^{26–29} dehydrogenative coupling of stannanes,³⁰ ring-opening polymerization of lactones,³¹ diphenyl carbamate synthesis,³² and ring-opening metathesis.³³ Recently, Braunstein et al.³⁴ reported a diphosphinoamine system anchored to alumina. However, to the best of our knowledge, there has been no report of a diphosphinoamine that can be linked to a polymer. Here we report the synthesis and characterization of the first polymeric PNP ligand system.

EXPERIMENTAL

General Method and Materials

Dichloromethane, chloroform, benzene, tetrahydrofuran (THF), methanol (MeOH), dimethylformamide (DMF), petroleum ether (bp = 60–80 °C), and acetonitrile were purified and dried under a nitrogen atmosphere with conventional methods.³⁵ All manipulations were carried out under an atmosphere of purified N₂ with a standard double manifold and Schlenk ware. Anionic polymerization was carried out under an argon atmosphere. [Cu(CH₃CN)₄]ClO₄³⁶ and CuCl³⁷ were prepared with the reported methods. Chlorodiphenylphosphine, *p*-vinylbenzyl chloride, and *n*-butyllithium (*n*-BuLi; 1.6 M in hexane) were purchased from Aldrich and used as supplied.

Measurements

¹H, ³¹P {¹H}, and ¹³C {¹H} NMR were conducted with a Bruker AMX 400 spectrometer in CDCl₃ as the solvent at 400, 162.2, and 100 MHz, respectively, with tetramethylsilane (for ¹H and ¹³C {¹H}) and H₃PO₄ (85%; for ³¹P {¹H}) as the external references. Solid-state ³¹P {¹H} magic-

angle-spinning (MAS) NMR was recorded on a 300 MHz Bruker DSX spectrometer at 121.1 MHz. IR spectra were recorded in the solid state as KBr pellets either on a Bruker Equinox 55 Fourier transform infrared (FTIR) spectrometer or on a PerkinElmer Spectrum One FTIR spectrometer. Elemental analyses were performed with a Thermo Finnigan Flash 1112 CHN analyzer, electrospray ionization mass spectrometry (ESIMS) was performed on an HP 1100 MSD electrospray ionization instrument, and high-resolution mass spectrometry (HRESMS) was performed on a Micromass Q-ToF micro. GPC was carried out with a Viscotek TDA model 300 system, which coupled a refractive-index detector, a differential viscometer, and a light scattering detector in series. The separation was achieved with two mixed-bed PLgel columns (5 μm, mixed C) maintained at 30 °C, with THF as the eluent. The molecular weights were determined with a conventional calibration curve constructed with polystyrene standards. The copper loading on polyvbzppn and styrene-vbzppn copolymer [where vbzppn, or **1**, is (PPh₂)₂N–CH₂–C₆H₄–CH=CH₂] was estimated with a Thermo Jarrell Ash Video 11E model atomic absorption spectrophotometer with a calibration curve constructed with four different standard solutions of copper (1, 2, 3, and 4 ppm copper). The wavelength of the lamp was 324.7 nm, and the bandwidth was 1.0 nm.

Synthesis of *p*-Vinylbenzyl Amine (CH₂=CH–C₆H₄–CH₂NH₂)

The amine was synthesized by a three-step procedure with the Staudinger reaction scheme. In the first step, *p*-vinylbenzyl chloride was converted into the corresponding azide, and this was followed by the formation of the iminophosphorane in the second step. Finally, the iminophosphorane was hydrolyzed to obtain the corresponding amine.

Synthesis of *p*-Vinylbenzyl Azide (CH₂=CH–C₆H₄–CH₂N₃)

To about 10 mL of dry DMF in a 100-mL, round-bottom flask, *p*-vinylbenzyl chloride (10 mmol, 1.41 mL) was added. To the same solution, sodium azide (11.5 mmol, 0.75 g) was added, and the contents were stirred at room temperature for 1 h. Then, 5 mL of distilled water was added, and the organic layer was extracted with benzene

and dried with anhydrous sodium sulfate. Pure *p*-vinylbenzyl azide was obtained as an oily liquid.

Yield: 99%. $^1\text{H NMR}^{38}$ (δ): 4.33 (2H, s, $-\text{CH}_2$), 5.28 (1H, d, H_a , $J_{\text{H-H}} = 10.8$ Hz), 5.77 (1H, d, H_b , $J_{\text{H-H}} = 17.6$ Hz), 6.71 (1H, dd, H_c , $J_{\text{H-H}} = 17.6$ Hz, $J_{\text{H-H}} = 10.8$ Hz), 7.29 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz), 7.43 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz). IR (cm^{-1}): $\nu_{(\text{N}=\text{N})} = 2096$.

Synthesis of *p*-Vinylbenzyl Iminophosphorane ($\text{CH}_2 = \text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{N}=\text{PPh}_3$)

The benzene solution of the azide derivative was evacuated under reduced pressure to remove the solvent. The compound was dissolved in 15 mL of dry THF, and this was followed by the addition of triphenyl phosphine (10 mmol, 2.63 g). The immediate evolution of nitrogen gas could be seen, and the reaction mixture was allowed to stir at room temperature for 3 h.

Yield: 98%. ESIMS m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{27}\text{H}_{24}\text{NP}$, 393.1; found, 394.1. $^1\text{H NMR}$ (δ): 4.37 (2H, d, $-\text{CH}_2$, $J_{\text{H-P}} = 18$ Hz), 5.14 (1H, d, H_a , $J_{\text{H-H}} = 10.8$ Hz), 5.68 (1H, d, H_b , $J_{\text{H-H}} = 17.6$ Hz), 6.69 (1H, dd, H_c , $J_{\text{H-H}} = 17.6$ Hz, $J_{\text{H-H}} = 10.8$ Hz), 7.32 (4H, d, Ph, $J_{\text{H-H}} = 7.6$ Hz), 7.43 (7H, m, Ph), 7.49 (2H, d, Ph, $J_{\text{H-H}} = 6.0$ Hz), 7.68 (6H, m, Ph). ^{31}P $\{^1\text{H}\}$ NMR (δ): 11.9.

Synthesis of *p*-Vinylbenzyl Amine

To the previously prepared iminophosphorane, 5 mL of distilled water was added, and the solution was refluxed for 5 h. The solvent was removed under reduced pressure to obtain crude *p*-vinylbenzyl amine, which was purified by column chromatography on silica gel with 15:1 $\text{CHCl}_3/\text{MeOH}$ as the eluent. The initial isolated fraction was unreacted triphenyl phosphine, and the next fraction was triphenyl phosphine oxide. The last fraction was the pure amine, and it was isolated in an approximately 98% yield.

$^1\text{H NMR}^{38}$ (δ): 3.85 (2H, br, s, $-\text{CH}_2$), 5.21 (1H, d, H_a , $J_{\text{H-H}} = 10.8$ Hz), 5.72 (1H, d, H_b , $J_{\text{H-H}} = 17.6$ Hz), 6.70 (1H, dd, H_c , $J_{\text{H-H}} = 10.8$ Hz, $J_{\text{H-H}} = 17.6$ Hz), 7.29 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz), 7.37 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz).

Synthesis of 1

p-Vinylbenzyl amine (10 mmol, 1.33 g) was suspended in 30 mL of dry and distilled benzene in a 100-mL, round-bottom flask. To this solution, triethylamine (25 mmol, 3.48 mL) was added,

and the solution was cooled to 0 °C. Chlorodiphenylphosphine (20 mmol, 3.54 mL) was added dropwise over a period of half an hour. The contents were then brought to room temperature and stirred for 4 h. Triethylamine hydrochloride was filtered through a G-2 filtration frit and washed three times with benzene. The filtrate was evacuated *in vacuo*, and the residue was repeatedly washed with distilled MeOH under nitrogen. Subsequently, the compound was dried *in vacuo* to obtain the diphosphinoamine (**1**) as a white, free-flowing powder in a 70% yield.

HRESMS m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{30}\text{NP}_2$, 502.1853; found, 502.1851. $^1\text{H NMR}$ (δ): 4.45 (2H, t, $-\text{CH}_2$, $J_{\text{H-P}} = 10.4$ Hz), 5.15 (1H, d, H_a , $J_{\text{H-H}} = 10.8$ Hz), 5.65 (1H, d, H_b , $J_{\text{H-H}} = 17.6$ Hz), 6.61 (1H, dd, H_c , $J_{\text{H-H}} = 17.6$ Hz, $J_{\text{H-H}} = 10.8$ Hz), 6.70 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz), 6.59 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz), 7.14 (10H, m, Ph), 7.24 (10H, m, Ph). ^{31}P $\{^1\text{H}\}$ NMR (δ): 59.9. ^{13}C $\{^1\text{H}\}$ NMR (δ): 55.8 (t, $-\text{CH}_2-$, $J_{\text{C-P}} = 13$ Hz), 113.4 ($=\text{CH}_2$), 125.9 (Bz), 128.1 (t, PPh_2 , $J_{\text{C-P}} = 3$ Hz), 128.8 (PPh_2), 129.1 (Bz), 132.9 (t, PPh_2 , $J_{\text{C-P}} = 11$ Hz), 136.2 (Bz), 136.7 ($\text{CH}=\text{}$), 139.2 (Bz), 139.3 (t, PPh_2 , $J_{\text{C-P}} = 14$ Hz). IR (cm^{-1}): $\nu_{(\text{C}=\text{C})} = 1628$.

Synthesis of Copper(I) Complexes of Bis(diphenylphosphino)-*p*-Vinylbenzyl Amine

Reaction with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4 \cdot \{\text{Cu}[(\text{PPh}_2)_2\text{N}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2]_2\}\text{ClO}_4$ (**2**)

To 15 mL of distilled CHCl_3 , phosphine (vbzpn_p; 0.5 mmol, 0.25 g) was added, and it was followed by $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (0.25 mmol, 0.08 g). The reaction mixture was stirred at room temperature for 1 h. The solution was subsequently concentrated to about 8 mL and then layered with 15 mL of petroleum ether to obtain colorless, single crystals of **2**.

Yield: 97%. ELEM. ANAL. Calcd. for $\text{CuC}_{66}\text{H}_{58}\text{N}_2\text{P}_4\text{ClO}_4 \cdot 2\text{CHCl}_3$: C, 58.12%; H, 4.27%; N, 1.99%. Found: C, 58.64%; H, 4.44%; N, 2.29%. $^1\text{H NMR}$ (δ): 4.10 (2H, br, s, $-\text{CH}_2$), 5.13 (1H, d, H_a , $J_{\text{H-H}} = 10.8$ Hz), 5.52 (1H, d, H_b , $J_{\text{H-H}} = 17.6$ Hz), 6.16 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz), 6.44 (1H, dd, H_c , $J_{\text{H-H}} = 17.6$ Hz, $J_{\text{H-H}} = 10.8$ Hz), 6.76 (2H, d, Ph, $J_{\text{H-H}} = 8.0$ Hz), 7.21–7.37 (15H, m, Ph), 7.45 (5H, m, Ph). ^{31}P $\{^1\text{H}\}$ NMR (δ): 86.6. ^{13}C $\{^1\text{H}\}$ NMR (δ): 51.2 ($-\text{CH}_2-$), 114.3 ($=\text{CH}_2$), 134.8 ($-\text{CH}=\text{}$), 125.9, 129.3, 131.5, 131.9, 132.2, 132.3, 135.9, 137.0. IR (cm^{-1}): $\nu_{(\text{ClO}_4)} = 1098, 1058$, $\nu_{(\text{C}=\text{C})} = 1625$.

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	2	3
Empirical formula	C ₃₃ H ₂₉ NP ₂	C ₆₇ H ₅₉ Cl ₄ CuN ₂ O ₄ P ₄	C ₆₆ H ₅₈ Cl ₄ Cu ₄ N ₂ P ₄
Formula weight	501.51	1285.38	1398.98
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/n	C2/c	P-1
Unit cell dimensions (Å)	<i>a</i> = 8.998(9) <i>b</i> = 9.919(10) <i>c</i> = 30.58(3) <i>β</i> = 90.967/(17) ^o	<i>a</i> = 24.005(5) <i>b</i> = 12.329(3) <i>c</i> = 43.495(10) <i>β</i> = 98.475(4) ^o	<i>a</i> = 10.527(7) <i>b</i> = 11.305(7) <i>c</i> = 13.746(9) <i>α</i> = 105.832(10) ^o <i>β</i> = 92.977(11) ^o <i>γ</i> = 98.299(112) ^o
Volume (Å ³)	2729(5)	12732(5)	1550.0(17)
<i>Z</i>	4	8	1
Density (calculated) (mg/m ³)	1.221	1.341	1.499
Absorption coefficient (mm ⁻¹)	0.181	0.660	1.671
<i>F</i> (000)	1056	5312	712
Crystal size (mm ³)	0.32 × 0.30 × 0.29	0.32 × 0.12 × 0.08	0.11 × 0.09 × 0.06
Reflections collected	23142	46466	15416
Independent reflections	6383 [<i>R</i> (int) = 0.0248]	11641 [<i>R</i> (int) = 0.0413]	5664 [<i>R</i> (int) = 0.0303]
Data/restraints/parameters	6383/0/441	11641/0/739	5664/0/361
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0521, ^a <i>wR</i> ₂ = 0.1259 ^b	<i>R</i> ₁ = 0.0681 ^a <i>wR</i> ₂ = 0.1571 ^b	<i>R</i> ₁ = 0.0544 ^a <i>wR</i> ₂ = 0.1185 ^b
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0696 ^a <i>wR</i> ₂ = 0.1354 ^b	<i>R</i> ₁ = 0.0952 ^a <i>wR</i> ₂ = 0.1726 ^b	<i>R</i> ₁ = 0.0802 ^a <i>wR</i> ₂ = 0.1303 ^b
Goodness of fit on <i>F</i> ^{2c}	1.076	1.102	1.045

^a $R_1 = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$

^b $wR_2 = [\sum (w|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$

^c Goodness of fit = $[\sum (F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$

Reaction with CuCl: Cu₄[(PPh₂)₂N—C₆H₄—CH₂—CH=CH₂]₂Cl₄ (**3**)

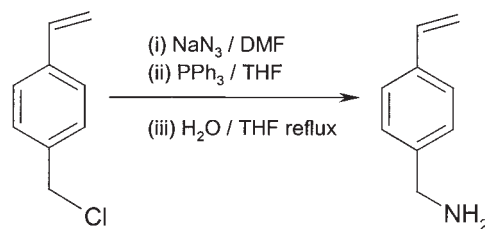
To 15 mL of a CHCl₃ solution containing vbzpnP (0.5 mmol, 0.25 g) was added CuCl (0.5 mmol, 0.05 g). CuCl dissolved completely after 1 h. Thereafter, the solution was evacuated under reduced pressure, and the residue was redissolved in about 8 mL of CH₂Cl₂. Petroleum ether (15 mL) was allowed to diffuse through the solution. Faint yellow crystals of **3** were obtained.

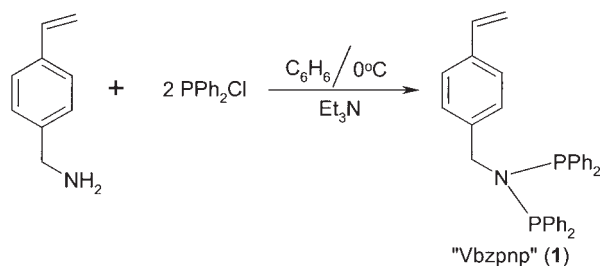
Yield: 98%. ELEM. ANAL. Calcd. for Cu₄Cl₄C₆₆H₅₈N₂P₄: C, 56.65%; H, 4.15%; N, 2.00%. Found: C, 56.32%; H, 4.66%; N, 2.43%. ¹H NMR (δ): 3.76 (2H, br, s, —CH₂), 5.06 (1H, d, H_a, *J*_{H—H} = 10.8 Hz), 5.42 (1H, d, H_b, *J*_{H—H} = 17.6 Hz), 5.60 (2H, d, Ph, *J*_{H—H} = 8.0 Hz), 6.33 (1H, dd, H_c, *J*_{H—H} = 17.6 Hz, *J*_{H—H} = 10.8 Hz), 6.52 (2H, d, Ph, *J*_{H—H} = 8.0 Hz), 6.93–6.97 (7H, m, Ph), 7.19–7.25 (13H, m, Ph). ³¹P {¹H} NMR (δ): 61.7. ¹³C {¹H} NMR (δ): 51.4 (—CH₂—), 113.7 (=CH₂), 128.3 (Bz), 128.4 (PPh₂), 128.8 (Bz), 130.5 (Bz), 131.5 (t, PPh₂,

*J*_{C—P} = 5 Hz), 132.5 (br, PPh₂), 135.3 (—CH=), 136.0 (PPh₂), 136.2 (Bz). IR (cm⁻¹): ν_(C=C) = 1627.

Anionic Polymerization: (PPh₂)₂N—CH₂—C₆H₄—(CH—CH₂)_{*n*}

The monomer vbzpnP (2.50 g, 4.50 mmol) was dissolved in 4 mL of dry THF in a Schlenk tube and subjected to three freeze–pump–thaw cycles. Subsequently, the solution was maintained at –78 °C in an ethyl acetate/liquid nitrogen slush bath. Then, 0.3 M *n*-BuLi (0.45 mL, 0.14 mmol)

**Scheme 1.** Synthesis of *p*-vinylbenzyl amine.



Scheme 2. Synthesis of **1**.

was added dropwise to the monomer solution. An intense green color was observed. The solution was then allowed to come to room temperature slowly. The color became dark orange at this stage. The reaction was stirred for 24 h and was concentrated, and 2 mL of distilled MeOH was added to quench the polymerization. A faint yellow solid was obtained upon the addition of MeOH. After thorough stirring, the solid was allowed to settle. The supernatant solution was syringed out, and the solid was dried *in vacuo*. The polyvzbznp so obtained was further purified three times by reprecipitation from a solution of dry THF with distilled MeOH.

Yield: 10%. ^1H NMR (δ): 0.88–1.55 (—CH₂—CH₂—), 4.24 (br, C₆H₄—CH₂—), 5.99–6.26 (br, C₆H₄—), 7.03–7.35 (m, PPh₂). ^{31}P { ^1H } NMR (δ): 59.5 (br, s). Number-average molecular weight (M_n) = 40,050; weight-average molecular weight (M_w) = 55,690; polydispersity index (PDI) = 1.39.

Reaction of Polyvzbznp with [Cu(CH₃CN)₄]ClO₄

In 15 mL of dry CHCl₃, polyvzbznp (25 mg, 0.05 mmol) was dissolved, and [Cu(CH₃CN)₄]ClO₄ (8.40 mg, 0.025 mmol) was added. The addition of copper(I) resulted in a white insoluble material that appeared as a gel. The contents were stirred at room temperature for 8 h, and then approximately 10 mL of diethyl ether was added. Subsequently, the solution was centrifuged. The supernatant was discarded, and fresh CHCl₃/ether (1:1 v/v) was added. The contents were centrifuged again. This procedure was repeated three to four times. The solid was dried *in vacuo* and was obtained in an almost quantitative yield.

ELEM. ANAL. Calcd. for (CuClO₄)_{0.85}C₆₆H₅₈N₂P₄·CH₃OH·2H₂O: C, 66.56%; H, 5.51%; N, 2.32%. Found: C, 65.99%; H, 5.23%; N, 2.39%. ^{31}P { ^1H } MAS NMR (δ): 85.5 (br, s). IR

(cm⁻¹): $\nu_{(\text{ClO}_4)}$ = 1098. Loading of copper: 0.0452 g of Cu/g of polymer.

Decomplexation of Copper(I)–Polyvzbznp

The crosslinked polymer (163 mg, 0.014 mmol) was suspended in 4 mL of DMF. The suspension was allowed to stir for 1 h to swell the polymer. Subsequently, the suspension was titrated with a DMF solution of NBu₄CN of a known concentration. With 1.5 equiv of cyanide, a clear solution was obtained. The removal of copper in this solution was confirmed by the absence of the ^{31}P signal at 86 ppm and the presence of a single ^{31}P resonance at δ = 59.8.

X-Ray Diffraction Studies

Crystals of **1**, **2**, and **3** were glued to the tip of a glass fiber along the largest dimension for data collection. Data were collected on a Bruker AXS single-crystal diffractometer equipped with a Smart Apex CCD detector and a sealed Mo K α source working at 1.75 kW and 50/35 (kV/mA). The intensity data were collected at 20 °C. All computations were performed with the WINGX package.³⁹ The data were corrected for Lorentz and polarization effects. The positions of heavy atoms were determined with SHELXS-86.⁴⁰ The remaining atoms were located from the difference Fourier map with SHELXL-97.⁴¹ Hydrogen atoms were included in the final stage of refinement on calculated positions bonded on their carrier atoms for **1**, whereas for complexes **2** and **3**, the hydrogen atoms were geometrically

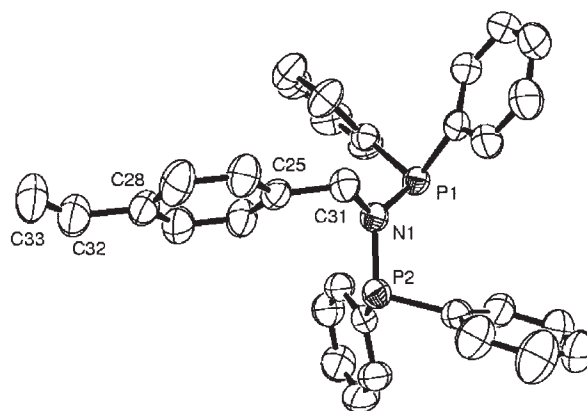


Figure 1. ORTEP plot of **1** at 50% thermal ellipsoid probability. The hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) in Compound **1**

Bond Length (Å)		Bond Angle (°)	
P(1)—N(1)	1.722(2)	P(1)—N(1)—P(2)	122.45(9)
P(2)—N(1)	1.7233(19)	C(31)—N(1)—P(1)	122.33(13)
N(1)—C(31)	1.486(2)	C(31)—N(1)—P(2)	113.27(14)
C(25)—C(31)	1.512(3)	N(1)—C(31)—C(25)	116.12(16)
C(32)—C(33)	1.284(5)	C(33)—C(32)—C(28)	127.5(4)

fixed. The crystallographic data for compounds **1**, **2**, and **3** are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis of Monomer **1**

In the first step, a primary amine (*p*-vinylbenzyl amine) was synthesized by the Staudinger reaction.⁴² It is a three-step process (Scheme 1) in which the corresponding azide is synthesized from *p*-vinylbenzyl chloride, and this is followed by a reaction with triphenyl phosphine to yield an iminophosphorane. Subsequently, the amine was generated by hydrolysis and purified by column chromatography with CHCl₃/MeOH (15:1) as the eluent.

The diphosphinoamine ligand (vbzppn) was synthesized (Scheme 2) by the treatment of the amine with 2 equiv of chlorodiphenylphosphine in the presence of triethylamine as the base. The ligand was purified by repeated washing with distilled MeOH and was quite stable. A singlet at 59.9 ppm was obtained with ³¹P {¹H} NMR in CDCl₃.

The ligand crystallized in a centrosymmetric space group adopting a C_s conformation (Fig. 1). Selected bond lengths and bond angles are given in Table 2. The central nitrogen adopted a more or less planar geometry with a P—N—P angle of 122.4°. The P—N distances were approximately 1.72 Å, with the two phosphorous atoms separated by a distance of 3.02 Å. The P—N—P bond angle and the P—N bond distances were very similar to those found for bis(diphenylphosphino)isopropylamine.¹⁹

Synthesis of the Copper(I) Complexes

2

The reaction of the monomer with [Cu(CH₃CN)₄] ClO₄ in a ratio of 2:1 in CHCl₃ yielded bischelate monomer **2**. The complex had a resonance

at 86.6 ppm in ³¹P {¹H} NMR that was characteristic of similar complexes and an intense broad band at 1098 cm⁻¹ (ClO₄⁻) in the IR spectrum. It was characterized by X-ray crystallography as well. The two phosphine ligands were bound to the metal in a chelating mode (Fig. 2). Copper adopted a distorted tetrahedral geometry with four phosphorus atoms in its coordination sphere (Table 3). The angle subtended by the ligand at the metal center was approximately 73°. Correspondingly, the P—N—P angle was reduced to about 105.8° from 122.4° in the free ligand. With chelation, there was a considerable decrease in the P—P distance from 3.02 Å in the free ligand to 2.72 Å in the complex.

3

A reaction of CuCl with vbzppn in a ratio of 1:1 in CHCl₃ afforded complex **3**. A singlet at 61.7 ppm was obtained in ³¹P {¹H} NMR for the complex, and the structure of the complex was confirmed to be a tetramer by X-ray crystallography. The Oak Ridge thermal ellipsoid plot (ORTEP) view of the complex is shown in Figure 3, and selected bond lengths and bond angles are listed in Table 4. The molecule was centrosymmetric, with four copper atoms in the

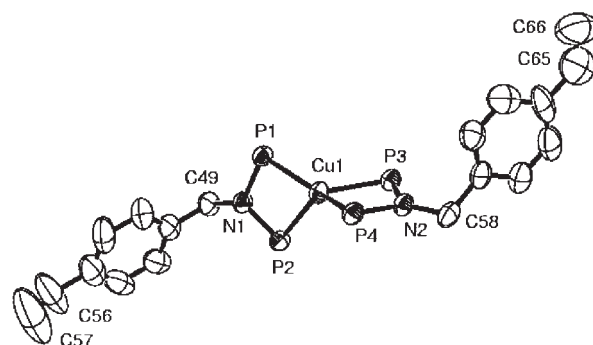


Figure 2. ORTEP plot of **2** at 50% thermal ellipsoid probability. The phenyl rings on phosphorus and hydrogen atoms have been omitted for clarity.

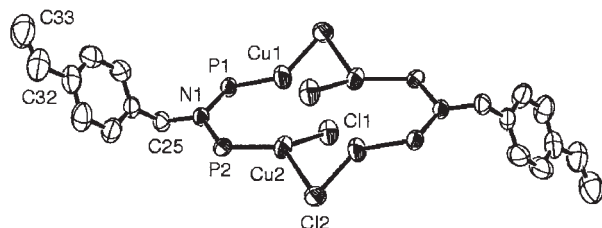
Table 3. Selected Bond Lengths (Å) and Bond Angles (°) in Complex **2**

Bond Length (Å)			
Cu(1)—P(1)	2.2704(11)	N(2)—P(3)	1.708(3)
Cu(1)—P(2)	2.2980(12)	N(2)—P(4)	1.709(3)
Cu(1)—P(3)	2.2786(12)	N(1)—C(49)	1.494(5)
Cu(1)—P(4)	2.2856(11)	N(2)—C(58)	1.488(5)
N(1)—P(1)	1.708(3)	C(56)—C(57)	0.924(13)
N(1)—P(2)	1.708(3)	C(65)—C(66)	1.134(10)
Bond Angle (°)			
P(1)—N(1)—P(2)	105.85(17)	N(1)—P(1)—Cu(1)	90.64(11)
P(3)—N(2)—P(4)	106.02(17)	N(1)—P(2)—Cu(1)	89.69(11)
P(1)—Cu(1)—P(2)	73.24(4)	N(2)—P(3)—Cu(1)	89.86(11)
P(1)—Cu(1)—P(3)	128.92(4)	N(2)—P(4)—Cu(1)	89.60(11)
P(1)—Cu(1)—P(4)	143.73(4)	C(49)—N(1)—P(1)	124.2(3)
P(2)—Cu(1)—P(3)	125.01(4)	C(49)—N(1)—P(2)	126.9(3)
P(2)—Cu(1)—P(4)	120.70(4)	C(58)—N(2)—P(3)	129.2(3)
P(3)—Cu(1)—P(4)	73.46(4)	C(58)—N(2)—P(4)	124.6(3)

same plane. In contrast to **2**, the bridged PNP angle was 116°. A similar Cu₄Cl₄ motif with two bridging diphosphines was found with bis(diphenylphosphino)methane.⁴³

Polymerization of Bis(diphenylphosphino)-*p*-Vinylbenzyl Amine

Several attempts were made to polymerize this vinyl monomer, but they were unsuccessful. These included free-radical polymerization under thermal conditions and living cationic polymerization. The P—N bond readily cleaved under these reaction conditions. Finally, anionic polymerization⁴⁴ of the monomer was attempted in THF with *n*-BuLi as the initiator in a ratio of approximately 32:1, and it was successful (Scheme 3). The dark orange solution was concentrated and quenched by the addition of distilled MeOH to obtain a faint yellow free-flowing powder. Polyvbzppnp was purified by reprecipitation with MeOH from a solution of dry THF. It

**Figure 3.** ORTEP plot of **3** at 50% thermal ellipsoid probability. The phenyl rings on phosphorus and hydrogen atoms have been omitted for clarity.

showed a broad singlet in ³¹P {¹H} NMR in CDCl₃ at 59 ppm and a broad band at 1098 cm⁻¹ for ClO₄⁻ (solid state) in the IR spectrum. It was soluble in chlorinated solvents and THF but insoluble in MeOH. The monomer could be recovered at the end of the reaction, and this indicated premature chain termination. As determined by GPC, *M*_n was 40,050, *M*_w was 55,690, and PDI was 1.39 for the polymer (polyvbzppnp).

Copolymerization of Bis(diphenylphosphino)-*p*-Vinylbenzyl Amine and Styrene

Copolymerization was also attempted with vbzppnp and unsubstituted styrene in a ratio of 1:10. A similar procedure was adopted for the preparation and purification. The ratio of phosphine and styrene was found to be 1:16 from ¹H NMR in the styrene–vbzppnp copolymer so obtained. Thus, smaller amounts of the diphosphinoamine were incorporated into the copolymer in comparison with the starting amount of diphosphinoamine used in the reaction. The molecular weights were smaller than the ones obtained for polyvbzppnp copolymer. *M*_w was 11,320, *M*_n was 21,150, and PDI was 1.7.

Complexation of Polyvbzppnp with Copper(I)

The treatment of polyvbzppnp with [Cu(CH₃CN)₄]ClO₄ in CHCl₃ yielded a crosslinked insoluble material. To confirm the coordination mode in the polymer, solid-state ³¹P {¹H} MAS

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) in Complex **3**

Bond Length (Å)			
Cu(1)—Cu(2)	2.7254(15)	Cu(2)—Cl(1)	2.382(2)
Cu(1)—Cu(2)#1	2.7537(15)	Cu(2)—Cl(2)	2.3415(19)
Cu(1)—P(1)	2.1789(16)	P(1)—N(1)	1.709(3)
Cu(2)—P(2)	2.1812(14)	P(2)—N(1)	1.714(3)
Cu(1)—Cl(1)#1	2.6912(18)	N(1)—C(25)	1.502(5)
Cu(1)—Cl(2)#1	2.2335(17)	C(32)—C(33)	1.282(9)
Bond Angle(°)			
P(1)—N(1)—P(2)	115.49(17)	Cl(1)—Cu(2)—Cl(2)	97.69(6)
P(1)—Cu(1)—Cl(1)	110.82(6)	P(2)—Cu(2)—Cu(1)	90.40(6)
P(1)—Cu(1)—Cl(1)#1	128.88(6)	Cl(2)—Cu(2)—Cu(1)	149.33(4)
P(1)—Cu(1)—Cl(2)#1	133.08(6)	Cl(1)—Cu(2)—Cu(1)	64.22(5)
P(1)—Cu(1)—Cu(2)	89.31(6)	C(25)—N(1)—P(1)	121.0(2)
Cl(1)—Cu(1)—Cu(2)	51.78(5)	C(25)—N(1)—P(2)	122.1(3)
P(2)—Cu(2)—Cl(2)	117.70(6)	N(1)—P(1)—Cu(1)	116.40(12)
P(2)—Cu(2)—Cl(1)	137.15(5)	N(1)—P(2)—Cu(2)	117.04(12)

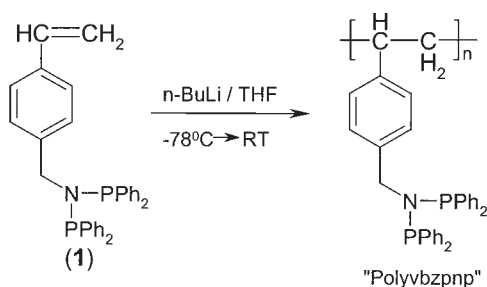
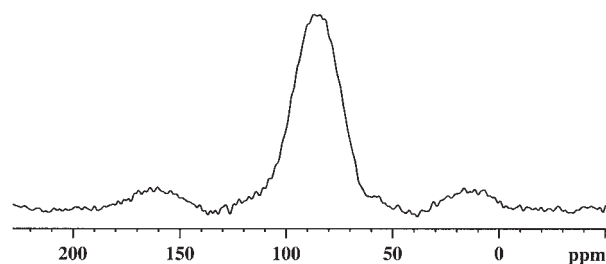
NMR was recorded, and it showed a broad singlet at 85.5 ppm (Fig. 4). This chemical shift for the polymer closely matched that of monomer **2**. This suggested that copper in polyvbznp also formed a bischelate. Because of this bischelate formation, the crosslinking of polymer chains occurred. A similar interchain process was reported by Ikegami et al.⁴⁵ in a soluble amide-based polymer with pendant PPh₂ units; coordination to palladium(II) led to crosslinking.

The copper loading in polyvbznp was estimated to be 0.0452 g of Cu/g of polymer by atomic absorption spectrophotometry, and this corresponded to a metal loading of approximately 85% (under the assumption that all P sites were accessible on the polymer and the CuP₄ complex could be formed). On the other hand, when a similar complexation reaction was attempted with the styrene–vbznp copolymer (vbznp/styrene = 1:16), a soluble material was obtained with a singlet at 87.0 ppm in ³¹P {¹H}

NMR in CDCl₃. The metal loading was determined by the presence of —PPh₂ groups, which in turn determined the extent of crosslinking and ultimately the solubility of the polymer.

Decomplexation of Copper(I)-Bound polyvbznp

The perchlorate counterion embedded in the polymer could be exchanged with tetrabutylammonium cyanide. When the polymer was swelled in chloroform, only 55% perchlorate could be exchanged from the polymer by the addition of cyanide. On the other hand, with more polar solvents such as DMF, the exchange increased to 90% (the percentage exchange was calculated by the integration of the band at 1098 cm⁻¹ for ClO₄⁻ in IR after the normalization of the spectrum with respect to the C—H stretch at 3052 cm⁻¹). Upon the addition of more than 1.5 equiv of cyanide to the crosslinked polymer suspended in DMF, the metal was removed via the formation of Cu(CN)₂⁻ species. This resulted in a

**Scheme 3.** Anionic polymerization of **1** with *n*-BuLi (RT = room temperature).**Figure 4.** ³¹P {¹H} MAS NMR spectrum of the copper(I)-loaded polymer.

clear solution of soluble polyvbznp. The removal of copper was confirmed by the ^{31}P resonance of the uncomplexed $-\text{PPh}_2$ units in the polymer at 59.8 ppm in ^{31}P $\{^1\text{H}\}$ NMR.

CONCLUSIONS

A novel diphosphinoamine ligand with a polymerizable side chain was successfully synthesized for the first time. The ligand was obtained in high purity and in a good yield. The ligand could only be polymerized via anionic polymerization because it decomposed when subjected to free-radical and cationic polymerization. Although the polymerization was incomplete, the unreacted monomer could be recovered at the end of the reaction. The synthesis of two new copper(I) complexes of the monomeric ligand was carried out to obtain a bischelate monomer in the presence of perchlorate and a chloride tetramer in almost quantitative yields. Polyvbznp crosslinked upon the addition of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$, and this resulted in an insoluble networked complex. Because diphosphinoamine ligands have been shown to be of great importance in transition-metal chemistry, the immobilization of these ligands on a polymer support has immense potential in the area of heterogeneous catalysis.

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