Article

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J. Comb. Chem., **1999**, 1 (1), 101-104• DOI: 10.1021/cc980013x • Publication Date (Web): 04 December 1998

Parallel Synthesis of Aminomethylphosphine Ligands

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Received September 5, 1998

Aminomethylphosphines ($R_aR_bPCHR_cNR_dR_e$) were prepared by condensation of R_aR_bPH, R_cCHO, and R_dR_eNH in THF at ambient temperature. A 96-member library of aminomethylphosphines was prepared in parallel using a combination of two phosphines (Ph_2PH, Cy_2PH), six aldehydes (PhCHO, *p*-$CF_3C_6H_4CHO$, 2,4,6-$(CH_3)_3C_6H_2CHO$, pyridine-2-carboxaldehyde, quinoline-2-carboxaldehyde, ferrocenecarboxaldehyde), and eight amines ($(CH_3)(PhCH_2)NH$, (*n*-C_6H_{13})$(CH_3)NH$, $(PhCH_2)$(*t*-Bu)NH, $(NCCH_2CH_2)NH(CH_3)$, $(CH_3)_2NCH_2CH_2NH(CH_3)$, $(CH_3)_2NCH_2CH_2CH_2NH(CH_3)$, $PhN(CH_2CH_2)_2NH$, $(CH_2)_5NH$).

Introduction

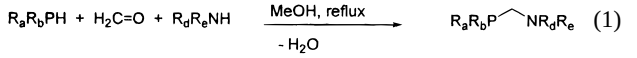
Recently, combinatorial chemistry techniques have been applied to the fields of inorganic and organometallic chemistry.[1] Examples from inorganic chemistry include the preparation of libraries of luminescent materials,[2] magnetoresistive materials,[3] thin film inorganic arrays,[4,5] ternary metal alloys,[6] binding agents for Ni(II) and Fe(III),[7] and zeolites.[8] In the field of organometallic chemistry, recent examples of combinatorial chemistry include the development of catalysts for the asymmetric ring-opening of epoxides,[9,10] the parallel synthesis of di(imine) ligands and metal complexes thereof,[11] and the preparation of libraries of phosphine-containing polypeptides for the Rh-catalyzed asymmetric hydrogenation of olefins.[12] In all of the organometallic examples cited above, the ligands (rather than the metal) provide the diversity. Thus, the design and preparation of libraries of ligands (either solid- or solution-phase) are very important. Several features must be considered in the selection of ligand libraries. First, the potential utility of a particular class of ligands for a particular catalytic application must be considered; in this regard, the strategy is the same as it is for "traditional" (noncombinatorial) organometallic chemistry and homogeneous catalysis. Second, potential diversity of a ligand library is an asset. Third, ligand synthesis and purification procedures must be readily adaptable to solution-phase parallel synthesis or solid-phase organic synthesis techniques.

In homogeneous catalysis, phosphines are extremely important supporting ligands in late-transition metal catalyzed processes such as hydrogenation, hydrosilation, hydroformylation, carbonylation, and olefin dimerization.[13,14] It would be advantageous to develop facile routes to libraries of organophosphines. Traditional syntheses of organophosphines utilize pyrophoric reagents (such as alkali metal phosphides or organolithium reagents) and require anaerobic, anhydrous conditions, careful manipulation at low temperatures, extensive purification, or other time-consuming procedures. In a combinatorial syntheses, such procedures would be inconvenient and impractical.

We were interested in preparing solution-phase libraries of organophosphines for our research in combinatorial organometallic chemistry. A convenient one-step synthesis of aminomethylphosphines is reported here. Also described are the parallel synthesis and characterization of a 96-member solution library of these aminomethylphosphines ("PCN" ligands) and the preparation of an aminomethylphosphine complex of Pd(II).

Results

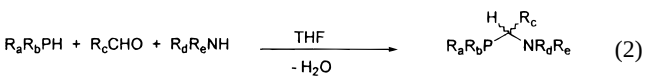
Synthesis of Aminomethylphosphines. The condensation of a secondary phosphine, formaldehyde, and an amine (primary or secondary) has been used to prepare aminomethylphosphines (eq 1).[15−19] Typical conditions for this reaction (a variation of the Mannich reaction) involve refluxing the reagents in protic solvents such as methanol.



(1)

The relatively mild reaction conditions, the large number of substructures available, and the lack of a protection/deprotection step for the phosphine functional group made this one-step synthesis of phosphines an attractive target for parallel synthesis. Aminomethylphosphines have been used as supporting ligands for a variety of hydrogenation[20,21] and hydroformylation[19,21] catalysts. We were interested in expanding the scope of the aminomethylphosphine synthesis to include aldehydes other than formaldehyde and avoiding the use of protic solvents, elevated temperatures, and extensive purification procedures.

The reaction of a secondary phosphine, a substituted aldehyde, and a secondary amine in THF at room temperature under rigorously anaerobic conditions cleanly yields the desired aminomethylphosphine (eq 2).



(2)

The reaction is successful under fairly concentrated (2 M) as well as dilute conditions (0.1 M). Dialkyl- and diarylphosphines can be used, as can arylaldehydes, demonstrating the generality of the reaction. Primary amines and dialkylamines

10.1021/cc980013x CCC: $18.00
Published on Web 12/04/1998

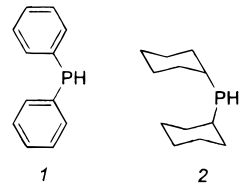


Figure 1. Diversity reagents **1**{*1*−*2*}: building blocks for aminomethylphosphine ("PCN") library (library size: 2 × 6 × 8 = 96).

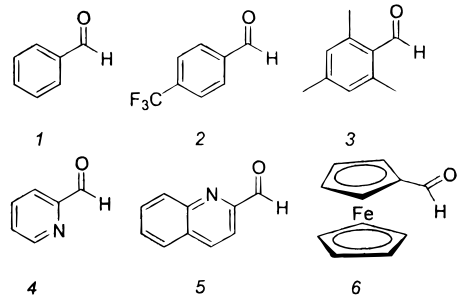


Figure 2. Diversity reagents **2**{*1*−*6*}: building blocks for aminomethylphosphine ("PCN") library (library size: 2 × 6 × 8 = 96).

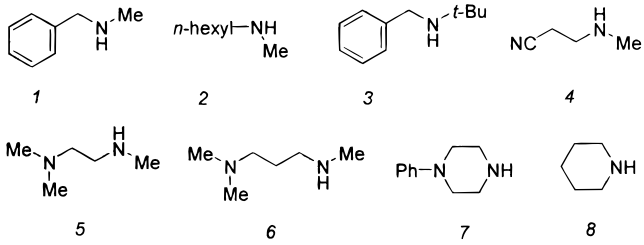
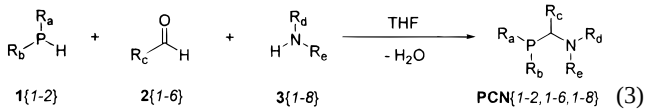


Figure 3. Diversity reagents **3**{*1*−*8*}: building blocks for aminomethylphosphine ("PCN") library (library size: 2 × 6 × 8 = 96).

also work well; however, di(aryl)amines and *N*-alkylanilines react sluggishly under these reaction conditions.

The crude product obtained from the reaction is typically >80% pure as determined by ^{1}H and ^{31}P NMR spectroscopy; however, further purification can be achieved through recrystallization or flash chromatography through neutral alumina.

Library Design, Synthesis, and Characterization. Although the number of commercially available secondary phosphines is low (ten), diverse arrays of amines and aldehydes are readily available. A 96-member library was prepared using a combination of two secondary phosphines, six aldehydes, and eight amines (eq 3). The substrates are shown in Figures 1−3.



(3)

Using robotic liquid-dispensing techniques in an inert atmosphere glovebox, 200 μL of a 1.0 M solution of diversity reagents **1**{*1*−*2*}, **2**{*1*−*6*}, and **3**{*1*−*8*} were dispensed into an 8 × 12 array of preweighed 1 mL glass vials. The plate was then sealed and shaken at room temperature overnight. Solvent was removed and the plate was dried in vacuo to afford the library of substituted aminomethylphosphines.

The aminomethylphosphines are extremely air-sensitive and cannot be readily characterized by GC-MS or HPLC. NMR spectroscopy was used as an alternate method of characterization. In particular, ^{31}P NMR spectroscopy is the preferred method of characterization, allowing the product to be readily distinguished from other phosphorus-containing products such as phosphine oxides and unreacted R_2PH.

Table 1. Characterization of PCN Library: Yield, Purity, and ^{31}P NMR Data for 20 Library Elements

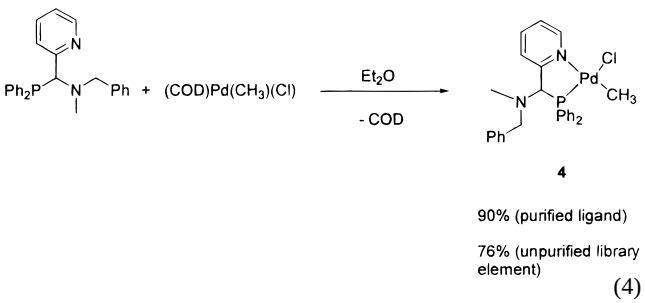
library ID	yield (%)	purity (wt %)[a]	^{31}P NMR (δ)
PCN{*2,4,6*}	82	83	−0.2
PCN{*1,5,5*}	87	88	−14.7
PCN{*1,4,8*}	88	97	−16.4
PCN{*2,6,7*}	89	99	1.8
PCN{*1,2,2*}	74	82	−14.9
PCN{*1,4,6*}	94	86*	−18.0
PCN{*2,2,8*}	80	>95*	−6.4
PCN{*2,2,1*}	54	89*	−4.1
PCN{*1,1,8*}	63	85	−19.4
PCN{*1,2,7*}	77	79	−17.2
PCN{*2,5,2*}	76	82	−0.1
PCN{*1,4,7*}	87	87	−16.2
PCN{*1,2,6*}	87	93	−15.1
PCN{*1,5,7*}	82	90	−15.0
PCN{*2,5,4*}	79	82	0.3
PCN{*1,4,1*}	85	91	−15.1
PCN{*2,2,5*}	80	90	−1.9
PCN{*2,1,8*}	81	>95*	−4.5
PCN{*2,1,1*}	80	80*	−1.8
PCN{*2,4,5*}	82	82	−0.3

[a] Asterisk (*) indicates that purity was estimated by ^{1}H and ^{31}P NMR.

Twenty elements of the library were sampled and characterized by ^{1}H and ^{31}P NMR spectroscopy. The results are summarized in Table 1. Yields ranged from 54 to 94%, and the majority (85%) of library elements were prepared in 74−90% yield. The purity (wt %) of the library elements ranged from 79 to 95%. The results of the library synthesis and characterization demonstrate that the preparation of the PCN ligands is highly amenable to parallel synthesis.

Coordination Chemistry. It was necessary to test whether the unpurified library elements could be used to prepare coordination complexes and to compare the resulting complexes with complexes prepared from prepurified PCN ligands. The reaction of (COD)Pd(CH_3)(Cl) (COD = 1,5-cyclooctadiene) with $Ph_2PCH(py)N(CH_3)(CH_2Ph)$ was investigated. In the first example, equimolar amounts of (COD)Pd(CH_3)(Cl) and recrystallized $Ph_2PCH(py)N(CH_3)(CH_2Ph)$ reacted in ether to form beige [($Ph_2PCH(py)N(CH_3)(CH_2Ph)$]Pd($CH_3$)(Cl) (**4**) in 90% yield.

In the second example, an unpurified element from the **PCN** library (library element **PCN**{*1,4,1*}, 91% purity) was dissolved in ether and a slight deficit (0.15 mmol) of (COD)Pd(CH_3)Cl was added. A beige solid formed, which was collected, washed, and dried in vacuo to yield compound **4** in 76% yield (based on Pd). The compound prepared in this



90% (purified ligand)

76% (unpurified library element)

(4)

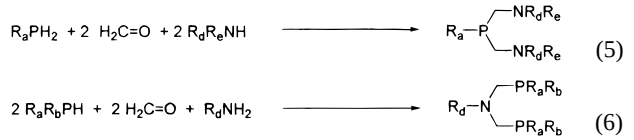
manner was pure by ^{1}H NMR and elemental analysis. Impurities present in the unpurified library element are removed by washing the precipitate with ether and pentane. A similar protocol has been used for the parallel synthesis of libraries of {PCN}PdMeCl complexes.[22]

Although the yield of **4** prepared from the library element is slightly lower than when it is prepared in a "traditional" organometallic synthesis, the samples are otherwise indistinguishable. Obviously, the amount of ligand purification that is necessary in the preparation of PCN complexes of other transition metals may vary, depending on the metal, the ancillary ligands, the solubility properties, potential catalytic applications, etc. The synthesis, coordination chemistry, and catalytic behavior of complexes such as **4** (and libraries thereof) will be reported in greater detail elsewhere.

Discussion and Conclusions

The condensation of a secondary phosphine with an aldehyde and an amine proceeded cleanly in THF to yield aminomethylphosphines, permitting the parallel synthesis of a 96-member solution library of these "PCN" ligands. This is one of the first reported parallel syntheses of organophosphines. Gilbertson and co-workers reported the preparation of a library of resin-bound oligopeptides which incorporated diphenylphosphinoserine sulfide or dicyclohexylphosphinoserine sulfide moieties.[23] At the end of the synthesis, the sulfide protecting group is removed, yielding a library of organophosphines.[12] The condensation of imines with resin-bound H-phosphonates [$(R_aO)(R_bO)P(=O)H$] has recently been reported for the solid-phase synthesis of α-aminophosphonates and α-aminophosphinic acids;[24,25] the condensation is similar to that reported here. One advantage of the PCN ligands reported here is that protection and deprotection of phosphorus are not necessary, resulting in an extremely facile one-step synthesis which is useful for both the preparation of individual PCN ligands as well as the parallel synthesis of libraries of these ligands.

Half of the amines and aldehydes selected for the library contain an additional, potentially chelating functional group (dimethylamino, nitrile, or pyridyl); thus, the PCN library contains a large number of potentially tri- and tetradentate PCN ligands. The inclusion of the potentially tri- and tetradentate PCN ligands in the library adds an additional element of diversity to libraries of transition metal complexes of the PCN ligands. Further diversity could be obtained by the use of other PCN substructures, such as di(aminomethyl)-phosphines[17] (eq 5) or di(phosphinomethyl)amines[16,21] (eq 6), which can be prepared by altering the reaction stoichiometry and using primary phosphines and amines, respectively.



(5)

(6)

The coordination chemistry of the PCN ligands and the parallel synthesis of libraries of metal complexes of the PCN ligands are currently being investigated and will be reported elsewhere.

Experimental Section

Unless otherwise noted, all manipulations were conducted under an atmosphere of dry, deoxygenated nitrogen in a Vacuum Atmospheres glovebox. Hexane, diethyl ether, THF, and toluene were sparged with nitrogen and passed though columns of activated Al_2O_3 and CU-0226S (Engelhart; a commerically available oxygen scavenger).[26] Dichloromethane was sparged with nitrogen and passed though activated alumina. Dicyclohexylphosphine was purchased from Strem; all other library reagents were purchased from Aldrich in the highest available purity and used without further purification.

NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{1}H and ^{13}C chemical shifts were referenced relative to residual protio solvent peaks and ^{13}C peaks, respectively; ^{31}P chemical shifts were referenced to an external standard (85% H_3PO_4). Elemental analyses were performed by QTI (Whitehouse, NJ).

Preparation of $R_aR_bPCHR_cNR_dR_e$; General Procedure. In a glovebox, R_aR_bPH, R_cCHO, and R_dR_eNH were combined in THF and the mixture was allowed to stir overnight at room temperature. THF was removed in vacuo, and the resulting oil or solid was dissolved in a minimal amount of pentane, recrystallized at −35 °C, and dried in vacuo. Three examples are given below.

$(PhCH_2)(CH_3)NCH(Ph)P(C_6H_{11})_2$. The reaction was set up as described above; 2.00 mL of $(C_6H_{11})_2PH$ (9.90 mmol), 1.20 mL of PhCHO (12.2 mmol), 1.30 mL of $(PhCH_2)(CH_3)$-NH (10.1 mmol), and 30 mL of THF were used. $(PhCH_2)$-$(CH_3)NCH(Ph)P(C_6H_{11})_2$ (3.30 g, 83%) was obtained as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 7.5−7.2 (m, 10, Ar), 4.23 (d, 1, Cy_2PCHPh), 3.57 (d, 1, NCH_aH_bPh), 3.45 (d, 1, NCH_aH_bPh), 2.21 (s, 3, N*Me*), 2.15−0.7 (br m, 22 total, cyclohexyl). ^{31}P NMR ($CDCl_3$): δ −1.78. Anal. Calcd for $C_{27}H_{38}NP$: C, 79.57; H, 9.40; N, 3.44. Found: C, 79.31; H, 9.26; N, 3.12.

$(PhCH_2)(CH_3)NCH(Ph)P(C_6H_5)_2$. The reaction was set up as described above; 2.00 mL of $(C_6H_5)_2PH$ (11.5 mmol), 1.20 mL of PhCHO (12.2 mmol), 1.30 mL of $(PhCH_2)(CH_3)$-NH (10.1 mmol), and 30 mL of THF were used. Upon isolation of the crude product, a colorless solid was obtained which was washed with pentane (10 mL) and dried (first crop = 2.97 g). The pentane washings were cooled to −35 °C, and an additional 0.66 g of $(PhCH_2)(CH_3)NCH(Ph)$-$P(C_6H_5)_2$ was collected. Total yield = 3.63 g = 77%. ^{1}H NMR ($CDCl_3$): δ 7.7−7.0 (m, 20 total, Ar), 4.64 (d, 1, Ph_2-$PCHPh$), 3.96 (d, 1, NCH_aH_bPh), 3.39 (d, 1, NCH_aH_bPh), 2.33 (s, 3, N*Me*). ^{31}P NMR ($CDCl_3$): δ −17.15.

$(NCCH_2CH_2)(CH_3)NCH(Ph)P(C_6H_5)_2$. Following the above procedure, 3.50 mL of $(C_6H_5)_2PH$ (20.1 mmol), 2.30 mL of PhCHO (23.4 mmol), 2.00 mL of $NCCH_2CH_2NH$-(CH_3) (21.4 mmol), and 10 mL of THF were combined. The reaction was stirred overnight. THF was removed in vacuo, yielding a colorless oil which solidified upon addition of pentane. The solid was collected, washed with pentane, and dried (6.02 g; 86%). ^{1}H NMR ($CDCl_3$): δ 7.75−7.05 (m, 15 total, Ar), 4.52 (d, 1, $CHPh$), 3.09 (m, 1H, NCH_aH_b), 2.70 (m, 1, NCH_aH_b), 2.46 (s, 3, N*Me*), 2.29 (td, 2, $NCCH_2$). ^{31}P NMR ($CDCl_3$): δ −15.25.

Library Synthesis. Library 1. An 8 × 12 array of preweighed 1.0 mL glass autosampler vials was assembled in an aluminum block. The arrangement of diversity reagents **1**{*1*−*2*}, **2**{*1*−*6*}, and **3**{*1*−*8*} in the plate is shown in the Supporting Information. Solutions (1.0 M) of diversity reagents **1**{*1*−*2*}, **2**{*1*−*6*}, and **3**{*1*−*8*} in THF were prepared. Aliquots (200 μL, 0.2 mmol) of **1**, **2**, and **3** were dispensed into each vial using a liquid-dispensing robot. The plate was then covered with a sheet of Teflon and a sheet of butyl rubber. An aluminum plate was then clamped into place over the microtiter plate assembly, sealing off each member of the library. The microtiter plate was shaken overnight. The aluminum plate and butyl rubber and Teflon sheets were removed from the microtiter plate, and solvent was removed by blowing a stream of dry N_2 over each vial. The plate was then dried in vacuo. The PCN ligands are very air-sensitive and should be stored and handled under an inert atmosphere.

Library Characterization. Individual library elements are denoted by **PCN**{*x*,*y*,*z*} (*x* = diversity reagent **1**, *y* = diversity reagent **2**, and *z* = diversity reagent **3**), as shown in eq 3. Twenty library elements were selected. The vials were weighed, and the contents of each vial were dissolved in 0.70 mL of a 0.10 M solution of $(Me_3Si)_2O$ in $CDCl_3$. Yields were calculated by comparing the integration of a selected peak (usually $R_aR_bPCHR_c$; d, δ = 4−5.5 ppm)) to that of the internal standard. Purity (wt %) was calculated by dividing the yield (as calculated by NMR) by a conversion factor *X* (*X* = weight of product obtained/theoretical yield.) In some cases, the calculated purity exceeded 100% due to product loss by evaporation or routine losses during transfer; in these cases, purity was qualitatively analyzed by ^{1}H and ^{31}P NMR. Yields and purity data are shown in Table 1. ^{1}H spectra are available in the Supporting Information.

[(Ph_2PCH(py)N(CH_3)(CH_2Ph)]Pd(CH_3)(Cl) (4). Method A. Solid (Ph_2PCH(py)N(CH_3)(CH_2Ph) (160 mg, 0.40 mmol) and (COD)PdMeCl (105 mg, 0.40 mmol) were combined. Et_2O (4 mL) was added, and the mixture was stirred. The reagents dissolved, and a beige precipitate formed. The reaction mixture was allowed to stir for 30 min, and the solid was collected, washed with pentane (5 mL), and dried in vacuo (190 mg; 90%). ^{1}H NMR (CD_2Cl_2): δ 9.50 (d, 1, py H_{ortho}), 7.90−6.72 (m, 18 total, Ar), 5.15 (d, 1, C*H*py), 3.82 (d, 1, NC$H_a$$H_b$Ph), 3.48 (d, 1, NC$H_a$$H_b$Ph), 2.37 (s, 3, N*Me*), 0.72 (d, 3, J_{P-H} = 2 Hz, PdCH_3). ^{31}P NMR (CD_2Cl_2): δ 48.9. Anal. Calcd for $C_{27}H_{28}N_2ClPPd$: C, 58.60; H, 5.10; N, 5.06. Found: C, 59.39; H, 5.25; N, 4.78.

Method B. PCN{*1*,*4*,*1*} (0.17 mmol, 91% purity) was dissolved in 3 mL of Et_2O. Solid (COD)PdMeCl (39 mg, 0.15 mmol) was added, and the mixture was stirred. A beige solid formed. After 30 min, pentane (5 mL) was added and the precipitate was collected, washed with pentane, and dried (63 mg; 76%). ^{1}H and ^{31}P NMR data matched those listed above. Anal. Calcd for $C_{27}H_{28}N_2ClPPd$: C, 58.60; H, 5.10; N, 5.06. Found: C, 58.44; H, 5.09; N, 4.94.

Acknowledgment. A.M.L. thanks Drs. T. Boussie, K. Hall, B. Jandeleit, C. Lund, V. Murphy, H. Turner, and J. van Beek for helpful discussions.

Supporting Information Available. ^{1}H NMR spectra from the library characterization (20 pages) and arrangement of the diversity reagents in the library (1 page). See any current masthead page for ordering information and Web access information.

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CC980013X