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New Bis(diphenylphosphino)aniline Derivatives: Synthesis and Spectroscopic Characterization

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ABSTRACT: *Six new multidentate bis(diphenylphosphino)amine [R—N(PPh$_2$)$_2$] ligands have been prepared from the reaction of aniline derivatives, R—NH$_2$, with Ph$_2$PCl in the presence of triethylamine. All of the compounds were obtained in good yields and were characterized by NMR, IR, and microanalysis.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:613–616, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20362

INTRODUCTION

Ligands bearing P—N—P backbone have been known since 1964 [1]. Several methods have been mentioned for the synthesis of aminophosphines and diphosphinoamines, among them the most common is aminolysis [2], namely the reaction of phosphine chloride with an amine usually provides the target compound, RNHPR$'_2$ or RN(PR$'_2$)$_2$, in high yields. The reaction condition for the synthesis of aminophosphines depends on the nature of chlorophosphine and the organic precursor. For the obvious electronic reasons, Ph$_2$PCl is more reactive toward a nucleophile than chlorodialkylphosphines [3]. Over the past years, studies of aminophosphines have attracted a considerable attention because aminophosphines consist of both soft and hard donor atoms to accommodate metal ions. This enables the synthesis of compounds containing transition metals, which have important applications in areas such as NMR shift reagents [4], selective metal extractions [5], organometallic chemistry, and catalysis [6–9]. Recently, new type of catalysts, ruthenium pyridine–phosphole complex [10] and chromium diphosphinoamine complexes [11] have been developed and are used in the transfer hydrogenation of ketones and the synthesis of 1-hexene, respectively.

Although anilines are well known and very cheap commercial reagents, the chemistry of diphosphinoamines with P—N—P skeletons has not been studied in detail. We report here the synthesis of some new multidentate aminophosphine ligands derived from aniline derivatives, possessing electron-donating substituents on an aryl ring. All compounds have been fully characterized by microanalysis: IR, ^{1}H NMR, ^{13}C NMR, and^{31}P–{^{1}H} NMR spectroscopy.

RESULTS AND DISCUSSION

Six new multidentate bis(diphenylphosphino)anilines were prepared from the commercially available starting materials, aniline derivatives, using the aminolysis method in dichloromethane as described in Scheme 1.

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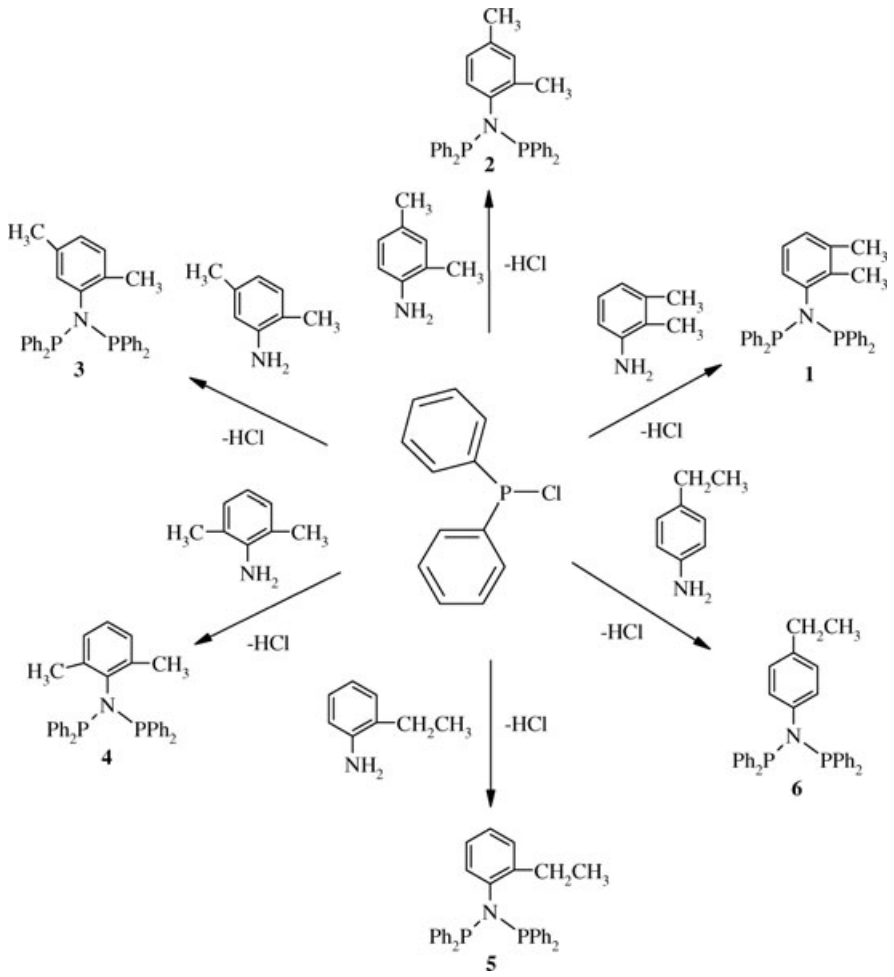

SCHEME 1 Aminolysis reactions of anilines with Ph_2PCl, Et_3N at 0°C in CH_2Cl_2.

The synthesis of bis(diphenylphosphino)anilines **1–6** has not been described in the literature so far. The structure of the compounds was confirmed by the spectroscopic analysis.

The reaction between anilines and Ph_2PCl in the presence of triethylamine is fast, and all the reaction products are soluble in dichloromethane, allowing the reaction to be monitored by ^{31}P NMR spectroscopy. Recently, the reactions of some aniline derivatives with Ph_2PCl in the presence of triethylamine have been thoroughly studied and different substances were obtained, depending on the relative ratio of the reagents, the electron-withdrawing groups and their positions on the aromatic ring and solvents such as diethyl ether and dichloromethane. Aminophosphines (Ph_2P—NHR) were found as the main products, and when the reaction conditions changed diphosphinoamines (R—$N(PPh_2)_2$) or iminodiphosphines (R—N=PPh_2—PPh_2) were also formed as the major products [12].

As shown in Scheme 1, we investigated the aminolysis reactions of aniline derivatives possessing electron-donating groups with Ph_2PCl in the presence of Et_3N (molar ratio 1:2:2) in CH_2Cl_2. ^{31}P–$\{^1H\}$ NMR investigation of the reaction mixtures shows that all the reactions were completed after 1 h to give the expected products, diphosphinoamines **1–6** (Scheme 1). ^{31}P–$\{^1H\}$ NMR spectra indicate that all compounds display the characteristic signals of bis(diphenylphosphino)amines between 56 and 69 ppm, and the results are in agreement with the earlier studies where the chemical shifts of the same functional groups generally appear between 60 and 70 ppm [13,14]. ^{31}P NMR chemical shifts (ppm) of the P—N—P function of our compounds are changed between 56 and 69 ppm, and the results are consistent with the mentioned studies. Two singlets at 61.4 and 29.0 were observed for the reaction mixture of **1** in its ^{31}P–$\{^1H\}$ NMR spectrum. The main signal at 61.4 was attributed to *N*-bis(diphenylphosphino)-2,3-dimethylaniline (**1**), and the small one was thought to be that of 2,3-dimethylanilodiphenylphosphine. When the mixture of **1** was washed with H_2O and

then with Et_2O, the minor signal at 29.0 ppm disappeared and only the one signal at 61.4 ppm was observed. Thus, compound **1** was obtained with a high yield as a pure product. The results on the byproduct are in agreement with the chemical shifts of arylaminodiphenylphosphines, which gave ^{31}P NMR resonances between 25 and 35 ppm [15]. There was no evidence for the formation of iminobiphosphines, producing two sets of doublets at $\sim +10$ to ~ -20 ppm [16], because no resonances were observed in this region in all reactions.

The $^{31}P–\{^1H\}$ NMR spectra of the reaction obtained from mixture after 1 h of the reaction of **2** and **3** show a single resonance at 61.4 ppm for compound **2** and at 60.2 ppm for compound **3**. No byproduct was observed in these reactions as seen in that of **1**. The property of **4** is really very interesting when compared to compounds **1–3**. A comparison of $^{31}P–\{^1H\}$ NMR spectra of **1–3** and **4** indicates that the position of the substituted groups is very important. So, the $^{31}P–\{^1H\}$ NMR spectrum of **4** shows a resonance at 56.8 ppm, at lower frequency of about 4 ppm from the other substances. After removal of the solvent, $Et_3N{\cdot}HCI$ was removed by washing the residue with water and **4** was isolated in high yields. Although compounds **1–3** are very stable in air, water, and organic solvents, compound **4** is sensitive to air. It is stable in air for 2 days and completely decomposed after that. Again $^{31}P–\{^1H\}$ NMR investigation of decomposed product showed that there are three different chemical shifts at 35.8–34.5 ppm as a doublet, 19.9 ppm as a singlet, and −22.5(−23.9) ppm as a doublet.

Notably, $^{31}P–\{^1H\}$ NMR spectrum of the reaction mixture of **6** shows a singlet at 68 ppm, a shift of exactly 7 ppm from that of **5**, possibly as a consequence of the position of an ethyl group on the aniline ring. This once again demonstrates that the steric and electronic effects of substituents on an aromatic ring for aminophosphines are very important. All compounds are colorless and are soluble in chlorinated solvents, Et_2O and THF, but a slow decomposition can occur in chlorinated solvents [17]. The compounds **1–6** are stable in air and moisture, except **4**.

The IR spectrum is useful in determination of $\nu_{P–N}$ bonds of aminophosphines and their coordination compounds [18]. We observed that all ligands showed characteristic vibrations about at 900–700 cm^{-1} of $\nu_{P–N–P}$ bonds, which are assigned to $\nu_{P–N–P}$ vibrations, producing the evidence for the synthesis of the compounds.

In conclusion, we have achieved the synthesis of six novel heterodonor tertiary phosphine ligands from the reaction of aniline derivatives bearing electron-donating groups, such as methyl and ethyl, and Ph_2PCl in a single step, with high yields. Further synthesis of their coordination compounds with transition metals and chalcogenides is in progress.

EXPERIMENTAL

All the starting materials are commercially available and were used without further purification. Solvents were dried using the appropriate reagents and were distilled prior to use. All manipulations were performed under an inert atmosphere of dry nitrogen using the standard Schlenk techniques. Infra red spectra were recorded as KBr pellet in the range 4000–400 cm^{-1} on a Mattson 1000 ATI Unicam FT-IR spectrometer. ^1H and ^{13}C NMR (100.6 MHz) spectra on Bruker AC 400 spectrometer, and $^{31}P–\{^1H\}$ NMR spectra at 162 MHz with δ referenced to external 85% H_3PO_4. Microanalysis was carried out by using Fisons EA 1108 CHNS-O instrument, and melting points were determined with the help of Gallenkamp MID 350 BM 2.5 apparatus.

General Procedure for Preparation of the Compounds **1–6**

Chlorodiphenylphosphine (3.74 g, 16.5 mmol) was added slowly to a solution of aniline derivatives (1.00 g, 8.25 mmol) and Et_3N (1.669 g, 16.5 mmol) in CH_2C1_2 (25 mL) at 0°C. The resulting white suspension was stirred for 2 h, and the solvent was removed under reduced pressure. The solid compounds were washed with degassed water (3 × 10 mL) and were dried in air.

Bis(diphenylphosphino)-2,3-dimethylaniline $[(Ph_2P)_2N–C_6H_3–(CH_3)_2]$ (**1**). Yield: 3.50 g, 87%. mp 120–122°C. ^1H NMR ($CDCl_3$) δ (ppm): 6.51–7.7 (m, 23H, ArH), 2.12 (s, 3H, CH_3), 1.53 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm): (C_{arm}, 146.7; 139.9; 137.7; 136.1; 134.6; 132.5; 129.9; 128.2; 127.7; 125.2), (C_{CH_3}, 20.8; C_{CH_3}, 15.1). $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 61.4 (s). IR, ν (cm^{-1}): 3049 (w), 2951 (w), 1570 (w), 1470 (m), 1437 (s), 1377 (w), 1238 (m), 1186 (m), 1094 (s), 914 (s), 882 (s) (P—N), 783 (w), 737 (s), 691 (s), 571 (m), 533 (m), 492 (m), 440 (m). $C_{32}H_{29}NP_2$: calcd C 78.51, H 5.97, N 2.86; found, C 78.66, H 5.75, N 3.01.

Bis(diphenylphosphino)-2,4-dimethylaniline $[(Ph_2P)_2N–C_6H_3–(CH_3)_2]$ (**2**). Yield: 3.72 g, 92%. mp 147–149°C. ^1H NMR ($CDCl_3$) δ (ppm): 6.47–7.52 (m, 23H, ArH), 2.25 (s, 3H, CH_3), 1.68 (s, 3H, CH_3). $^{13}C–NMR$ ($CDCl_3$) δ (ppm): (C_{arm}, 144.7;

139.9; 136.9; 135.6; 134.7; 132.4; 129.9; 128.4; 127.7; 126.8), (C_{CH_3}, 20.9; C_{CH_3}, 19.4). $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 61.4 (s). IR, ν (cm^{-1}): 3054 (w), 2918 (w), 1576 (w), 1491 (m), 1437 (s), 1371 (w), 1213 (m), 1186 (m), 1094 (s), 955 (w), 889 (s) (P—N), 811 (w), 743 (s), 696 (s), 589 (w), 558 (m), 498 (m). $C_{32}H_{29}NP_2$: calcd C 78.51, H 5.97, N 2.86; found C 78.10, H 5.55, N 2.93.

Bis(diphenylphosphino)-2,5-dimethylaniline $[(Ph_2P)_2N–C_6H_3–(CH_3)_2]$ (**3**). Yield: 3.65 g, 91.5%. mp 164–165°C. ^1H NMR ($CDCl_3$) δ (ppm): 7.16–7.65 (m, 23H, ArH), 2.20 (s, 3H, CH_3), 1.76(s, 3H, CH_3). $^{13}C–NMR$ ($CDCl_3$) δ (ppm): (C_{arm}, 146.7; 139.9; 135.5; 134.5; 133.8; 131.2; 130.6; 128.2; 127.8; 126.7), (C_{CH_3}, 20.8; C_{CH_3}, 19.1) $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 60.2 (s). IR, ν (cm^{-1}): 3076 (w), 2970 (w), 1589 (w), 1483 (m), 1437 (s), 1312 (w), 1233 (m), 1179 (m), 1113 (m), 1086 (m), 993 (m), 909 (s) (P—N), 855 (s), 803 (m), 737 (s), 691 (s), 590 (m), 525 (m), 473 (m). $C_{32}H_{29}NP_2$: calcd C 78.51, H 5.97, N 2.86; found C 78.20, H 5.78, N 2.96.

Bis(diphenylphosphino)-2,6-dimethylaniline $[(Ph_2P)_2N–C_6H_3–(CH_3)_2]$ (**4**). Yield: 3.8 g, 88%. mp 100–101°C. ^1H NMR ($CDCl_3$) δ (ppm): 6.9–7.82 (m, 23H, ArH), 1.607 (s, 6H, CH_3). $^{13}C–NMR$ ($CDCl_3$) δ (ppm): (C_{arm}, 145.7; 139.6; 138.5; 135.2; 134.3; 134.2; 129.3; 128.9; 127.9; 126.2), (C_{CH_3}, 20.5). $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 56.8 (s). IR, ν (cm^{-1}): 3057 (w), 2932 (w), 1595 (w), 1478 (m), 1437 (s), 1325 (w), 1179 (s), 1094 (m), 1034 (w), 878 (s) (P—N), 770 (w), 750 (s), 696 (s), 544 (m), 492 (m), 452 (m). $C_{32}H_{29}NP_2$: calcd C 78.51, H 5.97, N 2.86; found C 78.9, H 6.02, N 2.78.

Bis(diphenylphosphino)-2-ethylaniline $[(Ph_2P)_2N–C_6H_4–(C_2H_5)]$ (**5**). Yield: 3.26, 81%. mp 104–107°C. ^1H NMR ($CDCl_3$) δ (ppm): 6.65–7.66 (m, 24H, ArH), 2.62–2.56 (q, 2H, CH_2, $^3J_{HH} = 7.4$ Hz), 1.27–1.24 (t, 3H, CH_3, $^3J_{HH} = 7.4$ Hz). $^{13}C–NMR$ ($CDCl_3$) δ (ppm): (C_{arm}, 146.7; 142.6; 135.0; 132.4; 131.2; 130.4; 130.0; 128.5; 126.3; 125.8), (C_{CH_2}, 23.9; C_{CH_3},13.7).$^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 61.6 (s). IR, ν (cm^{-1}): 3049 (w), 2964 (w), 1589 (w), 1483 (m), 1437 (s), 1317 (w), 1226 (m), 1179 (m), 1100 (m), 1028 (w), 947 (m), 895 (s) (P—N), 855 (s), 803 (m), 743 (s), 696 (s), 544 (m), 486 (m). $C_{32}H_{29}NP_2$: calcd C 78.51, H 5.97, N 2.86; found C 78.15, H 5.77, N 2.95.

Bis(diphenylphosphino)-4-ethylaniline $[(Ph_2P)_2N–C_6H_4–(C_2H_5)]$ (**6**). Yield: 3.42 g, 85%. mp 104–107°C. ^1H NMR ($CDCl_3$) δ (ppm): 6.55–7.38 (m, 24H, ArH), 2.47–2.53 (q, 2H, CH_2, $^3J_{HH} = 7.5$ Hz), 1.11–1.15 (t, 3H, CH_3, $^3J_{HH} = 7.6$ Hz). $^{13}C–NMR$ ($CDCl_3$) δ (ppm): (C_{arm}, 145.1; 141.1; 140.5; 139.4; 135.3; 133.3; 131.2; 129.0; 128.5; 127.6), (C_{CH_2}, 28.0; C_{CH_3},15.6). $^{31}P–\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 68.5 (s). IR, ν (cm^{-1}): 3049 (w), 2970 (w), 1550 (m), 1478 (m), 1437 (s), 1306 (w), 1219 (s), 1173 (w), 1100 (m), 1020 (w), 895 (s) (P—N), 737 (s), 696 (s), 598 (m), 588 (m), 492 (m). $C_{32}H_{29}NP_2$: calcd C 78.51, H 5.97, N 2.86; found C 78.56, H 5.68, N 2.78.

REFERENCES

[1] Schmidpeter, A.; Böhm, R.; Groeger, H. Angew Chem, Int Ed Engl 1964, 3, 704.

[2] (a) Ewart, G.; Lane, A. P.; McKechnie, J.; Payne, D. S. J Chem Soc A 1964, 1543; (b) Lane, A. P.; Morton-Blake, D. A.; Payne, D. S. J Chem Soc A 1967, 1492.

[3] Agbassou, F.; Carpentier, J. F.; Hapiot, F.; Suisse, I.; Mortreux, A. Coord Chem Rev 1998, 1615, 178–180.

[4] Barkaoui, L.; Charrouf, M.; Rager, M. N.; Denise, B.; Platzer, N.; Rudler, H. Bull Soc Chim Fr 1997, 134, 167.

[5] Navrátil, O.; Herrmann, E.; Slezák, P. Collect Czech Chem Commun 1987, 52, 1708.

[6] (a) King, R. B. Acc Chem Res 1980, 13, 243; (b) Mague, J. T. J Cluster Sci 1995, 6, 217; (c) Bhattacharyya, P.; Woollins, J. D. Polyhedron 1995, 14, 3367.

[7] Ly, T. Q.; Slawin, A. M. Z.; Woollins, J. D. J Chem Soc, Dalton Trans 1997, 1611.

[8] Zubiri, I. M. R.; Clarke, M. L.; Foster, D. F.; Cole-Hamilton, D. J.; Slawin, A. M. Z.; Woollins, J. D. J Chem Soc, Dalton Trans 2001, 969.

[9] Molloy, K. G.; Petersen, J. L. J Am Chem Soc 1995, 117, 7696.

[10] Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. Organometallics 2003, 22(8), 1580.

[11] (a) Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. Chem Commun 2002, 8, 858; (b) Bowen, L. E.; Wass, D. F. Organometallics 2006, 25(3), 555; (c) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. Chem Commun 2005, 5, 620; (d) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S. Chem Commun 2005, 5, 622.

[12] Fei, Z.; Scopelliti, R.; Dyson, P. J. J Chem Soc, Dalton Trans 2003, 2772.

[13] Gaw, K. G.; Smith, M. B.; Steed, J. W. J Organomet Chem 2002, 664, 294.

[14] Fei, Z.; Dyson, P. J. Coord Chem Rev 2005, 249, 2056.

[15] Fei, Z.; Scopelliti, R.; Dyson, P. J. J Chem Soc, Dalton Trans 2003, 2772.

[16] Fei, Z.; Biricik, N.; Scopelliti, R.; Dongbin, Z.; Dyson, P. J. Inorg Chem 2004, 43(7), 2228.

[17] Lindner, E.; Mohr, M.; Nachtigal, C.; Fawzi, R.; Henkel, G. J. Organomet Chem 2000, 595, 166.

[18] Necas, M.; Foreman, St. M. R.; Marek, J.; Slawin, A. M. Z.; Woollins, J. D.; Novosad, J. New J Chem 2001, 25, 1256.